quadrivalent ruthenium by oxidation of trivalent ruthenium by the liberated bromine accounts for the secondary effect produced by free bromine.

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

THE HEATS OF DILUTION AND SPECIFIC HEATS OF BARIUM AND CALCIUM CHLORIDE SOLUTIONS[1]

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Introduction

The recent accurate and systematic investigations of the heats of dilution of various electrolytes carried out by Richards,[2] Lange[3] and their coworkers have been practically entirely limited to uni-univalent salts. The rise of the Debye and Hückel theory of complete dissociation has focused attention, however, on compounds with unsymmetrical valences, because, according to their ideas, the deviations of solutions from those predicted by the perfect gas laws are due partly to the electrical charges on the ions and when these are different the deviations are more marked. Hence a study of the heats of dilution of barium and calcium chloride solutions should prove of particular interest to the modern theories of solutions. Furthermore, one of us[4] had just completed electrochemical and viscosity experiments on barium chloride solutions and was therefore interested in this salt.

Determination of Specific Heats by the Direct Method

Introduction.—As in the previous papers of this series, the procedure in measuring the heats of dilution consisted in diluting a concentrated solution in several successive steps until the experimental errors became greater than the heat effect of the dilution. In addition to observing the rise in temperature of the calorimetric system, in order to calculate the amount of heat energy evolved it was necessary to know the heat capacity of the factors involved. The heat capacity of water and of the apparatus having been determined previously, the only factors remaining unknown were the heat capacities of the salt solutions. If the heat capacity at one

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author under the general direction of Dr. Lawrence P. Hall.

[2] Theodore W. Richards and Allan Winter Rowe, THIS JOURNAL, **43**, 770 (1921).

[3] J. Wüst and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925); E. Lange and F. Dürr, *ibid.*, **121**, 361 (1926); E. Lange and A. Eichler, *ibid.*, **129**, 285 (1927); E. Lange and E. Schwarz, *ibid.*, **133**, 129 (1928); E. Lange and G. Messner, *Z. Elektrochem.*, **33**, 431 (1927).

[4] Grinnell Jones and Malcolm Dole, unpublished results.

concentration is known, then the heat capacities of all the other concentrations may be found by performing the heat of dilution experiments at two temperatures and then calculating the change of the heat capacities of the factors by means of the Person–Kirchhoff equation. To find the heat capacity of the initial solution, a direct method must be used.

Review of Previous Values.—Specific heats of barium and calcium chloride have previously been measured by Thomsen,[5] Marignac[6] and Faasch[7] for barium chloride, and for calcium chloride by Thomsen,[5] Marignac,[6] Koch,[8] Dickinson, Mueller and George[9] and W. S. Tucker.[10] Of the data given by these investigators, Marignac's values would have sufficed for the present calculations since they were carried out at suitable concentrations, but although Richards and Gucker found Marignac to be an exceedingly accurate investigator,[11] it was decided to redetermine these values to a greater accuracy if possible.

The Apparatus.—Previous experimental methods of specific heat determinations have been reviewed recently by Richards and Gucker[11] and need not be considered here.

For this investigation the identical apparatus described by Gucker,[12] and further modified by Richards and Gucker,[13] was fortunately available. Many thanks are due to Dr. Gucker for so kindly lending the apparatus to us and for his interest and help in the carrying out of the experiments.

Materials and Solutions.—Commercial "C. P." barium chloride was dissolved, filtered, precipitated in freshly distilled alcohol, centrifuged, then again dissolved in water, recrystallized, centrifuged and dried in an oven at 120°. A spectroscopic test showed it to be free from strontium. For this direct determination of the specific heat, the solution used was that obtained by diluting the $BaCl_2 \cdot 50H_2O$ solution to $BaCl_2 \cdot 100H_2O$. It was analyzed gravimetrically and found to be $BaCl_2 \cdot 99.97H_2O$.

The calcium chloride was prepared by dissolving calcium nitrate in water, filtering, then precipitating the calcium as the carbonate, dissolving this in freshly distilled hydrochloric acid and finally recrystallizing from water, followed by drying in a centrifuge. A solution made up in the same way as the barium chloride solution proved to have the composition corresponding to $CaCl_2 \cdot 100.13H_2O$. All weighings throughout this paper were referred to the vacuum standard.

Experimental Procedure.—The experimental procedure was practically identical with that described by Gucker,[12] except that not so good

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[5] Thomsen, "Systematische Durchführung thermochemische Untersuchung," Stuttgart, pp. 110–115.

[6] Marignac, "Oeuvres completes," Vol. II, pp. 624–628.

[7] Faasch, "Dissertation," Rostock, **1911**, p. 57.

[8] W. Koch, Landolt-Börnstein, "Tabellen," 5th ed., **1923**, p. 1262.

[9] H. C. Dickinson, E. F. Mueller and E. B. George, "Bull. Bureau of Standards," Vol. **6**, p. 379.

[10] Wm. S. Tucker, *Phil. Trans. Roy. Soc.*, **215A,** 319 (1925).

[11] Theodore W. Richards and F. T. Gucker, THIS JOURNAL, **47**, 1892 (1925).

[12] Frank T. Gucker, *ibid.*, **50**, 1005 (1928).

[13] Theodore W. Richards and F. T. Gucker, *ibid.*, **51**, 712 (1929).

working conditions as he experienced can be claimed here. In his paper[14] he states that the two calorimeters never differed in temperature by more than 0.005° during the heating period. In the present investigation they differed greatly while being heated, probably by as much as 0.1°. The cause of this disconcerting inequality was different lags in the heating coils or in the calorimeters themselves which resulted, as far as could be told, from their being covered with spun gold. The standardization of the apparatus with water reduced this error appreciably; nevertheless, it must be admitted that the difficulty was present.[15] Separate check experiments showed the error of the procedure to be about 0.02% but, due to the uncertainties involved, the results might well be incorrect by as much as 0.05 or 0.1%.

Experimental Results.—In the actual procedure the temperature trends of the calorimeters before and after the heating period were plotted in order to insure that the trend had become constant before the reading was taken. Otherwise than this, the method was identical with that of Dr. Gucker. The experiments were carried out at two temperatures, from 19–21° and from 24–26°. The water standardization gave the same galvanometer deflections at both temperatures, but the barium and calcium chloride solutions were different. The results are summarized in the following tables.

Discussion of the Results.—From the viewpoint of F. Zwicky's theory,[12] the results are interesting because there is a decided increase in

TABLE I

WATER STANDARDIZATION DATA AT 20 AND 25°

Expt.	Av. temp. of heating period, °C.	Wt. of water *in vacuo*, g.	Galv. defl., cm.	Av. defl.
3	20.37, 25.01	245.26	9.00, 8.94	
4	20.12, 25.20	245.66	3.57, 3.57	3.57[a]
5	20.05, 25.01	245.26	8.52, 7.93	
6	19.67, 25.01	246.26	−4.20, −4.31	
12	20.01		−4.62	−4.38[b]
13	21.69	245.26	7.04	8.29[c]

[a] This value, which is intermediate between the two others, falls very near to a straight line drawn between the two other values when they all are plotted on a graph.

[b] The value −4.38 is the average of Expts. 6 and 12.

[c] The value 8.29 is the average of Expts. 3, 5 and 13. The total deflection due to one gram of water was taken as 12.67 cm. Expts. 12 and 13 were performed after the experiments on the salt solutions and constitute, therefore, a check on the constancy of the apparatus.

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[14] Ref. 12, p. 1013.

[15] Inasmuch as this particular research, which was the last of the experiments here described, had to be carried out in the short time of twelve days (the only time the machine was available before the summer vacation), it was not possible to attempt to overcome this difficulty.

TABLE II

SUMMARY OF RESULTS

Specific heat referred to water over the same temperature range

Expt.	Av. temp. of heating period, °C.	Wt. soln. *in vacuo*, g.	Galv. defl.	Wt. H_2O giving same galv. defl.	Sp. ht.
		$BaCl_2 \cdot 99.97H_2O$			
7	20.00	282.47	0.74	245.86	0.87039
	25.00		−5.29	246.37	.87206
8	20.02		0.05	245.91	.87057
	25.00		−5.52	246.35	.87212
		$CaCl_2 \cdot 100.13H_2O$			
10	19.87	268.02	6.54	245.41	.91564 (corrected to 20° C.)
	25.00		1.04	245.83	.91721
11	20.00		5.95	245.44	.91575
	25.00		0.56	245.87	.91736
		Averaged values for $BaCl_2 \cdot 99.97H_2O$			
	20.00				.8705
	25.00				.8721
		Averaged values for $CaCl_2 \cdot 100.13H_2O$			
	20.00				.9157
	25.00				.9173

specific heat between 20 and 25°. This shows that the change of specific heat with temperature is quite noticeable and that it is a field of research which needs further development.

Heats of Dilution and Specific Heats

Review of Previous Investigations.—Heats of dilution of barium chloride have been measured by Magie,[16] Pratt,[17] and Smith, Stearn and Schneider.[18] The first two workers measured the temperature change only to 0.001° and obtained results which agree only in sign with those of this paper, while Smith, Stearn and Schneider determined the differential heat of dilution, in concentrated solutions only, by adding smaller and smaller amounts of water to a definite amount of solution and then extrapolating to zero amount of water added. The differential heats of dilution are not comparable to the total heats of dilution with which we are concerned in this research.

In addition to these heats of *dilution* might be mentioned the interesting work on the heats of *solution* of barium chloride in water by Lehtonen,[19]

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[16] W. F. Magie, *Phys. Rev.*, **35**, 265 (1912).

[17] F. R. Pratt, *J. Franklin Inst.*, **185**, 663 (1918).

[18] G. McP. Smith, Allen E. Stearn and R. F. Schneider, THIS JOURNAL, **42**, 32 (1920).

[19] Lyyli Lehtonen, *Soc. Sci. Fennica Comm. Phys.-Math.*, **1**, No. 13 (1923).

and in water and mixtures of ethyl alcohol and water carried out by de Kolossowsky.[20]

The differential heats of dilution of calcium chloride solutions have been measured by W. S. Tucker[10] at 18°, and by Harrison and Perman[21] at 40, 50, 60, 70 and 80°. In neither research were smaller temperature changes than 0.001° measured, nor were measurements made in the range of low concentrations. Nernst and Orthmann[22] made one preliminary determination of the heat developed in the dilution of a moderately dilute solution of calcium chloride chiefly for the purpose of comparison with calcium nitrate, which at that concentration has a negative heat of dilution in contrast to calcium chloride, which has a positive heat of dilution. They were apparently solely interested in investigating the validity of the Debye and Hückel theory.

The Experimental Procedure.—The Richards adiabatic calorimeter method was used in this investigation for measuring the heats of dilution. The apparatus and the procedure have already been described in great detail by Richards and Rowe[23] and have been modified further by Richards and Gucker,[24] and improved by Richards, Mair and Hall.[25] The only variation of the procedure introduced in this investigation was to plot the temperature drifts of the calorimeter system before and after the solution and the water were mixed. The temperature readings were then made from the plot, thereby basing the final temperatures on several successive readings rather than on two. In this way there is no doubt that the temperature change of the system, in the most favorable cases, could be determined with an error of only 0.00001°. For example, in Fig. 1 are plotted the various temperatures of the system for Expt. 29 on calcium chloride. The total change was 0.00284° and agreed well with the temperature change in Expt. 30, which was 0.00285°. Needless to say, not all the experiments turned out as well as these two.

Experimental Results.—The method of calculating the results from the rise in temperature was practically the same as in the previous papers of this series. The temperature changes of the calorimetric system were corrected to 20 or 25° and then averaged before calculating any of the results. Since with two exceptions the heat capacities of the factors were used in the calculations, the temperature of the experiment was taken as the final temperature of the reaction. The two exceptions were the dilutions of $BaCl_2 \cdot 50H_2O$ to $BaCl_2 \cdot 100H_2O$ and $CaCl_2 \cdot 50H_2O$ to $CaCl_2 \cdot 100H_2O$, where the temperature of the reaction had to be the initial temperature

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[20] Nicolas de Kolossowsky, *J. chim. phys.*, **22**, 97 (1925).

[21] W. R. Harrison and W. P. Perman, *Trans. Faraday Soc.*, **23**, 1 (1927).

[22] W. Nernst and W. Orthmann, *Sitzb. Preuss. Akad. Wis.*, **1926**, 51.

[23] Theodore W. Richards and Allan W. Rowe, This Journal, **42**, 1621 (1920).

[24] Theodore W. Richards and F. T. Gucker, *ibid.*, **51**, 712 (1929).

[25] Theodore W. Richards, B. J. Mair and L. P. Hall, *ibid.*, **51**, 727 (1929).

because the heat capacities of the products were the data from which the heat capacities of the factors had to be calculated.

The specific heats are the specific heats referred to water over the same temperature range. They were calculated at 20 and 25° by using the value for the concentrated solution at 20° throughout the Person–Kirchhoff equation and the value at 25° throughout the equation. Heat capacities in mayers (joules per degree) at 20° were found by multiplying the specific heat by 4.1805,[26] and at 25° by multiplying the specific heat by 4.1780.[26] For calculating the heats of dilution at 20 and 25° the average specific heat

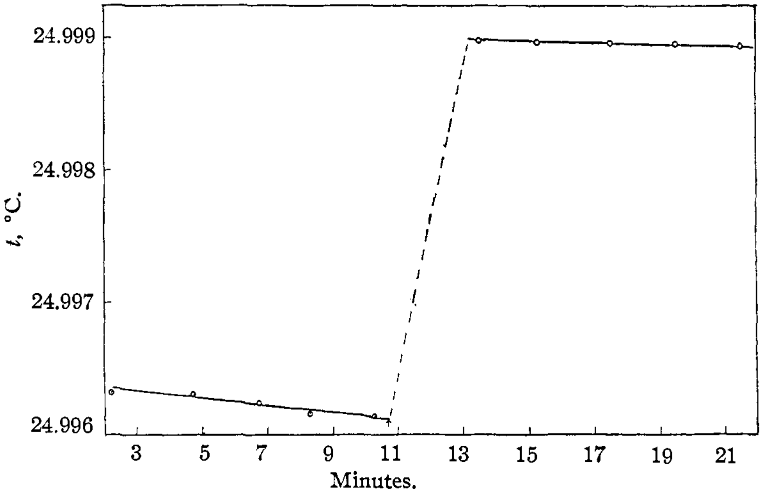

Fig. 1.—Temperature trends of system in Expt. 29 on calcium chloride.

TABLE III

SPECIFIC HEATS

Referred to water over the same temperature range

Concn. moles water per mole of salt	20°	22.5°	25°	Concn. moles water per mole of salt	20°	22.5°	25°
	Barium	Chloride			Calcium	Chloride	
50	0.7760	0.7775	0.7789	50	0.8487	0.8502	0.8516
100	.8705	.8713	.8721	100	.9156	.9164	.9172
200	.9298	.9303	.9307	200	.9553	.9557	.9561
200.3	.9299	.9304	.9308	400	.9768	.9770	.9772
390.2	.9625	.9627	.9629	800	.9881	.9882	.9883
400	.9635	.9637	.9639	1600	.9939	.9940	.9941
800	.9812	.9813	.9814	3200	.9969	.9969	.9970
1600	.9904	.9905	.9906				
3200	.9952	.9952	.9953				
6400	.9976	.9976	.9976				

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[26] The heat capacities in mayers of water. See Theodore W. Richards and F. T. Gucker, THIS JOURNAL, 47, 1890 (1925).

TABLE IV

HEAT CAPACITIES IN MAYERS

Concn. in moles H_2O per mole of salt	$BaCl_2$		$CaCl_2$	
	20°	25°	20°	25°
50	3.2440	3.2542	3.5480	3.5580
100	3.6391	3.6436	3.8277	3.8321
200	3.8873	3.8885	3.9936	3.9946
400	4.0279	4.0272	4.0835	4.0827
800	4.1019	4.1003	4.1308	4.1291
1600	4.1404	4.1387	4.1550	4.1534
3200	4.1604	4.1584	4.1675	4.1655
6400	4.1705	4.1680		

TABLE V

MOLAL HEATS OF DILUTION AND LOSS IN MOLAL HEAT CAPACITY ON DILUTION

Barium Chloride

Dilution in moles H_2O per mole salt	Heat of dilution (joules) at		Loss in heat capacity, mayers
	20°	25°	
50- 100	−145.0	90.7	− 47.1
100- 200	75.2	225.3	− 30
200- 400	210.9	305.7	− 16.3
400- 800	269.4	333.5	− 13.4
800- 1600	281.9	324.7	− 8.6
1600- 3200	244.3	285.9	− 8.3
3200- 6400	.....	259.1	.....
6400–12800	.....	107	.....
50- 200	− 69.8	316.0	− 77.1
50- 400	141.1	621.7	− 93.4
50- 800	410.5	955.2	−106.8
50- 1600	692.4	1279.9	−115.4
50- 3200	934	1566	−124
50- 6400	.....	1825	.....
50–12800	.....	1932	.....

Calcium Chloride

Dilution in moles H_2O per mole salt	Heat of dilution (joules) at		Loss in heat capacity, mayers
	20°	25°	
50- 100	638.4	808.7	−34.1
100- 200	467.9	579.4	−22.3
200- 400	397.9	470.1	−14.4
400- 800	358.2	409.9	−10.3
800–1600	302.7	347.8	− 9.0
1600–3200	....	276.1	....
3200–6400	....	215.1	....
50- 200	1106	1388	−56.4
50- 400	1504	1858	−70.8
50- 800	1862	2268	−81.1
50–1600	2165	2616	−90.1
50–3200	....	2892	....
50–6400	....	3107	....

over that range was used, since this involves no appreciable error. A negative sign for the heats of dilution means heat absorbed. The absolute value of the final temperature is the same as in the previous papers of this series (that is, the investigations which used the heat of dilution apparatus). The heat capacity of the apparatus devoid of water or solution was 76.4 mayers.

In all of the tables, a correction of −0.05° should be applied to all of the temperature readings. The absolute temperature is then correct to within ±0.02°.

Comparison with Earlier Data

In Table VI the data obtained in this research are tabulated with all other comparable values which are available in the literature. It might be mentioned that Pratt[17] published his values of the heats of dilution for barium chloride only in the form of a graph, which makes it impossible to obtain accurate values for comparison. In the specific heat column, (M.) stands for Marignac[6] and (T.) for Thomsen.[7]

TABLE VI

COMPARISON WITH EARLIER VALUES. SPECIFIC HEATS

				Richards and Dole		
Concn.	t, °C.	Sp. ht.	t, °C.	Sp. ht.	t, °C.	Sp. ht.
		Barium Chloride				
$50H_2O$	24.5	0.7799 (M.)	20	0.7760	25	0.7789
$100H_2O$	24.5	.8751 (M.)	20	.8705	25	.8721
$200H_2O$	24.5	.9319 (M.)	20	.9298	25	.9307
	18	.932 (T.)				
		Calcium Chloride				
$50H_2O$	22.5	0.8510 (M.)	20	0.8487	25	0.8516
$100H_2O$	22.5	.9154 (M.)	20	.9156	25	.9172
$200H_2O$	22.5	.9554 (M.)	20	.9553	25	.9561
	18	.957 (T.)				

HEATS OF DILUTION IN JOULES

Barium Chloride

	Magie[16]		Richards and Dole	
Dilution	t, °C.	Ht. of diln.	t, °C.	Ht. of diln.
50–100	24.5	29.5	25.0	90.7
100–200	24.5	80	25.0	225.3
200–400	24.5	100	25.0	305.7
400–800	24.5	146	25.0	333.5

Discussion of the Results

Although this is chiefly an experimental paper, it would not be amiss to draw a few conclusions from the results. In their investigation of the differential heats of dilution of barium chloride, Smith, Stearn and Schneider[18] made several measurements in the region of concentrated solutions, where the thermal effect on the addition of water is always negative. From this they concluded that the heats of dilution of barium chloride were always negative and so drew the curve on their graph. They also investigated strontium chloride, which they found to have just the opposite heat effect from barium chloride, *i. e.*, the differential heats of dilution were always positive. In both curves they found a sudden change in the region of 1.25 molal; they concluded from this that at that concentration the solutions of 1.25 molal strontium and barium chloride consisted chiefly of the intermediate ions $BaCl^+$ and $SrCl^+$. They explained the difference in the signs of the heats of dilution by the remarkable statement that the heat of hydration must be endothermic in one case and exothermic in the other.

In the light of modern theories of solutions, it is hardly necessary to explain the results in this way. In the first place, if there are complex ions, they are certainly not of the type $BaCl^+$, because the transference number of the barium ion in barium chloride solutions decreases with increasing concentrations, whereas if ions like $BaCl^+$ were present, the transference number would have to increase.[4] The complex ions, then, must be of the type $BaCl_3^-$ or $BaCl_4^{--}$ if they are present at all.

If we consider the very dilute solutions, we find excellent qualitative agreement with the Debye and Hückel theory. Both calcium and barium chloride have positive heats of dilution at very small concentrations, which the theory predicts.[27] The magnitudes of the thermal effects approach each other closely in dilute solutions, as would be expected from the complete dissociation theory. Hence in dilute solutions there is no need of assuming complex ions. Furthermore, in concentrated solutions there are so many effects such as heat of hydration, heat of polymerization of the water molecules, etc., that it is unnecessary if not actually unsound to explain any bend in the curve of the heat of dilution by merely *one* effect, such as that of the presence of complex ions. The heats of solution[19] of calcium, strontium and barium chlorides show a regular decrease in magnitude as the atomic weight increases, those for strontium chloride being half-way between those for calcium and barium chlorides; hence the different thermal effects of these solutions may be due to the intrinsic but regular difference in the atoms and not to any peculiarity of complex ions.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this program of research.

Summary

1. The specific heats of a concentrated solution of calcium and barium chloride have been measured directly.

2. By the indirect method the specific heats and heat capacities of all the solutions have been determined.

3. The heats of dilution and the loss in heat capacity on dilution have been calculated from the observations.

4. Qualitative agreement with the Debye and Hückel theory has been found in dilute solutions.

NEW YORK, N. Y.

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[27] N. Bjerrum, *Z. physik. Chem.*, **119**, 45 (1926).