It is a pleasure to acknowledge the helpful coöperation of a number of chemists. We mention in particular our indebtedness to Dr. J. L. McGhee, of Emory University, who has contributed greatly by his collaboration in the work of chemical analysis and otherwise; to Professor H. D. Jones, formerly our colleague and at the present time an industrial chemist, who has checked some of our observations and has made analyses by the method; to our colleague, Professor H. M. Martin, whose advice in problems of inorganic chemistry has been frequently sought; in fact, to the entire faculty of chemistry in this Institution for their cordial attitude of coöperation. We wish also to express our thanks to Mr. J. H. Christensen, student assistant in physics, for taking many observations, particularly with the hydroxides, and for making a number of checks on our work.

Summary

1. Each compound studied produces its own characteristic minimum, or minima, of light, regardless of the presence of other compounds.
2. The characteristic minima of those compounds for which quantitative tests have been made do not disappear until the concentration is reduced to about one part of the compound in 10^{11} parts of water.
3. These minima appear at points along the scale in the order of the chemical equivalents of the metallic elements of the compounds, or the differential time lag is some inverse function of the chemical equivalent.
4. The number of characteristic minima, with few exceptions, is equal to the number of known isotopes of the metallic element of the compound.
5. The method promises to be of value in quantitative as well as in qualitative analysis in work dealing with very small quantities of materials.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 188]

HEATS OF NEUTRALIZATION BY THE CONTINUOUS FLOW CALORIMETER

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The continuous flow calorimeter[1] served to locate a serious error in an accepted value[2] for the heat of neutralization of sodium hydroxide with hydrochloric acid, in agreement with the findings of Richards and Rowe,[3] which were published at the same time. Richards and his collaborators at Harvard have given a large body of data which seem to be of high precision, and repetition or extension of their measurements appears pointless

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[1] Keyes, Gillespie and Mitsukuri, THIS JOURNAL, **44**, 707 (1922).

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

[3] Richards and Rowe, THIS JOURNAL, **44**, 684 (1922).

unless the chemicals used, especially the alkalies, are pure to within about 0.1%. Now the continuous flow calorimeter demands large supplies of carefully controlled solutions. Furthermore, it furnishes merely temperature changes and cannot be used alone, therefore, to extend the data of Richards and his collaborators into temperature regions where no specific heat data exist. We have been forced to limit our efforts to verification of some of the results of Richards and his collaborators at the temperature of their experiments, and to test the applicability of the Kirchhoff equation[4] by a few direct measurements at other temperatures.

We supposed at first that we should be able to check the work of the Harvard investigators only with respect to the temperature changes due to the reactions, but found that enough experimental work was available by other workers to furnish independent specific heats, and therefore afford heats of reaction completely independent of the Harvard work.

The apparatus and method used were essentially the same as that of Keyes, Gillespie and Mitsukuri, with minor improvements of the method of controlling the speed of flow and with one change of technique which enabled the rise of temperature to be obtained at unusually slow rates of flow.

When the rate of flow is too small, the mixing at the double concentric nozzles is imperfect when the average effluent is neutral, but may be good enough when the average effluent is either acid or alkaline. It was found possible at such a rate of flow to determine the rise of temperature for a neutral effluent by plotting the change of temperature against excess of acid or of alkali as indicated by neutralizing 100 cc. of effluent. Excess of alkali was plotted as negative excess acid, and two intersecting straight lines were used to smooth the observations and to find the maximum rise of temperature.

Platinum thermometry was used as before. The two thermometers were tested from time to time for the fundamental interval and the delta value. It was necessary to have a new calorimeter constructed, and the inside of the Dewar space was silvered. The silvering reduced the heat loss considerably. The small difference in indication of the two thermometers was rendered of no influence by determining the difference of readings when pure water was run through both sides of the apparatus; it was found possible to set the temperature of the preliminary thermostat at such a value that the difference of readings was practically independent of the rate of flow within the necessary range, and this adjustment was made and the difference determined for each experiment. This difference was then applied as a correction to one thermometer, thus basing all temperatures on the indications of a single thermometer.

Chemicals Used. Ordinary distilled water of good quality was used. A good grade of hydrochloric acid was made up to constant boiling composition and distilled into three fractions. The middle third was further divided into three portions by distillation and the middle third kept. It was standardized gravimetrically by the silver chloride method. A precision within 0.1% was apparently obtained. The results were satisfactorily checked by reference to recrystallized acid potassium phthalate. Fresh solutions were used, though the carboy in which they were kept had been used for years to hold hydrochloric acid and tests of the acid by acidimetric titration and by the silver chloride method showed no change of the acid on standing even for several weeks.

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[4] When approximately integrated.

The alkalies were standardized acidimetrically by reference to the acid, using weight burets.

The carbonate content was determined by first passing acid into base in the presence of carbon dioxide-free air. Secondly, base was added to a new portion of the acid in a stream of carbon dioxide-free air.

A good grade of potassium hydroxide from alcohol was dissolved in water and freed from carbonate in the apparatus of Knobel,[5] who very kindly lent us his apparatus. In this apparatus potassium amalgam is formed by electrolysis in one of two flasks which communicate at the bottom under mercury, and decomposed by distilled water in the other. The resulting solution contained only 0.05 mole of potassium carbonate per hundred moles of total alkali.

For sodium hydroxide the apparatus was not suitable. An initial phase of sodium amalgam reacted very slowly and appeared unstable. After some time a new phase seemed to appear that would hardly react with water, so that sufficient hydroxide could not be obtained for an experiment even after a week of electrolysis. Hence, from sodium hydroxide partially freed from carbonate by sedimentation from a concentrated solution, a viscous amalgam was formed by electrolysis. This was washed many times with cold conductivity water and placed in a large bottle, the amalgam filling about one-fourth the volume of the bottle. Steam was then passed through the amalgam. The hot water reacted rapidly with it. By the time the bottle was filled with condensed liquid, sufficient alkali had been formed to make a strong solution. After the washing with conductivity water the operations were carried out in the absence of carbon dioxide. The solution contained less than 0.2 mole of sodium carbonate per hundred moles of total alkali.

Unfortunately such alkali was not available for all of the experiments and in such a case sodium hydroxide freed from carbonate by sedimentation was used. Owing in part to the large volumes taken, this method was not uniformly successful and the solutions used for the experiments contained sometimes more carbonate than is desirable in a precision experiment.

The Specific Heats of Aqueous Solutions of Sodium Chloride and of Potassium Chloride.—The continuous flow calorimeter gives temperature elevations to a high degree of precision and in order to calculate heats one should know the heat capacities of the products (or of the factors) of the reaction to an equal precision. In the present case the heat capacities of solutions of sodium and of potassium chloride were needed at several temperatures, and it proved necessary to construct original specific heat tables, smoothed for both temperature and concentration. Fortunately the work of Bousfield and Bousfield[6] proved to be very consistent with that of Richards and Rowe[7] at 20°, and with that of Randall and Bisson[8] at 25°, so that reliable results could be obtained without any attempt to utilize scattered data, or data without the appearance of special precision, of other investigators.

Bousfield and Bousfield[6b] determined over a series of concentrations the

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[5] Knobel, This Journal, **45**. 70 (1923).

[6] Bousfield and Bousfield, *Trans. Roy. Soc. London*, **211A**, 199 (1912); (b) **218A**, 119 (1919).

[7] Richards and Rowe, This Journal, **43**, 770 (1921).

[8] Randall and Bisson, *ibid.*, **42**, 347 (1920).

total heat in joules required to raise the temperature in steps of 13° from 0.5 to 39.5°. They had previously[6a] done the same for water. They recognized in their second paper that their values for water might be in error, and in fact they are, according to recent values of the Bureau of Standards,[9] but they believed their results for solutions to be comparable with those for water, and this belief is borne out by the present calculations.

To deduce specific heats from their data, the total heat in joules was differentiated graphically with respect to temperature (at each concentration), and the tangent was divided by the instantaneous value of the specific heat of pure water given by their earlier experiments and expressed in their equation for J_Θ (Reference 5, page 236). This gave the true specific heat referred to water at the same temperature. From the Bureau of Standards data[9] conversion factors were found by interpolation to convert specific heats in calories at $t°$ to 20°-calories. The so-converted values were smoothed at the desired temperatures with respect to concentration, plotting the deviation from linearity of $1 - C_p$ with concentration expressed in moles of substance per mole of water, and were finally interpolated by means of the deviation plots for evenly spaced values of the concentration as well as for the particular concentrations needed for the calculation of heats.

As a check on the results at 20°, the specific heats given by Richards and Rowe[7] for both salts at 18° in 18°-calories were used to find values at 20° in 20°-calories, using smoothed temperature coefficients from the data of Bousfield and Bousfield and the conversion factors from the Bureau of Standards data. Examination of Table I, in which these Richards and Rowe values (R-R) are given together with the values from Bousfield and Bousfield (B-B), show the excellent agreement. At the concentrations at which values were needed for calculations of heats, the agreement is perfect. At 25° the deviation curve through the Bousfield data for sodium chloride passed beautifully through the two points of Randall and Bisson. Because little use was made of the excellent work of the Bousfields in the compilation of the "International Critical Tables," specific heats from their data alone are given in Table I, rather than values, possibly better, derivable from more than one source. The specific heats of sodium chloride solutions have been given by Lipsett, Johnson and Maass[10] for both 20 and 25°. Since these were determined indirectly and are not altogether independent of the values of Richards and Rowe, they were not utilized for the present comparisons.

The values at 50° were determined entirely by extrapolation without the aid of check determinations, and cannot be regarded as accurate. They are given mainly as an aid to the correction of our calculations of heats,

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[9] Osborne, Stimson and Fiock, *Mech. Eng.*, 51, 125 (1929), Table 3.

[10] Lipsett, Johnson and Maass, THIS JOURNAL, **49**, 925, 1940 (1927).

which will be possible when accurate specific heats are determined at that temperature.

TABLE I

SPECIFIC HEATS FOR $NaCl \cdot hH_2O$ AND $KCl \cdot hH_2O$ IN 20°-CALORIES

B-B, from Bousfield and Bousfield; R-R, from Richards and Rowe

Salt..........	NaCl	NaCl	NaCl	NaCl	NaCl	KCl	KCl	KCl
Authors.......	B-B	R-R	B-B	B-B	B-B	B-B	R-R	B-B
	t							
h	20	20	25	32	50[a]	20	20	25
10	0.7920	...	0.7921	0.7916	0.7905	...	...	...
12.5	.8144	...	.8133	.8141	.8147	...	...	...
25	.8797	0.8786	.8804	.8816	.8836	0.8328	0.8319	0.8338
50	.9302	.9286	.9314	.9318	.9324	.9035	.9036	.9045
100	.9617	.9611	.9622	.9625	.9641	.9478	.9482	.9480
200	.9796	.9794	.9797	.9799	.9819	.9726	.9729	.9723
400	.9895	.9894	.9892	.9893	.9911	.9860	.9861	.9854
800	.9946	.9946	.9943	.9943	.9957	.9929	.9930	.9924
1600	.9972	.9972	.9969	.9968	.9980	.9965	.9965	.9960
∞	1.0000	1.0000	.99959	.99943	1.00038	1.0000	1.0000	.99959

[a] Severely extrapolated.

The specific heats actually used for heat calculations were interpolated with the aid of the same deviation plots used in constructing the tables, and were found for the final concentration of the solutions and for a temperature equal to the initial temperature plus one-half the temperature rise due to the reaction. Only at 50° did it make a difference of more than one calorie in the heat whether the specific heat was calculated for this mean, or for the initial temperature. The concentration at which the specific heat was calculated was not quite the concentration of moles of NaCl (from NaOH) per mole of water, but the total moles NaCl from NaOH, NaCl from Na_2CO_3, and $NaHCO_3$ from Na_2CO_3. Here the loss of heat capacity due to the presence of $NaHCO_3$ was assumed to be the same as for NaCl, which was safe, as the total error made, if the NaCl and $NaHCO_3$ from the small concentration of Na_2CO_3 had both been neglected in the calculation of the heat capacity, would have been only 2.7 calories in the worst case. The water formed during the reaction was naturally taken into account in calculating the concentration.

The calculation of the results was in general the same as before,[1] except for some small added corrections. The effect of carbonate in the alkali was allowed for in the same way. The necessary corrections were applied to give $-\Delta H$, the heat evolved at constant pressure, for the reaction

$$NaOH \cdot 0.5(h-1)H_2O + HCl \cdot 0.5(h-1)H_2O = NaCl \cdot hH_2O - \Delta H, \text{ at } t^\circ \qquad (1)$$

where h is the number of moles of water associated with 1 mole of salt in the product of the neutralization. Atomic weights were used as in the Harvard calculations, namely, "International Critical Tables" values with the exception that 1.008 was used for hydrogen. Consistently with their recent work, the heats are given in 20°-calories.

Since the concentrations of the acid and alkali were not identical, the results were corrected to the form of Equation 1 by the use of heats of dilution, obtained directly from the Harvard work[7,11,12] or indirectly with the aid of their recent heats of dilution and Kirchhoff's law. These corrections never exceeded 3 calories.

The treatment of the potassium chloride data was the same as for sodium chloride, and the corrections smaller.

Table II

Results of the Continuous-Flow Calorimetry

No. 6 is the recomputed value from the previous work[1]

No.	Salt	t	h	x	t'	$1/h'$	C_p	$-\Delta H$	$-\Delta H$(R)
1	NaCl	20	1080.7	0.255	20.354	0.000930	0.9961	13784	13773
2	NaCl	20	566.5	.50	20.678	.001783	.9924	13803	13823
3	NaCl	24.99	1101.4	.15	25.333	.000911	.9957	13582	...
4	NaCl	32.27	568.8	.38	32.917	.001771	.9922	13211	...
5	NaCl	32.27	566.0	.20	32.953	.001774	.9922	13274	...
6	NaCl	32.3	520.5	.42	33.008	.001921	.9916	13284	...
7	NaCl	50.04	52.87	.10	57.04	.01895	.9359	13237	...
8	NaCl	50.04	99.91	.13	53.58	.01003	.9642	12676	...
9	KCl	20	547.8	.05	20.705	.001827	.9896	13864	13861

The results of the calorimetry are given in Table II. t, h and $-\Delta H$ refer to Equation 1; x is the number of moles of sodium carbonate or potassium carbonate per 100 moles of base in the alkaline solution used for the experiment. t' and $1/h'$ are the temperature and the moles of salt per mole of water for which the specific heat, C_p, was interpolated from the deviation plots representing the Bousfield data. In the last column, $-\Delta H$(R) gives the interpolated values for the same concentration and temperature (20°) furnished by the data of Richards and collaborators, as noted. For this interpolation the deviations from linearity of the heat versus $1/h$ were calculated and plotted against the square root of $1/h$; taking the square root removed an excessive bend in the plots. The values of the heat for infinite dilution used were the extrapolated values found in the summary of Richards and Rowe[3] for the formation of potassium chloride, and of Richards and Hall[13] for the formation of sodium chloride. At the time our experiments were concluded the 1929 articles from the Harvard laboratory had not been published and our results for sodium chloride differed from the interpolated values from the older work of Richards and Rowe by about 25 calories, but it will be seen from Table II that our results are in good agreement with the recent values.

In order now to compare our six results at temperatures other than 20°, it is necessary to have temperature coefficients of the heat of neutralization.

[11] Richards and Gucker, This Journal, 51, 712 (1929).

[12] Richards, Mair and Hall, *ibid.*, 51, 727 (1929)

[13] Richards and Hall, *ibid.*, 51, 731 (1929).

The values of Richards and Rowe need corrections, according to the 1929 articles. Using the latest data for sodium hydroxide and hydrochloric acid, and the (R-R) specific heats for sodium chloride given in Table I, new values of the temperature coefficient were calculated from Kirchhoff's law. They lie near a gently sloping line, when plotted against the concentration ($1/h$), and intercept the axis of zero concentration very close to the value of Noyes, Kato and Sosman.[14] Since, however, ideas have necessarily been used in the interpolation of some of the specific heat data on which the values of the temperature coefficient in the dilute region are based, we see no guarantee that this temperature coefficient curve is substantially correct at low concentrations, and it is not here reproduced. We have used it, however, in an effort to compare our results at various temperatures with the interpolated Harvard values at 20°. From this curve, interpolated values of the temperature coefficient were read off for the necessary concentrations, and our results were corrected to 20° by means of them, assuming, of course, that the coefficient is constant over the whole temperature interval, which cannot be the case from 20 to 50°. The comparison is given in Table III.

TABLE III

ATTEMPTED COMPARISON OF DATA BY THE USE OF TEMPERATURE COEFFICIENTS

Temperature.........	24.99	32.27	32.27	32.3	50.04	50.04
Dilution (h).........	1101	569	566	521	52.9	99.9
Percentage deviation..	0.45	0.24	0.71	0.70	0	−1.22

The percentage deviation is the heat of reaction (evolution) calculated from our results minus the corresponding results of Richards and Hall,[13] in percentage of the latter results. Bearing in mind the close agreement shown at 20° in Table II, which was only reached after their recent revision, we do not believe that the disagreement shown in Table III (unless, it may well be, at 50°, in view of the unsatisfactory specific heats at that temperature) is mainly due to experimental error in our heats. Neither does it seem to be principally due to a variation of the temperature coefficient with temperature. The suggestion is strong that the temperature coefficients, extrapolated into the dilute region, cannot be trusted.

Summary

From the measurements of Bousfield and Bousfield, specific heat tables, apparently quite accurate, were deduced for sodium chloride solutions at 20, 25 and 32°, and for potassium chloride solutions at 20 and 25°.

Some data were obtained for the formation by neutralization of sodium and potassium chlorides. The results were computed in the form

$$NaOH \cdot 0.5(h-1)H_2O + HCl \cdot 0.5(h-1)H_2O = NaCl \cdot hH_2O - \Delta H, \text{ at } t°$$

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[14] Noyes, Kato and Sosman, THIS JOURNAL, 32, 159 (1910).

Our experiments at 20° agree very closely for both chlorides with the exact results of Richards and his collaborators for 20°, but when our experiments at other temperatures are compared with them with the aid of temperature coefficients, the agreement is poor. The concentrations at which the discrepancies are significant are rather low, and it appears that the temperature coefficients are not known at sufficiently low concentrations to establish the extrapolated value at zero concentration.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

DOUBLE SALT FORMATION AMONG THE CARBONATES AND BICARBONATES OF SODIUM AND POTASSIUM

BY ARTHUR E. HILL

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When aqueous solutions of the carbonates and bicarbonates of sodium and potassium are brought to crystallization, five solid phases of the general nature of double salts have been found and identified with certainty. The best known of these is Trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, which has been known for a long period of time and which has been studied from its lower temperature of formation, 21.26°, up to 50° by Hill and Bacon,[1] and more recently up to 89° by Wegscheider and Mehl;[2] at this temperature the latter investigators also believe that two new double salts are formed, for which the evidence is, however, less conclusive than for toe five here under discussion. Known also for a long time, but incorrectly classed as a definite compound in the earlier literature, is the hydrated solid solution $(K_2, Na_2)CO_3 \cdot 6H_2O$, which was shown by Hill and Miller[3] to exist in contact with alkali carbonate solutions over a rather wide range of concentrations, from 34° downward. The anhydrous double carbonate $KNaCO_3$ has been shown[3] to be stable in contact with solution from 25.12° upward to at least 50°, and probably much higher. Recently, in a study of the reciprocal salt pair $K_2CO_3 + 2NaHCO_3 \rightleftarrows Na_2CO_3 + 2KHCO_3$, Hill and S. B. Smith[4] found a new double salt of the formula $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, belonging to the class of double salts without common ion which Meyerhoffer[5] has called tetragene salts. This salt was found only in four-component solutions, and its occurrence and the limits of its field were determined, it was thought, with surety. At the same time that this paper was published, there appeared the valuable and comprehensive work of Teeple upon the

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[1] Hill and Bacon, THIS JOURNAL, 49, 2487 (1927).

[2] Wegscheider and Mehl, *Monatsh.*, 49, 283 (1928).

[3] Hill and Miller, THIS JOURNAL, 49, 669 (1927).

[4] Hill and Smith, *ibid.*, 51, 1626 (1929).

[5] Meyerhoffer, *Z. anorg. Chem.*, 34, 147 (1902).