

results of measurements of the electromotive force of concentration cells. At still higher concentrations, the conductance approaches that of metallic conductors. At approximately 2 *N* a solution of sodium in liquid ammonia has an equivalent conductance of approximately 83,000 and a specific conductance of 0.0164×10^4 . A saturated solution of sodium in liquid ammonia has a specific conductance approximately half that of mercury at 0°.

The conductance curves of sodium, lithium and potassium, as well as of mixtures of sodium and potassium, are similar in form but are displaced as regards the value of the conductance. The difference in the conductance of the more dilute solutions corresponds approximately to the difference in the conductance of the positive ions of these metals. This is in agreement with the conclusion reached above, that the negative carriers in the case of these three solutions are identical.

It appears that the solutions of the metals in liquid ammonia form the connecting link between electrolytic and metallic conductors. It has been definitely shown that the conduction process in the case of these solutions is an ionic one. There is nothing to distinguish the more concentrated solutions from actual metallic substances. It may be concluded, therefore, that the process of conduction in the case of ordinary metals is effected by means of the same negative carrier. Since this carrier is negatively charged and has sub-atomic dimensions, we may conclude that it is identical with the negative electron as it appears in radio-active and other phenomena.

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THE HEATS OF DILUTION AND THE SPECIFIC HEATS OF DILUTE SOLUTIONS OF NITRIC ACID AND OF HYDROXIDES AND CHLORIDES AND NITRATES OF LITHIUM, SODIUM, POTASSIUM, AND CESIUM.

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In a recent paper an indirect but accurate method of determining the specific heats of dilute solutions was described,¹ together with data and results concerning hydrochloric acid. The method depends upon the law of Kirchhoff, and bases the values for the more dilute solutions upon the change of heat capacity which occurs during dilution, as calculated from the temperature coefficient of the heat of dilution. The specific heats of the initial concentrated solutions must have been determined directly.

¹ Richards and Rowe, *THIS JOURNAL*, 42, 1621 (1920).

The method and calculation of a single case having been detailed in the previous paper, the data concerning a variety of solutions of common electrolytes may be presented as briefly as possible. For the sake of convenience the description will be divided into four parts: (1) the preparation of materials and the specific heats of the concentrated solutions; (2) the experimental data concerning the dilution; (3) the results for the heats of dilution, and (4) the results for the specific heats of the dilute solutions. To these are added the determination of the temperature coefficient of the heat of neutralization, which can be simply calculated from the results, and other relations of the results to one another.

The Preparation and Specific Heats of the Initial Solutions.

Lithium chloride in suitable quantity, prepared especially for this research by a trustworthy American firm of manufacturing chemists, and free from appreciable impurities, except a small percentage of common salt, was dissolved in more than 7 liters of water. On account of the hygroscopic nature of the substance an excess was taken. Careful titrations (by the volumetric Volhard method with excess of silver nitrate and thiocyanate) determined the concentration, and seemed to show that a solution obtained by suitable dilution of the original was LiCl , 24.98 H_2O . Nevertheless, 48.697 g. of the solution yielded in two identical gravimetric trials 14.315 g. of silver chloride, indicating only LiCl , 24.72 H_2O . As is well known, the Volhard method, unless the precipitate is removed, indicates too little chlorine, because the thiocyanate overshoots the end-point by attacking some of the silver chloride.

Accordingly, the proper amount of water, calculated from the last mentioned gravimetric results, was added to obtain exactly LiCl , 25 H_2O . Since the concentration was determined by reference to the chlorine, the presence of a small amount of sodium chloride could not greatly affect the results.

The specific heat of this solution was found to be 0.8955.

Sodium Chloride.—A very pure specimen of common salt was dried over caustic alkali and by subsequent heating. 50.369 g. of a carefully made solution yielded in two identical experiments 14.154 g. of silver chloride, showing the solution to be NaCl , 25.07 H_2O . The specific heat of this solution was found by direct determination to be 0.8779. This agrees closely with 0.878—the mean of the most trustworthy of results heretofore published by others.¹ A small error in this estimate would have only a very slight effect on the specific heats of the dilute solutions.

¹ The values for this and other specific heats have been sought, where possible, directly from the original articles. Where observations had not been made at the desired concentration, the value tabulated has been determined by interpolation. Similarly, in the value obtained by calculation, we have made the necessary computations using the original data of the investigators where possible. The sources are detailed once for all below. Space is too valuable to give every result for each substance in full. Per-

Potassium chloride (C. P. from a reliable firm).—1.195 kg. was dissolved in 7200 g. of pure water, and on evaporation 41.175 g. of the solution was found in two closely agreeing trials to yield 5.862 g. of solid, indicating KCl, 24.93 H₂O. After adding the appropriate amount of water, 50.190 g. of the solution in two closely agreeing trials gave 13.6964 g. of silver chloride, indicating KCl, 25.02 H₂O. The specific heat of this solution was found to be 0.8319.

Cesium Chloride.—Rubidium chloride was not available in adequate quantity; but of cesium chloride we had enough, with care, to obtain significant results. Values for rubidium chloride may doubtless be obtained with considerable accuracy from the mean of the values for the potassium and cesium salts. The latter was prepared from pollucite from Maine, the initial preparation having been carried out by Dr. J. W. Shipley. The salt was purified according to the suggestion of H. L. Wells by crystallization of the dichloriodide, which gives an excellent means of separation, even from rubidium. 135.51 g. of the dry salt was dissolved in 860.91 g. of water, making a solution of the concentration CsCl, 50 H₂O.

The specific heat of this solution was found by direct measurement to be 0.8216.

Nitric acid (dilute) was made from pure redistilled acid and water and analyzed with weight burets by means of a carefully made standard sodium hydroxide solution. Three values (indicating 10.031, 10.032 and 10.032 H₂O) left no doubt as to its concentration. Its specific heat was son, *Ann. chim. phys.*, **3**, 33, 437 (1851); *Ann.*, **80**, 136 (1851). Schueller, *Ann. Phys.*, **136**, 70 (1869); Marignac, *Ann. Suppl.*, **8**, 335 (1872); Winkelmann, *Diss. Bonn.*, *Ann. Phys.*, **149**, 1 (1873); Marignac, *Ann. chim. phys.*, **5**, 8, 410 (1876); Hammerl, *Compt. rend.*, **90**, 694 (1880); Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882; Bluemcke, *Ann. phys.*, **23**, 161 (1884); Drecker, *ibid.*, **34**, 952 (1888); Mathias, *Compt. rend.*, **107**, 524 (1888). In this paper he indicates the empirical relation $n = (A + N)c/(B + N)$ where N = the number of mols of solvent per mol of solute, A and B are constants and c the specific heat of the solvent—in the present case equal to 1. By substituting two of the observed values of Thomsen, the equations may be solved for A and B . v. Strombeck, *Z. physik. Chem.*, **11**, 139 (1893); *J. Franklin Inst.*, Aug., 1892. Jacquerod, *Thèse*, Geneva, 1901.

Magie (*Phys. Rev.*, **25**, 171 (1907)) has evolved an empirical relation of the general form spec. heat = $(WN + A + Bp)/(WN + S)$, where W is the molecular heat of the solvent and N the number of mols, S the weight of a gram molecule of the solute, p the dissociation factor based upon the recalculated conductivity measurements of Kohlrausch and Holborn ("Leitvermoegeen der Elektrolyte") and A and B are constants. Substituting two of Thomsen's observed values, Magie solved for A and B . Bakowski (*Z. physik. Chem.*, **65**, 727 (1909)) subsequently printed a similar formula. See also Jacquerod, *J. chim. phys.*, **7**, 129 (1909); Noyes and Falk, *THIS JOURNAL*, **34**, 454 (1912); Pashskii, *J. Russ. Phys.-Chem. Soc.*, **43**, 166 (1911). He points out an empirical relation which is essentially a modification of that of Magie. Applied to aqueous solutions it takes the form $sD = X + AY - BXYa$, where s is the specific heat of the solution, D , the density, X the grams of solvent and Y the grams of solute in 1 cc. of the solution; a is the dissociation factor and A and B are constants.

taken as 0.763, as the most probable average of the more trustworthy published results.

Lithium nitrate, purified by frequent recrystallization, was made up into a solution of which (in two concordant trials) 65.117 g. yielded 8.6377 g. of the dry salt on evaporation. Its molal formula was therefore LiNO_3 , 25.03 H_2O . It contained still a little sodium nitrate, but not enough to vitiate the results. The specific heat of this solution was found to be 0.8803.

Sodium nitrate (1360 g.) was dissolved in 7.2 liters of water. Weighed portions of the solution on evaporation *in vacuo* indicated the composition NaNO_3 , 24.77 H_2O . To this solution the calculated amount of water was added to produce NaNO_3 , 25 H_2O , and the product was analyzed by means of the method of Busch,¹ using "nitron" ($\text{C}_{20}\text{H}_{16}\text{N}_4$). The results were 3% too low. Hence we once more evaporated the solution quantitatively *in vacuo*. In two trials 36.693 g. gave 5.821 g. of salt, indicating NaNO_3 , 25.03 H_2O . The specific heat of this solution was taken as 0.865, from the mean of the most trustworthy values.

Potassium nitrate solution was prepared in the same way, from similar excellent material. 39.025 g. of the solution in two concordant trials gave 7.1592 g. of solid indicating KNO_3 , 24.96 H_2O . The most probable specific heat seemed to be 0.833.

Cesium nitrate solution was made by dissolving 210.01 g. of very pure cesium nitrate in 1375.2 g. of water. The specific heat of this initial solution, CsNO_3 , 60 H_2O , was found to be 0.8395.

The **lithium hydroxide** available was less satisfactory. The best preparation which a well known firm could make especially for this work contained 11% of carbonate, 0.1% of sulfate and 0.78% of chloride. The two former impurities were eliminated by excess of barium hydroxide, precipitating the excess of barium as in the case of the other hydroxides;² but the chloride remained, together with a negligible amount of carbonate. Therefore the results can hardly be considered as more than preliminary. A mitigating circumstance lay in the fact that the heat of dilution of the chloride is almost exactly identical with that of the hydroxide, hence the error introduced by this impurity could not be large. The solution was prepared of such concentration that its alkalimetric titration indicated LiOH , 25 H_2O .

No data concerning the specific heat of this solution could be found. This basic quantity was therefore, computed from an earlier careful determination³ of LiOH , 100 H_2O (sp. ht. = 0.9813). The computation is easily made by means of the Kirchhoff equation, reversing the

¹ M. Busch, *Ber.*, **38**, 861 (1905).

² Richards and Rowe, *Proc. Am. Acad.*, **49**, 183 (1913).

³ *Ibid.*, p. 198.

calculation commonly used throughout this paper, with the help of the data for the dilution $\text{LiOH}, 25 \text{ H}_2\text{O} + 75 \text{ H}_2\text{O}$. The value 0.952 is thus found for the specific heat of $\text{LiOH}, 25 \text{ H}_2\text{O}$. The Magie formula with the help of the specific heats of the sodium and potassium solutions leads to the value 0.94, which is perhaps as near the more exact value given above as could be expected from this formula.

Sodium and potassium hydroxide solutions were prepared from sufficiently pure materials, removing and excluding carbon dioxide, in ways already sufficiently outlined. The specific heats of the solutions were chosen as follows: $\text{NaOH}, 10 \text{ H}_2\text{O}$, 0.855; and $\text{KOH}, 10 \text{ H}_2\text{O}$, 0.755, from the weighted average of many published results.

In general it may be said that although the material used in the preparation of the solutions described above was not of the highest grade of purity, such as would be used in researches upon atomic weights, nevertheless it was probably all of purity as high as was warranted by the other experimental refinements. The three kinds of results obtained are so different from one another that the effects of possible impurities upon the results tabulated in Tables II, III and IV below differed greatly according to circumstances. The heats of dilution would be much more affected by impurities than the changes of heat capacity, since the former data differed widely with different substances, whereas the latter are very similar. The most serious impurity in the case of the dilution of the hydroxides is usually dissolved carbon dioxide in water, which would evolve nearly 0.5 calorie per milligram on neutralization. With moderate dilution this might cause but little error, but evidently in the case of the greatest dilutions where over 7 liters of water per mol were present, a small percentage of carbon dioxide might cause appreciable error. Definite tests showed that the water used in these cases was pure enough for the purpose.

The Direct Determination of the Specific Heats of the Concentrated Solutions.

The data obtained concerning these solutions may be separated into two classes, the first including the data for the specific heats of several of the initial solutions, not adequately found by others, upon which the other data rest; and the second, including the data concerning dilution, which are the main subjects of the present paper.

The present section of the paper deals with those concentrated solutions in which the figures already published by others showed variations so great as to cause uncertainty, or those cases in which data were lacking altogether.

Determinations of the specific heats of the most concentrated solutions were made according to the method which has already been described

in full detail in a preceding paper¹—a definite weight of the solution being raised in temperature by the heat given out by neutralization of a known weight of dil. sulfuric acid in an enclosed, sunken receptacle, and the result being compared with a similar procedure carried out with a definite weight of pure water, calculated to the same temperature.

The calorimetric outfit had a total heat capacity of 134.06 cal. per degree (which includes that of the acid and alkali evolving the heat), in addition to that of the liquid to be determined. The following tables record the rise of temperature observed in a calorimeter having the heat capacity just mentioned, together with the number of grams of solution used in each case. Under the same conditions this same reaction raised 450.17 grams of water 4.070° when 19.35° was the final temperature, and 4.059° when 20.31° was the temperature.

In the table following are given in successive columns: first, the number of the experiment; second, the weight of solution used; third, the rise of temperature observed from the neutralization 109.36 g. of sulfuric acid in the inner vessel; fourth, the final temperature; and fifth, the calculated value of the specific heat from the foregoing data for the rise obtained in pure water.

TABLE I.—DIRECT DETERMINATION OF SPECIFIC HEATS OF INITIAL SOLUTIONS.

523.17 g. of solution taken for all experiments except those with cesium nitrate.

No.	$t_2 - t_1$.	t_2 .	Specific heat.
LiCl, 25 H ₂ O.			
1.....	3.944	19.70	0.8951
2.....	1.936	20.29	0.8954
3.....	1.9385	19.94	0.8959
4.....	1.946	19.37	0.8957
			0.8955
NaCl, 25 H ₂ O.			
1.....	3.9985	20.31	0.8774
2.....	4.001	19.80	0.8784
3.....	4.002	19.95	0.8776
4.....	4.005	19.38	0.8786
5.....	4.009	19.32	0.8777
			0.8779
KCl, 25 H ₂ O.			
1.....	4.1715	19.65	0.8325
2.....	4.1645	20.35	0.8321
3.....	4.1715	19.99	0.8314
4.....	4.1745	19.68	0.8316
			0.8319

¹ T. W. Richards and A. W. Rowe, *Proc. Am. Acad.*, **49**, 173 (1913); *Z. physik. Chem.*, **84**, 585 (1913). See especially pp. 190 and 601, respectively.

TABLE I (*Continued*).

No.	t_2-t_1 .	t_2 .	Specific heat.
CsCl, 50 H ₂ O.			
1.....	4.2135	19.65	0.8216
2.....	4.154	19.54	0.8217
3.....	4.153	19.54	0.8219
4.....	4.1455	20.40	0.8212
			0.8216
LiNO ₃ , 25 H ₂ O.			
1.....	3.995	19.58	0.8808
2.....	3.9895	20.31	0.8800
3.....	3.999	19.30	0.8806
4.....	3.991	20.21	0.8799
			0.8803
NaNO ₃ , 25 H ₂ O.			
1.....	4.036	19.35	0.8700
2.....	4.0325	19.71	0.8698
3.....	4.0265	20.46	0.8690
4.....	4.0295	19.96	0.8698
			0.8697
KNO ₃ , 25 H ₂ O.			
1.....	4.1685	19.58	0.8335
2.....	4.165	20.05	0.8329
3.....	4.1615	19.99	0.8340
4.....	4.1625	20.25	0.8329
			0.8333
CsNO ₃ , 60 H ₂ O.			
497.17 g. taken in Expt. 1; 533.17 g. taken in subsequent experiments.			
1.....	4.326	19.88	0.8394
2.....	4.0795	20.13	0.8394
3.....	4.0775	20.21	0.8397
4.....	4.088	19.39	0.8396
			0.8395

If space were less valuable it would be interesting to compare these results with those found by others, but this comparison must be omitted. It may be mentioned, however, that Marignac found NaCl, 25 H₂O to have the specific heat 0.877, Thomsen 0.882, whereas our value is 0.8779; for KCl, 25 H₂O Marignac found 0.833, Thomsen 0.825 and others values ranging from 0.825 to 0.863, as compared with our value 0.8319; for NaNO₃, 25 H₂O Marignac found 0.870, Thomsen 0.863, Magie 0.872, as compared with our value 0.8697; with nitric acid similarly, Marignac's results as usual were amazingly correct and Thomsen's and Magie's less near ours. The surprising accuracy of Marignac's early determinations speaks very well for the precision of that admirable experimenter, whose

work has perhaps never received the full credit which it deserves, either in this direction or in some others. His method was a very simple and comparatively crude one, but by many repetitions and by its consistent and uniform prosecution, it seems to have yielded in his hands an unusually satisfactory outcome. Our experience with the more dilute solutions given in the following tables confirms this conclusion.

The Dilution of the Concentrated Solutions.

The solutions named in the foregoing table as well as some others, were diluted at two different temperatures, t_1 and t_2 , according to a technique precisely similar to that indicated on pp. 1627 to 1632 of the previous paper. Averages of the data obtained are recorded in the following tables which are arranged precisely in the manner employed in the case of hydrochloric acid, just referred to, all the apparatus and details of experimentation having been exactly similar. Each of the figures given for rise of temperature (Δt_1 or Δt_2) is the average of at least two experiments. In every case enough trials were made to be sure of the thermometer readings to within 0.0005°.

TABLE II.—RISE OF TEMPERATURE ON DILUTION AT DIFFERENT TEMPERATURES.

Factors in reaction.	s_c .	Calorimeter.	t_2 °C.	$\Delta\theta =$ $t_2 - t_1$ °C.	Δt_1 °C.	Δt_2 °C.	$\Delta t_2 - \Delta t_1$ °C.
LiCl, 25 H ₂ O + 25 H ₂ O....	0.8955	A'a	20.76	5.05	+0.147	+0.159	+0.012
LiCl, 25 H ₂ O + 75 H ₂ O....	0.8955	Bc	20.73	5.12	+0.113	+0.127	+0.014
LiCl, 25 H ₂ O + 175 H ₂ O....	0.8955	Ab	20.74	5.15	+0.072	+0.083	+0.011
LiCl, 25 H ₂ O + 375 H ₂ O....	0.8955	Ac	20.75	5.12	+0.041	+0.047	+0.006
NaCl, 25 H ₂ O + 25 H ₂ O...	0.8779	Aa	20.5	4.93	-0.248	-0.210	+0.038
NaCl, 25 H ₂ O + 75 H ₂ O...	0.8779	Bc	20.6	4.96	-0.193	-0.162	+0.031
NaCl, 25 H ₂ O + 175 H ₂ O...	0.8779	Ab	20.6	5.12	-0.1145	-0.096	+0.0185
NaCl, 25 H ₂ O + 375 H ₂ O...	0.8779	Ac	20.7	5.20	-0.063	-0.050	+0.013
KCl, 25 H ₂ O + 25 H ₂ O....	0.8319	A'a	20.5	4.99	-0.225	-0.196	+0.029
KCl, 25 H ₂ O + 75 H ₂ O....	0.8319	Bc	20.6	5.10	-0.173	-0.148	+0.025
KCl, 25 H ₂ O + 175 H ₂ O....	0.8319	Ab	20.6	5.03	-0.103	-0.088	+0.015
KCl, 25 H ₂ O + 375 H ₂ O....	0.8319	Ac	20.7	5.13	-0.046	-0.056	+0.010
CsCl, 50 H ₂ O + 50 H ₂ O...	0.8216 ^a	A'a	20.2	4.35	-0.1115	-0.096	+0.0155
CsCl, 100 H ₂ O + 100 H ₂ O..	0.8995 ^b	A'a	20.1	4.35	-0.033	-0.028	+0.005
CsCl, 200 H ₂ O + 200 H ₂ O..	0.9464 ^b	A'a	20.0	4.51	-0.010	-0.009	+0.001
HNO ₃ , 10 H ₂ O + 15 H ₂ O..	0.763	Aa	19.7	3.45	+0.247	+0.337	+0.090
HNO ₃ , 10 H ₂ O + 40 H ₂ O..	0.763	Bc	20.8	5.15	+0.066	+0.160	+0.094
HNO ₃ , 10 H ₂ O + 90 H ₂ O..	0.763	Ac	19.8	3.68	+0.022	+0.063	+0.041
HNO ₃ , 10 H ₂ O + 190 H ₂ O..	0.763	Ac	19.7	3.67	+0.008	+0.031	+0.023
HNO ₃ , 10 H ₂ O + 390 H ₂ O..	0.763	Ac	19.8	3.84	+0.003	+0.016	+0.013
LiNO ₃ , 25 H ₂ O + 25 H ₂ O..	0.8803 ^a	Aa	20.3	4.77	+0.016	+0.037	+0.021
LiNO ₃ , 25 H ₂ O + 75 H ₂ O..	0.8803	Bb	20.0	4.01	+0.0185	+0.033	+0.0145

^a Obs. by direct measurement.

^b Calc. by Kirchoff's Rule (See Table III). The Cs salts were diluted progressively owing to small amount of available material.

TABLE II (Continued).

Factors in reaction.	s_c .	Calori- meter.	t_2 °C.	$\frac{\Delta\theta}{t_2-t_1}$ °C.	Δt_1 °C.	Δt_2 °C.	$\frac{\Delta t_2 - \Delta t_1}{t_2 - t_1}$
LiNO ₃ , 25 H ₂ O + 175 H ₂ O...	0.8803	Ab	20.0	3.94	+0.015	+0.025	+0.010
LiNO ₃ , 25 H ₂ O + 375 H ₂ O...	0.8803	Ac	20.3	4.02	+0.0105	+0.017	+0.006
NaNO ₃ , 25 H ₂ O + 25 H ₂ O.	0.8697	Aa	20.27	4.02	-0.487	-0.451	+0.036
NaNO ₃ , 25 H ₂ O + 75 H ₂ O.	0.8697	Bc	20.35	4.93	-0.406	-0.366	+0.040
NaNO ₃ , 25 H ₂ O + 175 H ₂ O.	0.8697	Ab	20.50	4.99	-0.249	-0.224	+0.025
NaNO ₃ , 25 H ₂ O + 375 H ₂ O.	0.8697	Ac	20.59	5.01	-0.136	-0.122	+0.014
KNO ₃ , 25 H ₂ O + 25 H ₂ O.	0.8333	Aa	20.05	4.51	-0.715	-0.675	+0.040
KNO ₃ , 25 H ₂ O + 75 H ₂ O.	0.8333	Bc	20.18	3.88	-0.591	-0.555	+0.036
KNO ₃ , 25 H ₂ O + 175 H ₂ O.	0.8333	Ab	20.41	4.96	-0.375	-0.347	+0.028
KNO ₃ , 25 H ₂ O + 375 H ₂ O.	0.8333	Ac	20.52	5.07	-0.208	-0.192	+0.016
CsNO ₃ , 60 H ₂ O + 40 H ₂ O.	0.8395 ^a	Bb	19.5	3.87	-0.176	-0.1635	+0.0125
CsNO ₃ , 100 H ₂ O + 100 H ₂ O	0.8945 ^b	A'a	20.2	4.31	-0.079	-0.0705	+0.0085
CsNO ₃ , 200 H ₂ O + 200 H ₂ O	0.9427 ^b	A'a	20.0	4.63	-0.023	-0.0215	+0.0015
LiOH, 25 H ₂ O + 25 H ₂ O...	0.952	Aa	19.6	3.55	+0.119	+0.143	+0.024
LiOH, 25 H ₂ O + 75 H ₂ O...	0.952	Bc	19.9	3.83	+0.097	+0.121	+0.024
LiOH, 25 H ₂ O + 175 H ₂ O...	0.952	Ac	19.8	3.67	+0.065	+0.078	+0.013
LiOH, 25 H ₂ O + 375 H ₂ O...	0.952	Ac	19.8	3.77	+0.040	+0.046	+0.006
NaOH, 10 H ₂ O + 15 H ₂ O.	0.855	A'a	20.1	3.98	+0.006	+0.124	+0.118
NaOH, 10 H ₂ O + 40 H ₂ O.	0.855	Ab	20.0	4.26	-0.167	-0.057	+0.104
NaOH, 10 H ₂ O + 90 H ₂ O.	0.855	Ac	19.8	3.88	-0.131	-0.072	+0.059
NaOH, 5.76 H ₂ O + 94.24 H ₂ O.....	0.834	Ac	19.8	2.95	+0.242	+0.302	+0.060
NaOH, 5.76 H ₂ O + 94.24 H ₂ O.....	0.834	Ac	19.8	3.99	+0.220	+0.302	+0.082
NaOH, 10 H ₂ O + 190 H ₂ O.	0.855	Ac	19.8	3.78	-0.078	-0.044	+0.034
NaOH, 5.76 H ₂ O + 194.24 H ₂ O.....	0.834	Ac	19.7	4.10	+0.100	+0.144	+0.044
NaOH, 10 H ₂ O + 390 H ₂ O.	0.855	Ac	19.8	3.88	-0.041	-0.023	+0.018
KOH, 10 H ₂ O + 15 H ₂ O...	0.755	Bb	19.8	3.25	+0.638	+0.724	+0.086
KOH, 10 H ₂ O + 40 H ₂ O...	0.755	Bc	20.7	4.82	+0.319	+0.412	+0.093
KOH, 10 H ₂ O + 90 H ₂ O...	0.755	Ac	19.7	3.67	+0.158	+0.203	+0.045
KOH, 10 H ₂ O + 190 H ₂ O...	0.755	Ac	19.8	3.77	+0.080	+0.105	+0.025
KOH, 10 H ₂ O + 390 H ₂ O...	0.755	Ac	19.8	3.70	+0.041	+0.055	+0.014

^a Obs. by direct measurement.

^b Calc. by Kirchoff's Rule (See Table III). The Cs salts were diluted progressively, owing to small amount of available material.

The results just given may be used for calculating two different but allied quantities, namely, the heat of dilution on the one hand and the specific heat of the dilute solution on the other. The mode of calculation is sufficiently explained in the previous paper (p. 1632). There follow the results for the heat of dilution of the several solutions. The table is, of course, an amplification of that immediately preceding. The atomic weights used are those of the international table: O = 16.00; H = 1.008; Li = 6.94; Na = 23.0, K = 39.10, Cl = 35.46; etc.

TABLE III.—HEATS OF DILUTION AND THEIR TEMPERATURE COEFFICIENTS.

Factors in reaction.	Heat cap of factors. K_M .	$\Delta\theta$ ° C.	U $K_M f \Delta t_1$ calories.	U' $K_M f \Delta t_2$ calories.	$\frac{\Delta U}{\Delta\theta}$ $= K_M - K'_M$ cal./° C.	Heat of dilution U_{20° calories.
LiCl, 25 H ₂ O + 25 H ₂ O....	891.7	5.05	+133.1	+143.7	+2.1	+142
LiCl, 25 H ₂ O + 75 H ₂ O....	1792.5	5.12	+266.6	+231.6	4.9	+228
LiCl, 25 H ₂ O + 175 H ₂ O....	3594.1	5.15	+263.0	+302.0	7.6	+296
LiCl, 25 H ₂ O + 375 H ₂ O....	7197.3	5.12	+298.0	+343.0	8.8	+337
NaCl, 25 H ₂ O + 25 H ₂ O....	897.1	4.93	-225.0	-191.4	+6.8	-195
NaCl, 25 H ₂ O + 75 H ₂ O....	1797.9	4.96	-354	-298	11.1	-305
NaCl, 25 H ₂ O + 175 H ₂ O....	3599.5	5.12	-418	-351	13.1	-359
NaCl, 25 H ₂ O + 375 H ₂ O....	7202.7	5.20	-461	-366	18.2	-379
KCl, 25 H ₂ O + 25 H ₂ O....	887.1	4.99	-203	-177	+5.2	-180
KCl, 25 H ₂ O + 75 H ₂ O....	1787.9	5.10	-315	-270	8.9	-275
KCl, 25 H ₂ O + 175 H ₂ O....	3589.5	5.03	-375	-321	10.8	-328
KCl, 25 H ₂ O + 375 H ₂ O....	7192.7	5.13	-409	-336	14.2	-346
RbCl, 50 H ₂ O + 50 H ₂ O....	[-134]
RbCl, 100 H ₂ O + 100 H ₂ O....	[-78]
CsCl, 50 H ₂ O + 50 H ₂ O....	1778.3	4.35	-201	-173	+6.4	-174
CsCl, 100 H ₂ O + 100 H ₂ O....	3573.5	4.35	-119	-102	4.0	-103
CsCl, 200 H ₂ O + 200 H ₂ O....	7172.6	4.51	-73	-66	1.6	-66
HNO ₃ , 10 H ₂ O + 15 H ₂ O....	455.8	3.45	+116	+157	+11.5	+160
HNO ₃ , 10 H ₂ O + 40 H ₂ O....	906.2	5.15	+61	+148	16.9	+135
HNO ₃ , 10 H ₂ O + 90 H ₂ O....	1807.0	3.68	+41	+115	20.1	+119
HNO ₃ , 10 H ₂ O + 190 H ₂ O....	3608.6	3.67	+31	+113	22.3	+119
HNO ₃ , 10 H ₂ O + 390 H ₂ O....	7211.8	3.84	+26	+117	23.7	+122
LiNO ₃ , 25 H ₂ O + 25 H ₂ O....	907.6	4.77	+15	+34	+4.0	+33
LiNO ₃ , 25 H ₂ O + 75 H ₂ O....	1808.4	4.01	+34	+61	6.7	+61
LiNO ₃ , 25 H ₂ O + 175 H ₂ O....	3609.9	3.94	+54	+93	9.8	+93
LiNO ₃ , 25 H ₂ O + 375 H ₂ O....	7212.9	4.02	+77	+123	11.4	+120
NaNO ₃ , 25 H ₂ O + 25 H ₂ O....	916.0	4.02	-452	-419	+8.2	-421
NaNO ₃ , 25 H ₂ O + 75 H ₂ O....	1816.8	4.93	-752	-678	15.0	-683
NaNO ₃ , 25 H ₂ O + 175 H ₂ O....	3618.4	4.99	-913.2	-822.6	18.2	-829
NaNO ₃ , 25 H ₂ O + 375 H ₂ O....	7221.6	5.01	-995	-893	20.4	-905
KNO ₃ , 25 H ₂ O + 25 H ₂ O....	909.4	4.51	-662	-625	+10.5	-625
KNO ₃ , 25 H ₂ O + 75 H ₂ O....	1810.2	3.88	-1093	-1024	17.7	-1027
KNO ₃ , 25 H ₂ O + 175 H ₂ O....	3611.8	4.96	-1370	-1269	20.4	-1277
KNO ₃ , 25 H ₂ O + 375 H ₂ O....	7215.0	5.07	-1521	-1404	23.0	-1416
RbNO ₃ , 100 H ₂ O + 100 H ₂ O....	[-255]
CsNO ₃ , 60 H ₂ O + 40 H ₂ O....	1791.6	3.87	-319	-296	+5.8	-293
CsNO ₃ , 100 H ₂ O + 100 H ₂ O....	3587.5	4.31	-289	-258	7.2	-260
CsNO ₃ , 200 H ₂ O + 200 H ₂ O....	7183.5	4.63	-169	-158	2.3	-158
LiOH, 25 H ₂ O + 25 H ₂ O....	902.1	3.55	+109	+131	+6.2	+133
LiOH, 25 H ₂ O + 75 H ₂ O....	1802.9	3.83	+178	222	11.5	+223
LiOH, 25 H ₂ O + 175 H ₂ O....	3604.5	3.67	+238	285	13.0	+288
LiOH, 25 H ₂ O + 375 H ₂ O....	7207.7	3.77	+292	337	11.8	+338
NaOH, 10 H ₂ O + 15 H ₂ O....	457.4	3.98	-3	+58	+13.8	+56
NaOH, 10 H ₂ O + 40 H ₂ O....	907.8	4.26	-149	-53	+22.5	-55
NaOH, 10 H ₂ O + 90 H ₂ O....	1808.5	3.88	-240	-132	+27.8	-127

TABLE III (Continued).

Factors in reaction.	Heat cap of factors. K_M .	$\Delta\theta$ ° C.	U $K_M f \Delta t$ calories.	U' $K_M f \Delta t$ calories.	$\frac{\Delta U}{\Delta\theta}$ $= K_M - K'_M$ cal./° C.	Heat of dilution U_{20}° calories.
NaOH, 5.76 H ₂ O + 94.24						
H ₂ O.....	1818.0	2.95	+447	+556	+37.5	+564
NaOH, 5.76 H ₂ O + 94.24						
H ₂ O.....	1818.0	3.99	+406	+556	+37.5	+564
NaOH, 10 H ₂ O + 190 H ₂ O..	3610	3.78	-286	-161	+33.1	-156
NaOH, 5.76 H ₂ O + 194.24						
H ₂ O.....	3610.5	4.10	+367	+529	+39.5	+541
NaOH, 10 H ₂ O + 390 H ₂ O..	7223.0	3.88	-300	-168	+34.0	-161
KOH, 10 H ₂ O + 15 H ₂ O...	448.6	3.25	+292	+332	+12.3	+334
KOH, 10 H ₂ O + 40 H ₂ O...	899.0	4.82	+293	+378	17.6	+366
KOH, 10 H ₂ O + 90 H ₂ O....	1799.8	3.67	+287	+370	22.6	+376
KOH, 10 H ₂ O + 190 H ₂ O...	3601.4	3.77	+290	+384	24.9	+388
KOH, 10 H ₂ O + 390 H ₂ O...	7204.6	3.70	+300	+402	27.6	+408

Yet another table, depending upon both of those given before, records the steps in the calculation of the specific heats of the dilute solutions as follows. The results for rubidium in both the foregoing and the following tables are interpolated between those for potassium and cesium, and are, of course, only probable approximations.

TABLE IV.—CHANGE OF HEAT CAPACITY, AND SPECIFIC HEATS.

Factors in reaction.	$K_M =$ heat cap. of factors.	$K_M - K'_M =$ $\Delta U_M / \Delta\theta$.	$K'_M =$ heat cap. of product. (ent./° C.)	Molal wt. of product.	Product.	Sp. heat of product. $S'_d = K'_M / M$.
LiCl, 25 H ₂ O.....	441.3	492.8	LiCl, 25 H ₂ O	0.8955
LiCl, 25 H ₂ O + 25 H ₂ O...	891.7	2.1	889.6	943.2	LiCl, 50 H ₂ O	0.9432
LiCl, 25 H ₂ O + 75 H ₂ O...	1792.5	4.9	1787.6	1844.0	LiCl, 100 H ₂ O	0.9694
LiCl, 25 H ₂ O + 175 H ₂ O...	3594.1	7.6	3586.5	3645.6	LiCl, 200 H ₂ O	0.9838
LiCl, 25 H ₂ O + 375 H ₂ O...	7197.3	8.8	7188.5	7248.2	LiCl, 400 H ₂ O	0.9918
NaCl, 25 H ₂ O.....	446.7	508.86	NaCl, 25 H ₂ O	0.8779
NaCl, 25 H ₂ O + 25 H ₂ O...	897.1	6.9	890.2	959.3	NaCl, 50 H ₂ O	0.9280
NaCl, 25 H ₂ O + 75 H ₂ O...	1797.9	11.2	1786.7	1860.1	NaCl, 100 H ₂ O	0.9605
NaCl, 25 H ₂ O + 175 H ₂ O...	3599.5	13.3	3586.2	3661.7	NaCl, 200 H ₂ O	0.9794
NaCl, 25 H ₂ O + 375 H ₂ O...	7202.7	18.2	7184.5	7264.9	NaCl, 400 H ₂ O	0.9889
KCl, 25 H ₂ O.....	436.7	524.96	KCl, 25 H ₂ O	0.8319
KCl, 25 H ₂ O + 25 H ₂ O...	887.1	5.2	881.4	975.4	KCl, 50 H ₂ O	0.9036
KCl, 25 H ₂ O + 75 H ₂ O...	1787.9	8.9	1779.0	1876.2	KCl, 100 H ₂ O	0.9482
KCl, 25 H ₂ O + 175 H ₂ O...	3589.5	10.8	3578.7	3677.8	KCl, 200 H ₂ O	0.9731
KCl, 25 H ₂ O + 375 H ₂ O...	7192.7	14.2	7178.5	7281.0	KCl, 400 H ₂ O	0.9859
RbCl, 50 H ₂ O.....	(880)	1021.7	RbCl, 50 H ₂ O	[0.8613]
RbCl, 100 H ₂ O.....	(1774)	1922.5	RbCl, 100 H ₂ O	[0.9228]
RbCl, 200 H ₂ O.....	(3574)	3722.1	RbCl, 200 H ₂ O	[0.9575]
RbCl, 400 H ₂ O.....	(7175)	7325.7	RbCl, 400 H ₂ O	[0.9794]

TABLE IV (Continued).

Factors in reaction.	$K'M =$ heat cap. of factors.	$K'M - K'M =$ $\Delta U_M / \Delta \theta$.	$K'M =$ heat cap. of product. (cal./° C.)	Molal wt. of product.	Product.	Sp. heat of product. $S_d = K'M/M$.
CsCl, 25 H ₂ O.....	878.9	1069.7	CsCl, 50 H ₂ O	0.8216
CsCl, 50 H ₂ O + 50 H ₂ O.	1778.3	6.4	1771.9	1969.9	CsCl, 100 H ₂ O	0.8995
CsCl, 100 H ₂ O + 100 H ₂ O.	3573.5	4.0	3569.4	3771.5	CsCl, 200 H ₂ O	0.9464
CsCl, 200 H ₂ O + 200 H ₂ O.	7172.6	1.6	7171.0	7374.7	CsCl, 400 H ₂ O	0.9723
HNO ₃ , 10 H ₂ O + 15 H ₂ O.	455.8	11.5	444.3	513.42	HNO ₃ + 25 H ₂ O	0.8654
HNO ₃ , 10 H ₂ O + 40 H ₂ O.	906.2	16.9	889.3	963.8	HNO ₃ + 50 H ₂ O	0.9227
HNO ₃ , 10 H ₂ O + 90 H ₂ O.	1807.0	20.1	1786.9	1864.6	HNO ₃ + 100 H ₂ O	0.9583
HNO ₃ , 10 H ₂ O + 190 H ₂ O.	3608.6	22.3	3586.3	3666.2	HNO ₃ + 200 H ₂ O	0.9782
HNO ₃ , 10 H ₂ O + 390 H ₂ O.	7211.8	23.7	7188.1	7269.4	HNO ₃ + 400 H ₂ O	0.9888
LiNO ₃ , 25 H ₂ O.....	457.2	519.4	LiNO ₃ + 25 H ₂ O	0.8803
LiNO ₃ , 25 H ₂ O + 25 H ₂ O	907.6	4.0	903.6	969.8	LiNO ₃ + 50 H ₂ O	0.9400
LiNO ₃ , 25 H ₂ O + 75 H ₂ O	1808.4	6.5	1801.9	1870.5	LiNO ₃ + 100 H ₂ O	0.9703
LiNO ₃ , 25 H ₂ O + 175 H ₂ O	3609.9	9.2	3600.7	3672.0	LiNO ₃ + 200 H ₂ O	0.9856
LiNO ₃ , 25 H ₂ O + 375 H ₂ O	7212.9	11.6	7201.6	7275.0	LiNO ₃ + 400 H ₂ O	0.9931
NaNO ₃ , 25 H ₂ O.....	465.6	535.4	NaNO ₃ , 25 H ₂ O	0.8697
NaNO ₃ , 25 H ₂ O + 25 H ₂ O	916.0	8.2	907.8	985.8	NaNO ₃ , 50 H ₂ O	0.9209
NaNO ₃ , 25 H ₂ O + 75 H ₂ O	1816.8	15.0	1801.8	1886.6	NaNO ₃ , 100 H ₂ O	0.9549
NaNO ₃ , 25 H ₂ O + 175 H ₂ O	3618.4	18.2	3600.2	3688.2	NaNO ₃ , 200 H ₂ O	0.9760
NaNO ₃ , 25 H ₂ O + 375 H ₂ O	7221.6	20.4	7201.2	7291.4	NaNO ₃ , 400 H ₂ O	0.9876
KNO ₃ , 25 H ₂ O.....	459.0	551.5	KNO ₃ , 25 H ₂ O	0.8319
KNO ₃ , 25 H ₂ O + 25 H ₂ O	909.4	10.5	898.9	1001.9	KNO ₃ , 50 H ₂ O	0.8972
KNO ₃ , 25 H ₂ O + 75 H ₂ O.	1810.2	17.7	1792.5	1902.7	KNO ₃ , 100 H ₂ O	0.9421
KNO ₃ , 25 H ₂ O + 175 H ₂ O.	3611.8	20.4	3591.4	3704.3	KNO ₃ , 200 H ₂ O	0.9695
KNO ₃ , 25 H ₂ O + 375 H ₂ O.	7215.0	23.0	7192.0	7307.5	KNO ₃ , 400 H ₂ O	0.9842
RbNO ₃ , 100 H ₂ O.....	(1789)	1949.0	RbNO ₃ , 100 H ₂ O	[0.9180]
RbNO ₃ , 200 H ₂ O.....	(3585)	3750.7	RbNO ₃ , 200 H ₂ O	[0.9558]
RbNO ₃ , 400 H ₂ O.....	(7186)	7353.9	RbNO ₃ , 400 H ₂ O	[0.9772]
CsNO ₃ , 60 H ₂ O.....	1071.0	1275.8	CsNO ₃ , 60 H ₂ O	0.8395
CsNO ₃ , 60 H ₂ O + 40 H ₂ O	1791.6	5.8	1785.8	1996.4	CsNO ₃ , 100 H ₂ O	0.8945
CsNO ₃ , 100 H ₂ O + 100 H ₂ O	3587.5	7.2	3580.3	3798.0	CsNO ₃ , 200 H ₂ O	0.9427
CsNO ₃ , 200 H ₂ O + 200 H ₂ O	7183.5	2.3	7181.2	7401.2	CsNO ₃ , 400 H ₂ O	0.9703
LiOH, 25 H ₂ O.....	451.7	474.3	LiOH, 50 H ₂ O	0.9520
LiOH, 25 H ₂ O + 25 H ₂ O..	902.1	6.2	895.9	924.7	LiOH, 50 H ₂ O	0.9689
LiOH, 25 H ₂ O + 75 H ₂ O..	1802.9	11.5	1791.4	1825.5	LiOH, 100 H ₂ O	0.9813
LiOH, 25 H ₂ O + 175 H ₂ O..	3604.5	13.0	3591.5	3627.1	LiOH, 200 H ₂ O	0.9902
LiOH, 25 H ₂ O + 375 H ₂ O..	7207.7	11.8	7195.9	7229.3	LiOH, 400 H ₂ O	0.9954
NaOH, 10 H ₂ O + 15 H ₂ O..	457.4	13.8	443.6	490.4	NaOH, 25 H ₂ O	0.9046
NaOH, 10 H ₂ O + 40 H ₂ O..	907.8	22.5	885.3	940.0	NaOH, 50 H ₂ O	0.9418
NaOH, 10 H ₂ O + 90 H ₂ O..	1808.5	27.7	1780.8	1841.6	NaOH, 100 H ₂ O	0.9670
NaOH, 5.76 H ₂ O + 94.24 H ₂ O.....	1818.0	37.5	1780.5	1841.6	NaOH, 100 H ₂ O	0.9668
NaOH, 5.76 H ₂ O + 94.24 H ₂ O.....	1818.0	37.5	1780.5	1841.6	NaOH, 100 H ₂ O	0.9668

TABLE IV (Continued).

Factors in reaction.	$KM =$ heat cap. of factors.	$K'M =$ $\Delta UM/\Delta\theta$.	$K''M =$ heat cap. of product. (cal./° C.)	Molal wt. of product.	Product.	Sp. heat of product. $S_d = K''M/M$.
NaOH, 10 H ₂ O + 190 H ₂ O	3610.0	33.1	3576.9	3643.2	NaOH, 200 H ₂ O	0.9818
NaOH, 5.76 H ₂ O + 194.24 H ₂ O.....	3619.1	38.6	3580.5	3643.2	NaOH, 200 H ₂ O	0.9828
NaOH, 10 H ₂ O + 390 H ₂ O	7213.3	34.0	7179.3	7246.4	NaOH, 400 H ₂ O	0.9907
KOH, 10 H ₂ O + 15 H ₂ O...	448.60	12.3	436.3	506.5	KOH, 25 H ₂ O	0.8614
KOH, 10 H ₂ O + 40 H ₂ O..	899.0	17.6	881.4	956.9	KOH, 50 H ₂ O	0.9211
KOH, 10 H ₂ O + 90 H ₂ O..	1799.8	22.6	1777.2	1859.7	KOH, 100 H ₂ O	0.9556
KOH, 10 H ₂ O + 190 H ₂ O..	3601.4	24.9	3576.5	3659.3	KOH, 200 H ₂ O	0.9773
KOH, 10 H ₂ O + 390 H ₂ O..	7204.6	27.6	7177.0	7262.5	KOH, 400 H ₂ O	0.9882

In order to verify the foregoing results and to exhibit experimentally the probable error of a single experiment, a number of individual dilutions were made (after the foregoing trials had been finished) at various temperatures. The actual results obtained from these experiments were then compared with the heats of dilution calculated for the appropriate temperature (t_2) from the data given in the foregoing tables. The differences between the results of these individual experiments and the calculated values are given in the final column of the table below. It will be seen that only 6 of the 23 experiments show an error of more than one calorie in the observed value, and that the experimental errors are about equally positive and negative. Since each of the values given in the foregoing tables represents an average of at least two determinations, the final results in these tables appear to be as trustworthy as could be expected, in the light of these check determinations. Nevertheless, as stated in the preceding paper, one cannot but wish that the thermometer could have been relied upon to within 0.0001°. Such inaccuracy as may be found later in the work should probably be referred to the calibration of the thermometer, which, although conducted with meticulous care, remains the least certain part of the investigation.

The most serious possible cause of error lies in the calibration of this thermometer. If the degrees at the opposite ends of the range 16° to 20° were different in length, the difference would appear with large percentage effect in the essential value $\Delta t_2 - \Delta t_1$. However, the evidence inherent in the results indicates that such an error did not exist in important degree. In the first place, the error would produce an opposite effect with a minus heat of dilution to that which it would produce with a plus heat of dilution. We find, however, that in 4 typical comparable cases, such as potassium chloride and potassium hydroxide (one of which absorbs heat, whereas the other gives out heat on dilution), the

values of the temperature coefficients are essentially alike. Yet more convincing is the fact that the actual direct determination of the specific heats of the dilute solutions agrees very closely with that found with the help of the dilution method under discussion.¹ Other verifications are given later in this paper.

The control determinations follow.

TABLE V.—CONTROL DETERMINATIONS.

Final conc.	t_2 °C.	$t_2 - t_1$ °C.	U_M (obs.)	U_M (calc.)	Diff.
Dilution of NaCl, 25 H ₂ O:					
50 H ₂ O	17.09	-0.237	-216	-216	≠0
100 H ₂ O	18.18	-0.177	-325	-325	≠0
200 H ₂ O	18.28	-0.104	-379	-382	+3
400 H ₂ O	20.04	-0.052	-379	-379	≠0
400 H ₂ O	20.05	-0.052	-379	-379	≠0
Dilution of KCl, 25 H ₂ O:					
50 H ₂ O	19.01	-0.205	-185	-185	≠0
100 H ₂ O	18.59	-0.159	-290	-288	-2
200 H ₂ O	17.96	-0.095	-346	-347	+1
400 H ₂ O	19.15	-0.049	-357	-358	+1
Dilution of HNO ₃ , 10 H ₂ O:					
50 H ₂ O	18.30	+0.117	+108	+107	+1
400 H ₂ O	18.09	0.0155	77	+77	≠0
Dilution of NaNO ₃ , 25 H ₂ O:					
50 H ₂ O	18.69	-0.468	-435	-439	+4
100 H ₂ O	18.08	-0.386	-715	-712	-3
200 H ₂ O	16.33	-0.246	-901	-896	-5
400 H ₂ O	17.11	-0.130	-951	-952	+1
Dilution of KNO ₃ , 25 H ₂ O:					
50 H ₂ O	17.83	-0.701	-648	-648	≠0
100 H ₂ O	17.82	0.577	-1067	-106	-1
200 H ₂ O	17.53	0.362	-1324	-1328	+4
400 H ₂ O	18.60	0.198	-1448	-1448	≠0
Dilution of KOH, 10 H ₂ O:					
50 H ₂ O (b)	19.09	+0.383	+351	+350	+1
200 H ₂ O	19.80	0.105	383	383	≠0
400 H ₂ O	18.17	0.049	358	357	+1
400 H ₂ O	19.76	0.055	402	402	≠0

The comparison of the results with those of Marignac and Thomsen (whose work, although not comprehending so many alkali metals, most nearly covered the same ground) shows reasonably close agreement. The results for four salts included in both investigations in which Marignac's temperature range most nearly approached ours (16° to 20°) are as follows:

¹ Richards and Rowe, THIS JOURNAL, 42, 1633 (1920).

Comparison of the New Results with Marignac's and Thomsen's.

SPECIFIC HEATS OF HECTOHYDRATED SOLUTIONS.

	Thomsen.	Marignac.	Richards and Rowe.	Difference. (R. and R.)—M
NaCl.....	0.962	0.9596	0.9605	+0.0009
KCl.....	0.948	0.9483	0.9482	—0.0001
NaNO ₃	0.950	0.9545	0.9549	+0.0004
KNO ₃	0.942	0.9430	0.9421	—0.0009

Average difference, ± 0.0006

Average error of Marignac, $+0.0001$

Marignac's figures are evidently somewhat better than Thomsen's. Not quite all of Marignac's results show as good agreement with the new ones, but the wider differences are usually due to a widely different temperature range (20–50°). The most serious discrepancy is for KNO₃, 50 H₂O, which Marignac makes 0.9005, whereas the new value is 0.8972. Here Thomsen's result, 0.901, agrees with Marignac's rather than with ours, nevertheless we have been able to find no especial reason for error in ours. On the whole, each investigation supports the other.

Collation and Interpretation of Results.

The outcome must now be tabulated systematically in order to clarify the mutual relations of the figures. The essential results are given below in 3 tables, giving respectively (Table VI) the heats of dilution at 20°; (Table VII) the temperature coefficients of these values (which are equal to the change of heat capacity during the dilution); and (Table VIII) the molal heat capacities. A few words of description and explanation follow each. The values for the specific heats calculated from the last named results have already been given in Table IV. These do not lend

TABLE VI.—HEATS OF DILUTION IN JOULES AT 20°.

Initial solution.	Final solutions (total mols. water).			
	50 H ₂ O.	100 H ₂ O.	200 H ₂ O.	400 H ₂ O.
HCl, 25 H ₂ O.....	+982	+1538	+1868	+2111
LiCl, 25 H ₂ O.....	+594	+953	+1237	+1409
NaCl, 25 H ₂ O.....	—815	—1275	—1501	—1584
KCl, 25 H ₂ O.....	—752	—1150	—1371	—1446
KCl, 50 H ₂ O (calc.)..	—397	—619	—694
(RbCl, 50 H ₂ O).....	(—560)	(—886)	(—1066)
CsCl, 50 H ₂ O.....	—727	—1158	—1434
HNO ₃ , 25 H ₂ O.....	—105	—171	—171	—159
LiNO ₃ , 25 H ₂ O.....	+137	+255	+389	+502
NaNO ₃ , 25 H ₂ O.....	—1760	—2855	—3465	—3783
KNO ₃ , 25 H ₂ O.....	—2613	—4293	—5338	—5919
RbNO ₃ , 100 H ₂ O...	(—1066)	(—1689)
CsNO ₃ , 60 H ₂ O.....	—1225	—2312	—2972
LiOH, 25 H ₂ O.....	+556	+932	+1204	+1413
NaOH, 25 H ₂ O.....	+4	—297	—418	—439
KOH, 25 H ₂ O.....	+134	+176	+226	+309

themselves to logical comparison; they are inferior to gram-molecular heat capacities for purposes of physico-chemical reasoning, although practically useful.

The results for hydrochloric and nitric acids and sodium and potassium hydroxides have been reduced to the 25 H₂O initial basis, in order to make their circumstances parallel with those of the other salts. All the data are given in the c. g. s. system, for the benefit of those desiring to use them in this system, assuming 1 calorie 20° = 4.180 joules. Those preferring the calorie standard can, of course, easily construct a similar table from the foregoing figures.

Several interesting points are brought out by this table. Especially it is seen that whereas the heat of dilution of the lithium compounds is always positive, that of the sodium compounds included in the table is always negative, except in the case of very concentrated sodium hydroxide. The chlorides have an effect more positive than that of the nitrates in all six cases. Potassium chloride and nitrate resemble the sodium salts closely; but the hydroxides are very different—sodium hydroxide absorbs heat (except with very concentrated solutions) on dilution, whereas potassium hydroxide gives out heat at every stage of the dilution. Sodium hydroxide is practically "thermo neutral" on diluting from 25 H₂O to 50 H₂O. This last named peculiarity (as well as the similar behavior of nitric acid between 100 and 200 H₂O) was discovered by Thomsen,¹ although his results are not exactly comparable with ours because of his having found them at a different temperature. The data for cesium, now available for the first time, are seen to be like those for potassium in general character. Those for rubidium are obtained by interpolation between those for these two similar metals. In the case of the chloride the gap to be bridged is large, and the results doubtful; in that of the nitrate the result is probably more trustworthy.

These results are plotted in the accompanying diagram (Fig. 1), which depicts them in the most nearly linear relationship. Heats of dilution are plotted as ordinates, and fractions of a gram mol of salts present for each mol of water are plotted as abscissas. The left-hand edge of the diagram represents infinite dilution. The values usually lie upon smooth, almost linear curves. Dilution from 200 H₂O to 400 H₂O is seen usually to involve a dilution-heat (either positive or negative) of about 10 to 20% (with cesium salts much more) of the total dilution heat up to that point. In no case, apparently, has the limit of the dilution heat been reached at 400 H₂O. The extrapolation to infinite dilution evidently indicates additional heat of dilution, usually about equal to that evolved in dilution from 200 H₂O to 400 H₂O, but occasionally a somewhat greater

¹ Thomsen, "Thermochem. Untersuch.," [III] 1883, p. 84.

quantity. The eccentricity of sodium hydroxide stands out in the middle of the diagram.

The relation, if any, of these results to the degree of ionization is worth discovering. Evidently their verdict is qualitatively similar to that of conductivity. Let us take, for instance, the case of sodium chloride, NaCl , 25 H_2O , which is about 2.13 N . For a moment, putting aside the

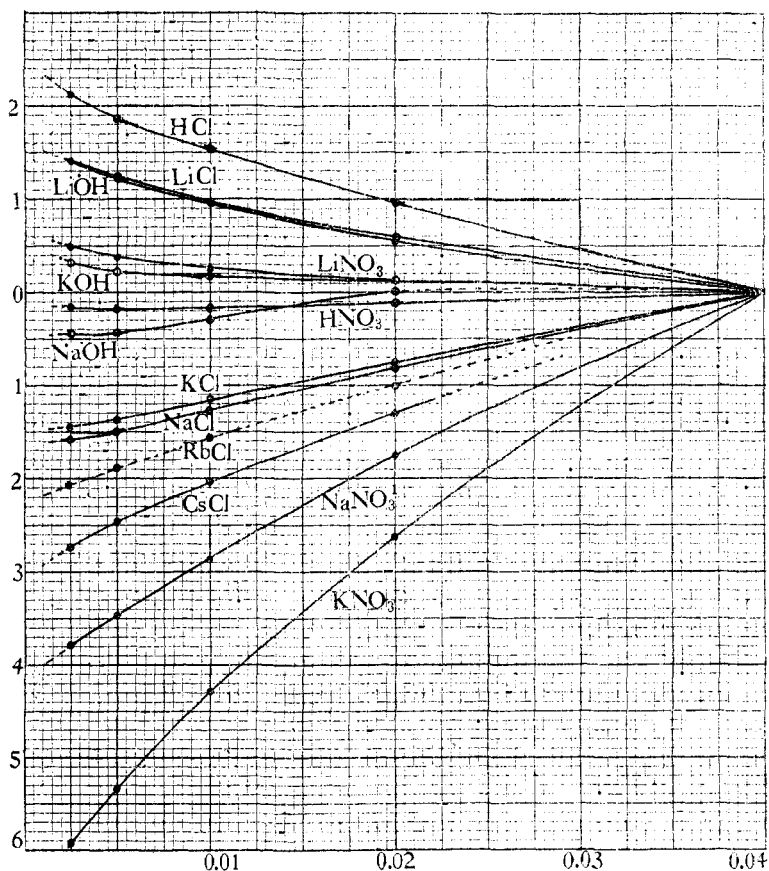


Fig. 1.—Heats of dilution of chlorides, nitrates and hydroxides. Heats of dilution are plotted in kilojoules as ordinates; abscissas represent fractions of mol of salt per mol of water. The left hand edge represents infinite dilution. Extrapolation, interpolation or doubtful data are represented by dotted lines.

doubt which now exists as to the best method of determining the degree of dissociation, let us assume on the basis of Kohlrausch's conductivity measurements that the dissociation of this solution is 57%. The chief phenomenon concerned in further dilution may be supposed to be ionization, since probably whatever molecular hydration exists had almost

attained saturation with so much water present. The almost perfectly straight line corresponding to sodium chloride tells us that (as regards dilution heat) NaCl, 50 H₂O is half way between its condition as 25 H₂O and that at infinite dilution. Then, half of the salt associated at 25 H₂O must be dissociated at 50 H₂O, if dilution heat is taken as a criterion, or the dissociation at 50 H₂O must be 78%. This, although qualitatively in the expected direction, is much more than the additional dissociation indicated by conductivity—the degree of dissociation corresponding to NaCl 50 H₂O (or about 1.086 *N*) being 67%. Evidently the curve for lithium chloride corresponds somewhat more closely to the conductivity data, for it curves upward; but none of the curves agrees exactly with the indications of electrolytic conductivity. No attempt will be made here to decide the question as to whether the defects in the criterion of dissociation on the one hand, or the question as to the possibility of the presence of some other heat-evolving phenomenon besides dissociation on the other hand, may constitute the cause of the discrepancy. In any case the full understanding of the phenomenon of dissociation must take these data into account.

Although the curves thus do not yet yield a very satisfactory theoretical outcome, their practical usefulness is none the less worth attention. As a matter of fact they serve as a convenient means for determining at once the heat of dilution from any concentration within the experimental range to any other within that range. All that is necessary is to calculate the fraction of mol of salt for one mol of water in each of the solutions and read off the corresponding ordinates, subtracting one from the other. Of course, similar curves might be drawn giving as abscissas molal concentration in the usual sense (mols per liter) with the help of the known specific gravities of these solutions, by any one who desired to use the curves frequently in relation to such solutions; for this, space is lacking here.

Let us turn to a systematic tabulation of the second series of quantities. These also are recorded in the c. g. s. system of energy and heat capacity, the figures being obtained by multiplying those in the ($K_M - K_{M'}$) column of Table IV by 4.180. The word mayer is a convenient designation for the heat capacity which is warmed 1.000° C. by 1.000 joule of energy.

The results for the acids and sodium and potassium hydroxides are given in this table upon the basis *MA* 25 H₂O instead of *MA* 10 H₂O for the sake of uniformity.

Attention should be called to the fact that all of these results are positive in spite of the fact that many of the heats of dilution themselves are negative. With two slight exceptions (marked as questionable above and probably due to experimental error) the temperature coefficient increases with increasing dilution, as would be expected, since it is equal

to the loss of heat capacity suffered by the system. These values may be plotted after the fashion of the graph on p. 1634 of the previous paper; when so plotted they show almost linear relationships like hydrochloric acid. The diagram is not printed here, since its essentials are given by an allied relationship to be recorded later.

TABLE VII.—TEMPERATURE COEFFICIENTS OF HEATS OF DILUTION IN JOULES PER °C. (15° TO 20°), OR LOSS OF HEAT CAPACITY (IN MAYERS).

Initial solution.	Final solutions (total mols water).			
	50 H ₂ O.	100 H ₂ O.	200 H ₂ O.	400 H ₂ O.
HCl, 25 H ₂ O.....	17.1	30.9	30.1 (?)	38.5
LiCl, 25 H ₂ O.....	8.8	20.5	31.8	36.8
NaCl, 25 H ₂ O.....	28.8	46.8	55.6	76.1
KCl, 25 H ₂ O.....	21.7	37.2	45.1	59.4
CsCl, 50 H ₂ O.....	26.8	43.9	50.6
HNO ₃ , 25 H ₂ O.....	22.6	35.9	45.1	51.0
LiNO ₃ , 25 H ₂ O.....	16.7	27.2	38.5	48.5
NaNO ₃ , 25 H ₂ O.....	34.3	62.7	76.1	85.3
KNO ₃ , 25 H ₂ O.....	43.9	74.0	85.3	96.1
CsNO ₃ , 60 H ₂ O.....	24.2	54.3	64.0
LiOH, 25 H ₂ O.....	25.9	48.1	54.3	49.3 (?)
NaOH, 25 H ₂ O.....	36.4	58.5	80.7	84.4
KOH, 25 H ₂ O.....	22.2	43.1	51.4	64.0

The usual loss of heat capacity on diluting the 100 H₂O solution to 200 H₂O is seen to be about 10 mayers. Only in the cases of the cesium salts and sodium hydroxide does it rise much above this value.

The total molal heat capacities of the several solutions may now be compared. In the following table these values have not been reduced to the c. g. s. system, since they are usually more conveniently discussed on the assumption that the heat capacity of water between 16° and 20°

TABLE VIII.—MOLAL HEAT CAPACITIES OF 65 SOLUTIONS.

	(In cal. 18°/°C.)				
	25 H ₂ O.	50 H ₂ O.	100 H ₂ O.	200 H ₂ O.	400 H ₂ O.
HCl.....	427.3	873.5	1770.9	3571.4	7174.1
LiCl.....	441.3	889.6	1787.6	3586.5	7188.5
NaCl.....	446.7	890.2	1786.7	3586.2	7184.5
KCl.....	436.7	881.4	1779.0	3578.7	7178.5
(RbCl).....	[880]	[1774]	[3574]	[7175]
CsCl.....	878.9	1771.9	3569.4	7171.0
HNO ₃	444.3	889.3	1786.9	3586.3	7188.1
LiNO ₃	457.2	903.6	1801.9	3600.7	7201.6
NaNO ₃	465.6	907.8	1801.6	3600.2	7201.2
KNO ₃	459.0	898.9	1792.5	3591.4	7192.0
(RbNO ₃).....	[1789]	[3585]	[7186]
CsNO ₃	1785.8	3580.3	7181.2
LiOH.....	451.7	895.9	1791.4	3591.5	7195.9
NaOH.....	443.6	885.3	1780.8	3578.7	7179.3
KOH.....	436.3	881.4	1777.2	3576.5	7177.0

is exactly unity. They are therefore recorded in terms of the commonly used nameless unit of heat capacity, calorie (18°) per degree C.

This table, like those previously given, affords much food for thought. The two acids, in the most concentrated solutions, show much lower molal heat capacities than any of the salts with corresponding ions. On dilution, however they gain more rapidly than the salts, and in the dilute solutions they approximate the interpolated values for the rubidium salts. Lithium and sodium salts, although so different as to heats of dilution, have nearly the same effect on the molal heat capacity. In every case (excepting the isolated cases of lithium chloride and nitrate in the two most concentrated solutions) each series of salts as well as each of the five series of hydroxide solutions (in vertical rows) shows decreasing heat capacity with increasing atomic weight. The values for rubidium chloride and nitrate, obtained by interpolation in this series, are obviously fairly trustworthy. Hence the specific heats calculated from them and given in Table IV are likewise fairly trustworthy.

The systematic comparison of each solution with each other of the same concentration by means of the method of tabulation given below (Table IX) would be of interest, but lack of space prohibits more than one such table.

TABLE IX.—MOLAL HEAT CAPACITIES OF DIHYDRATED SOLUTIONS.

	Cl.	NO ₃ .	OH.
H.....	3571	3586
Li.....	3587	3601	3591
Na.....	3586	3600	3579
K.....	3579	3591	3577
Rb.....	(3574)	(3585)
Cs.....	3569	3580

Evidently the nitrates, as would be expected, all have greater molal heat capacities than the corresponding chlorides. This rule holds for all concentrations. The march in the values for the alkali compounds is manifest.

One of the most interesting conclusions to be drawn from the data comes from the comparison of the changes of heat capacity on dissolving the several salts in water. These, of course, may be easily found where the heat capacities of the dry salts have been determined, by simply subtracting heat capacities of the solutions from the sums of the heat capacities of the water and the dry salts taken separately. The specific heats of the chlorides of lithium, sodium and potassium have been determined by Weber¹ and by Russell² to be respectively 0.282, 0.211, 0.166, indicating the molal heat capacities respectively 11.9, 12.4 and 12.4 cal./ $^{\circ}$ C. or

¹ R. Weber (in 1895) found 0.215 for NaCl; Landolt u. Börnstein, "Tabellen," 1912, p. 785.

² A. S. Russell found 0.208 for NaCl, *Physik. Z.*, 13, 59 (1912).

49.8, 51.8 and 51.8 mayers. Since Elsa Deuss¹ (1911) found the atomic heat capacity of rubidium to be approximately the same as that of potassium and Eckardt and Graefe² found that of cesium only a little less (6.4 cal./° C.), it appears probable that the molal heat capacity of cesium chloride is about 51.4 mayers. Lithium, sodium and potassium nitrates (with specific heats respectively about 0.39, 0.28 and 0.24) must have molal heat capacities about 113, 100 and 100 mayers respectively, and cesium nitrate is probably about the same as potassium in this respect. These data then give us the means of calculating approximately the values in question, after the fashion shown in this example:

HEAT CAPACITIES.		
	Cal./° C.	(Mayers.)
Molal heat capacity of KCl.....	12.4	51.8
Molal heat capacity 100 H ₂ O.....	1801.6	7530.7
	1814.0	7582.5
Molal heat capacity KCl + 100 H ₂ O.....	1779.0	7436.2
	35.0	146.3
Difference.....		

The difference of 35.0 cal. per degree C. (or 146 mayers) represents the loss of heat capacity on dissolving one gram mol of potassium chloride in 1.8 liters of water. It is a strikingly large amount.

The following table gives data computed in this way for a number of typical substances of which the specific heats in the solid state are sufficiently well known for the purpose in view.

LOSS OF HEAT CAPACITY ON DISSOLVING SALTS, ETC., IN WATER.
(Mayers).

	25 H ₂ O.	50 H ₂ O.	100 H ₂ O.	200 H ₂ O.	400 H ₂ O.
LiCl.....	88	101	118	119	125
NaCl.....	67	96	114	123	143
KCl.....	109	133	146	154	168
CsCl.....	...	143	175	193	199
LiNO ₃	84	101	112	123	133
NaNO ₃	38	71	99	113	122
KNO ₃	64	108	134	150	161
CsNO ₃	166	196	205

The accompanying diagram, Fig. 2, plots the values for 6 of these salts. Lithium chloride and nitrate are omitted because these two curves (almost identical) cause confusion with the sodium chloride curve which they cross, being somewhat less oblique. The 6 curves serve, however, sufficiently to show the diversities and similarities of the data. The curves for the cesium salts are concave downwards, the others concave upwards. All the curves excepting these for sodium chloride and potas-

¹ Elsa Deuss, *Viertelj. nat. Ges. Zürich*, **56**, 15 (1911).

² Eckardt and Graefe, *Z. anorg. chem.*, **23**, 378 (1900).

sium chloride are very smooth. These two latter are probably somewhat in error as to the 200 H₂O value. A compromise curve has been drawn in each of these cases. Possibly these two become much more oblique as they approach infinite dilution. This point must be left for

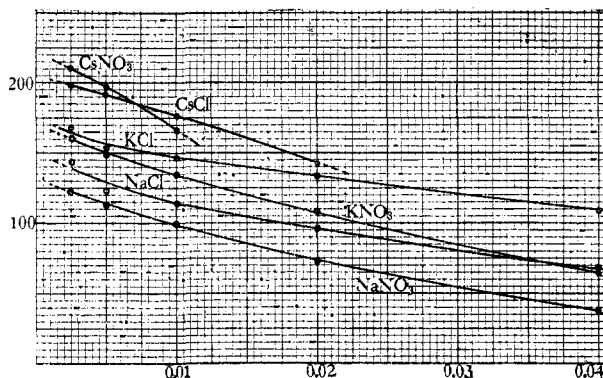


Fig. 2.—Loss of heat capacity on dissolving salts in water (dilute solution). Losses of heat capacity per mol of salt are plotted in mayers in the direction of ordinates, and fractions of mol of salt per mol of water as abscissas.

future more exact investigation. With both chlorides and nitrates the order is as would be expected: cesium, potassium, sodium; but probably in more concentrated solutions the cesium curves would cross the potassium curves.

From these curves the change of heat capacity on dissolving any amount of any one of these salts in any intermediate quantity of water may be found with great ease, and therefore the specific heat of the solution in question. The change in the heat capacity (ΔK_M) is simply read off as the ordinate corresponding to the particular point on the particular curve having the desired abscissa (*i. e.*, the fraction of a molecule of salt for each molecule of water). From this value of the change in heat capacity the specific heat is very easily calculated by the following obvious equation in which C is the mol. heat capacity of dry salt expressed in mayers:

$$\frac{\text{Wt. H}_2\text{O} + (C - \Delta K_M)/4.18}{\text{mol. wt. sol.}} = \text{sp. heat}$$

Thus for example, the specific heat of CsCl, 75 H₂O (abscissa 0.0133 . .) is

$$\frac{1351.2 + (51.4 + 165.)/4.18}{1351.2 + 132.81 + 35.46} = 0.8012.$$

The advantage of this curve over a mere plotting of the known specific heats is that a possible small error in drawing or reading the curve can have only a negligible effect on the result.

Inquiry into the cause of the large loss of heat capacity indicated by all the curves is not without interest. At least three different effects may reasonably be imagined to occur together when a salt solution is diluted. In the first place the dissociation of the salt may be increased; secondly there may be increased hydration and thirdly the polymerization of the water may be affected.

The first of these tendencies would probably decrease the heat capacity of the system, for it is well known that when ions are *de-ionized*, as for example, in neutralization of acids and alkalies, there is a considerable *increase* in heat capacity, indicating a *decrease* when *ionization* takes place, at least in the case of hydrogen and hydroxyl ions, and presumably in the case of other ions also. Hydration likewise causes change in heat capacity, as Marignac showed long ago, since crystal water has only about the specific heat of ice.

The third possible effect, namely, the change in the polymerization of the water would probably have much less influence than either of the other two, and its amount would not be easy to predict, since so little is precisely known concerning the nature of water. This third influence must therefore be neglected in the discussion; but it is probably not more than a slightly modifying influence.

Perhaps the loss of heat capacity produced by ionization is due primarily to hydration of the ions, which would presumably take on more water of hydration than undissociated salt. If this is the case, the first two tendencies just mentioned really become merged; that is to say, the loss of heat capacity is to be ascribed wholly to solvation, the first loss in a concentrated solution being due partly to the hydration of the undissociated salt, and the further loss on dilution being due chiefly to the further hydration of the ions, as their percentage increases during dilution. This seems to be the most reasonable interpretation of the results. In this connection Fig. 3, which plots the data for three salts in such a way as to depict more satisfactorily the behavior of concentrated solutions, is interesting.

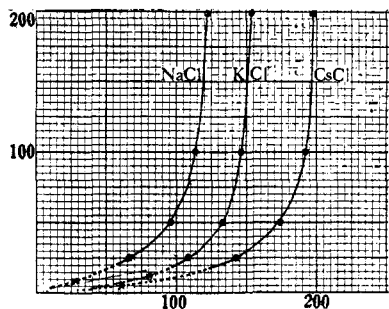


Fig. 3.—Loss of heat capacity on dissolving salts in water (concentrated solutions). Mols of water per mol of salt are plotted as ordinates, and losses of heat capacity (in mayers) as abscissas. Crosses indicate the limit of solubility. The extrapolated broken lines (supersaturated solution) evidently tend toward the origin.

It is striking that the different data under consideration are all of the same order. For example, the loss of heat capacity on forming solutions of the chlorides of sodium, potassium and cesium from the dry salt and 100 H₂O

are respectively 114, 146 and 175 mayers, whereas the heat of neutralization of acids and alkalis of similar concentration show an increase of heat capacity of about 200 mayers. Evidently the change of heat capacity involved in the formation of a single ion is in the neighborhood of from 50 to 100 mayers; and evidently, moreover, the phenomenon is a specific one not of exactly the same magnitude with all ions, but differing in systematic fashion among the various elements. Although the differing values with different substances might be due merely to differing degrees of dissociation (each ion having the same effect), there is no plausible reason for believing that cesium nitrate (in 0.13 *N* solution) is nearly twice as much dissociated as sodium nitrate at the same dilution. More probably the heat capacity loss (due presumably to hydration) is different with each ion, the degree of dissociation being not very different in the different cases. It is only reasonable to believe that the extent of solvation would be determined to a noticeable extent by the varying electro-affinity of the dissolved ions.

If the provisional assumption is made that the loss of heat capacity of the more dilute solution is due to ion-formation, the several values given by any one curve should be a means of determining approximately the several degrees of dissociation of the several solutions of the substance represented by that curve. In fact, although exact coincidence with the verdict of electrolytic conductivity is not indicated, an approximate correspondence is shown—a correspondence somewhat better than that shown by the heats of dilution.

As a first rough approximation, let us neglect the hydration of the undissociated salt, and calculate the degree of ionization on the assumption that all the loss of heat capacity is due to ionization. For example with sodium chloride, the maximum loss of heat capacity seems to be about 155 mayers (at infinite dilution). At concentration NaCl, 25 H₂O (1.09 *N*) the loss is 67, indicating a dissociation of $67/155 = 44\%$ instead of 57 as computed from conductivity. At 50 H₂O (2.13 *N*) the value is $96/155 = 62\%$ instead of 67% as computed, while at 400 H₂O the dissociation is 77% instead of 81%. The indeterminable allowance for the hydration of the undissociated salt would decrease all these values, and make the correspondence (especially in more concentrated solutions) even less satisfactory than it is. Nevertheless, qualitatively these figures point in the direction of the ordinary interpretation of dissociation rather than toward the more recent view that conductivity is of no importance as a guide to its extent. One can hardly believe that the marked change in heat capacity which occurs for example between the dilutions 50 H₂O and 400 H₂O (this change is 56 mayers in the case of cesium chloride) should be due to nothing more than further hydration of molecules or ions already existing in intimate conjunction with 50 H₂O. In any case

this argument, like that from the heats of dilution, is worthy of further consideration and research, which it will receive in the near future.

It is well known that this loss of heat capacity under discussion is often accompanied by a considerable change of volume.¹ The contractions on dissolving the salts do not at all follow the order given above, however—cesium chloride causing much less contraction than potassium chloride, and potassium chloride much less than sodium chloride. On the other hand, if the changes in volume on forming the ions from the elements are taken into account,² a distinct parallelism is seen, for during the formation from the elements of solutions of cesium, potassium and sodium chloride, about 55, 42 and 30 cc. contractions respectively, occur—numbers not very far from proportional to the figure above.

The situation is however, too complex for treatment at present, since the compressibilities of the elements enter into it, and other tendencies concerned are too little known for quantitative treatment. One can hardly help believing that the adjustment of affinities, by causing compression of at least a part of the solvent molecules concerned, diminishes their heat capacity, expelling a portion of the kinetic heat energy which they contain. If this were the only effect, heats of dilution would always be positive; but superposed upon this is the heat of dissociation, which probably plays a yet larger rôle. Evidently we are dealing with a complex of superposed effects, among which it is not at present possible to single out certainly the detailed behavior of any one. Nevertheless this detailed behavior can be ascertained, if at all, only by the careful study of all possible data concerning the question in hand, among which the data given in this paper are essential ones.

The Temperature Coefficient of the Heat of Neutralization.

According to Kirchhoff's law the temperature coefficient of any reaction can be calculated very simply from the heat capacities of the factors and products of that reaction. In the foregoing data we have the heat capacities of several acids and bases as well as of their corresponding salts in dilute solutions. Therefore the change in the heat of neutralization with the temperature can be computed from these data.

In one respect only are the data as given insufficient. On mixing HCl, 100 H₂O with NaOH, 100 H₂O the product is NaCl, 201 H₂O, whereas the foregoing data give the heat capacity for only NaCl, 200 H₂O. This lack is not serious, since it may be remedied by calculation which does not introduce a possible error as great as the probable error of experiment. Clearly an extra mol of water must have very nearly its full heat capacity when it is added to a dilute solution, since it can hardly be greatly affected by the presence of a small concentration of salt. A very close approx-

¹ G. P. Baxter and C. C. Wallace, *THIS JOURNAL*, **38**, 70 (1916).

² This was done by Baxter and Wallace on page 96 of the article just quoted.

imate evaluation of the effect may be obtained as follows. The average difference in molal heat capacity between the 100 H₂O and 200 H₂O solutions is 1798.5 cal./° C. That is to say, 1801.6 grams of water have lost only 3.1 in heat capacity, on the average, on being added to the salt solution. Similarly, 200 H₂O more on being added to the 200 H₂O solution, increase the average heat capacity by 3601.1, losing only 2.1 in heat capacity. Thus it is safe to say that a single H₂O (18.016 g.) cannot add more than 18.005 nor less than 17.985 to the heat capacity of a solution containing already 200 H₂O. Evidently no appreciable error can be committed if we take 18.0 as the added heat capacity of the 201st molecule of water. The heat capacity of NaCl, 200 H₂O is 3586.2; from which that of NaCl, 201 H₂O is found to be 3604.2.¹

Turning now to the dilution results we find that the average value for the heat capacity of NaOH, 100 H₂O is 1780.6, while that of HCl, 100 H₂O taken from the previous paper² is 1770.9. Subtracting the sum of these two quantities from the heat capacity of NaCl, 201 H₂O just given, we get the quantity $K - K_0 = 52.7$. This value according to Kirchoff's equation is — $\frac{U'_M - U_M}{\Delta\theta} = - \frac{\Delta U}{\Delta\theta}$.

The following table contains results for the various temperature coefficients of the heats of neutralization calculated in this way from the foregoing data; a mol of each of the salts being dissolved in 100 mols of water:

TEMPERATURE COEFFICIENTS OF HEATS OF NEUTRALIZATION.
(In calories and kilojoules per 1° C.)

	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
Average.....	—52.1	—49.7	—0.218	—0.209

These values are somewhat larger than those found by Thomsen. They show systematic progression.

An elaborate series of direct determinations of the heats of neutralization (of which quantities the above figures give the temperature coefficients) have been made, and will form the subject of a future communication.

We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for generous grants, which alone made possible the purchase of the expensive apparatus needed for this research.

¹ The specific heat of this solution was determined directly as 0.9798—which would make the heat capacity in question 3605.3. This is as good an agreement as could be expected. The indirect result is the more trustworthy.

² Richards and Rowe. *loc. cit.*, p. 1632.

Summary.

1. Berthelot's application of Kirchhoff's law has been applied systematically for the first time.

2. The heats of dilution of nitric acid, of the hydroxides of lithium, sodium and potassium, and of the chlorides and nitrates of lithium, sodium, potassium and cesium have been determined at about 16° and about 20° . These are recorded in Table III in calories and in Table VI in joules. Approximate values for rubidium salts were found by interpolation.

3. Some of these heats of dilution are positive and some negative. Sodium hydroxide and nitric acid show change of sign on progressive dilution. Distinct relationship to the periodic system is shown in the progression of values, but some eccentricities, particularly in sodium salts, are manifest.

4. From these results the temperature coefficients of the heats of dilution were found, as given in Tables IV (calories) and VII (joules). These latter are all positive.

5. From these latter values the specific heats of the various solutions are calculated; and it is shown how, by a simple method of plotting the heat capacity changes, all intermediate solutions may likewise be determined with considerable accuracy.

6. The loss of heat capacity on dissolving salts in water is shown to be of the same order as the gain of heat capacity on neutralizing acids by alkalis, in such sense that the heat capacity is diminished 50 to 100 mayers by such fraction of each gram ion as is formed from a gram molecule in solutions containing 100 H_2O . Presumably the nature of the ion determines the exact magnitude of this loss of heat capacity.

7. Heats of dilution and changes of heat capacity are shown to afford a possible partial clue to the extent of electrolytic dissociation.

8. The temperature coefficient of the heat of neutralization of solutions containing 100 H_2O is shown to vary somewhat with the nature of the alkali and of the acid, and to average about 51 calories or 213 joules per degree C. Therefore the gain of heat capacity on neutralization is 213 mayers.

9. These results are only a beginning, but are hoped to afford a suggestion, nevertheless, of the wealth of interesting knowledge which may be acquired by detailed study of such data.