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THE SPECIFIC HEATS OF CRYSTALLIZED SALTS.

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The physical structure of double salts and salts containing water of crystallization has long been a subject of discussion. It was hoped that some light might be thrown on this subject by a study of their specific heats at various temperature ranges. These figures would also be of considerable value in other calculations of a thermodynamic nature, and very little work had been done at temperatures below 0°. Accordingly the research was undertaken.

The various sulfates of copper were chosen for this work because of the number of possible salts that could be made, their permanence, purity, and ease of analysis. Baker & Adamson's analyzed chemicals were used throughout the work, but were always checked by analyses made on the sample actually used. The double salts were made by crystallizing them out at about 30° from saturated solutions of the calculated amounts of the single salts. To these a little sulfuric acid was added to prevent the formation of basic salts. The crystals were crushed and washed with distilled water four times, dried in a centrifuge, and then powdered and air dried to constant weight. Electrolytic determination of the per cent of copper was in each case within the limit of accuracy of the method. Anhydrous copper sulfate was made from the pure hydrated salt by grinding and drying for several days at 250° on a sand bath with stirring until constant weight, very nearly that calculated, was attained. The salt was bottled hot and used with minimum exposure. The other salts could be bought in a high state of purity. These were checked only by drying tests to find the amount of included water, which was in all cases negligible. Details of the analyses will be given later.

The specific heats of the single salts used have been determined at short temperature ranges between +15° and +100° by various experimenters of half a century ago. Regnault[1] in 1841, Pape[2] in 1864, Kopp[3] in 1864, and Schüller[4] in 1869, worked on them as part of a comprehensive study of the specific heat of compounds. While their determinations were of the greatest importance at that time, and were undoubtedly performed with the greatest accuracy then obtainable, they cannot be too closely

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[1] Regnault, *Ann. chim.*, [3] 1, 129 (1841).

[2] Pape, *Pogg. Ann.*, 122, 408 (1864).

[3] Kopp, *Ann. Suppl.*, [3] 1, 289 (1864–5).

[4] Schüller, *Pogg. Ann.*, 136, 70, 235 (1869).

relied upon at present, owing to the short temperature interval used, and the crudities of the calorimeters and thermometers that were then available.

The subject was not touched upon again until in 1906 and 1907 Nordmeyer[1] and his collaborators made a few experiments on salts in connection with a crude method that he used to determin the specific heats of metals. It consisted in pouring a weighed amount of the substance into a weighed amount of liquid air and weighing again. He found that about 50 calories were taken up to evaporate a gram of air. He did not work with any of the salts studied in this research.

Nernst[2] and his followers, Koref, Lindemann, Magnus, and Pollitzer have worked out a very elaborate electrical method for determining specific heats of all sorts of substances *at* very low temperatures and through very short ranges at very low temperatures. They wrap the substance in a vacuum with a calibrated wire, cool in liquid hydrogen, measure the temperature by the wire, pass a known amount of electrical energy through the wire, and measure the temperature again. They do not show that the temperature is uniform throughout the substance. From their results they have evolved a deeply mathematical vibration heat theorem.[3] This has, however, been severely criticized from a mathematical point of view by Kohnstamm and Ornstein[4] and will not be taken up here. As yet, Nernst has not worked with sulfates.

The adiabatic calorimeter proved of great advantage in this research. Thirty grams of salt required between 10 and 20 minutes to become completely warmed, and a very large possibility of error is eliminated with the correction for cooling. The calorimeter was of the type frequently used in the Harvard laboratory, and an exact duplicate of the one used by the writer in a previous research.[5]

The crucibles which contained the salts were made of spun copper, $2^1/_2''$ long and $^3/_4''$ in diameter. One end was conical to prevent them from splashing when they fell into the calorimeter, the other end was fitted with a watertight screw cap. This cap was so tight that when the crucible was cooled empty and the air inside contracted, no outside air was drawn in. The crucibles weighed about 60 grams apiece and had a water equivalent of about 5 grams when cooled with liquid air, $5^1/_2$ grams when cooled with solid carbon dioxide. They did not need to be so heavy, but the extra weight did no harm. To cool the crucibles out of contact with the cooling medium, they were put, pointed end up, into steel tubes,

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[1] Nordmeyer, *Ann. Phys.*, [4] **22**, 99 (1906); *Ber. physik. Ges.*, **5**, 173 (1907).

[2] Nernst, *Sitzber. kgl. Pr. Akad. Wiss.*, **1910**, 262; **1911**, 306, 494; *Electrochem. Z.*, **16**, 269; **17**, 5 (1911).

[3] Einstein, "Heat Theorem," *Ann. Phys.*, [4] **22**, 184 (1906).

[4] *Proc. K. Akad. Wet. Amsterdam*, **14**, 802 (1912).

[5] Richards and Jackson, *Z. physik. Chem.*, **70**, 414 (1909).

which they fitted closely. These tubes were eight inches long and had insulating handles of slightly larger glass tubing cemented on. The tubes had flat spun bottoms. It was found that a soldered joint leaked when cooled in liquid air, due to contraction.

These tubes were cooled by immersion in Dewar cylinders containing the cooling mixture of liquid air or solid carbon dioxide and alcohol. The mixture was replenished as often as necessary and the salts were cooled for 6 hours or more. The salt that took the longest time to warm in the calorimeter was tried once with only $3^1/_2$ hours cooling. The result was normal, as was one when the salt was cooled 17 hours. This shows that 6 hours gave complete cooling.

The temperature of the liquid air was taken with a pentane thermometer. This could not be read in practice closer than half a degree, and was undoubtedly the least accurate part of the determination. It was standardized by putting it into a tall unsilvered Dewar cylinder, filling the cylinder with liquid air, letting it evaporate to one-third of its volume, refilling, evaporating again, and again refilling. When this was again evaporated to a third of its volume, a constant reading of the thermometer of —184.0° was made through the liquid and glass while the thermometer bulb and entire column were submerged. This reading remained constant for nearly an hour, until the liquid evaporated down so as to expose part of the pentane column. Since liquid oxygen thus made boils at —182.5°,[1] the thermometer read 1.5° too low. When immersed in solid carbon dioxide and alcohol it read —79.3°, 0.9° too low.

The temperature of the paste of solid carbon dioxide and alcohol was not taken, since it is constant at —78.4° within wide limits.

The Beckmann thermometer used to determin the change in temperature of the calorimeter was of the best. It was made by Dr. Geissler and had a scale of 5.7° graduated to hundredths, and legible with a glass to thousandths. It had been used and calibrated by Burgess[2] in his work at Harvard, and subsequently restandardized with the greatest accuracy by Rowe and Barry.[3] They compared it with French, German, and American standard instruments. In no case was the correction between two points a tenth-degree apart greater than +0.005° or less than —0.002°. It was set high, 0° on the scale being equivalent to 20.4°, since the work was done in hot weather.

The manipulation in carrying out a determination was of the simplest. The calorimeter with fittings was weighed full of water. A constant was then subtracted, which represented the weight of the calorimeter and fittings less their water equivalent. The difference was therefore

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[1] Dewar, *Chem. Centr.*, 1, 1193 (1901).

[2] Richards and Burgess.

[3] Not yet published.

the total water equivalent. The temperature of the outer bath was then adjusted until the temperature of the inner bath was constant. This was then read and recorded. The pentane thermometer was then read, if liquid air was used. Then the steel tube was seized by the handle and drawn out of the cooling mixture, the cover of the calorimeter was raised, the tube inclined over the opening and the crucible slid into the calorimeter. Immediately a handful of cracked ice was dropped into the outer bath and a stream of ice water was run in. The thermometers in the inner and outer baths registered almost identical changes. This was continued with adjustment of the stream until the calorimeter again reached equilibrium, when the final temperature was read and recorded.

The crucible must have gained a little heat during transference but this must be almost a constant quantity, since the manipulation was very uniform. Since the water equivalent of the empty crucible was determined in exactly the same way as the specific heat of the salts, and was subtracted in computation, this error disappears from the final results. The amount of heat needed to warm the air in the empty crucible was negligible.

The method of calculation was as follows: the water equivalent of the calorimeter times its temperature equals the total heat evolved. The water equivalent of the crucible times its temperature change equals the heat taken by the crucible. Subtracting this from the total heat leaves the heat taken by the salt. Divide this number by the weight of the salt times its temperature change and the result is the specific heat of the salt.

A specimen determination is given.

Weight of crucible No. 1.....	60.35	Wt. calorimeter and water..	1064.6
$+CuSO_4K_2SO_4.6H_2O$........	89.74	Constant, subtract.........	283.6
Weight of salt used..........	29.39	Total water equivalent.....	781.0

COOLED FROM 8.30 A.M.

Time.	Temperature.		Time.	Temperature.	
	Inner.	Outer.		Inner.	Outer.
3 : 02	5.257	5.25	3 : 09	2.70	2.57
3 : 03	5.256	5.25	3 : 10	2.65	2.35
3 : 04	5.256	5.25	3 : 13	2.570	2.26
3 : 05	dropped in		3 : 17	2.540	2.27
3 : 06	3.1	3.1	3 : 21	2.529	2.27
3 : 07	2.95	2.90	3 : 22	2.529	2.27
3 : 08	2.78	2.65	3 : 23	2.529	2.27

Initial temp., —191.5°; final temp., +22.9°; change of temp., 214.4°.

Calorimeter change, 2.727°; corrected, 2.751°; water equiv. of crucible, 4.97.

I. 2.751 × 781.0 = 21.48, total heat evolved.
II. 4.97 × 214.4 = 1065, taken by crucible.
III. difference 1083, taken by salt.
IV. 29.39 × 214.4 = 6300.
V. 1083 ÷ 6300 = 0.171 specific heat.

The sources of possible error are as follows: the water equivalent of the calorimeter was probably known to one part in a thousand. Its change of temperature could be read within 0.003°, or one part in 500, when working with solid carbon dioxide, one part in 900 when working with liquid air. The water equivalent of the crucible would introduce a constant error of about one part in 500 with solid carbon dioxide, one part in 250 with liquid air. The temperature change of the crucible and salt was known within one part in a thousand with solid carbon dioxide, one part in 400 with liquid air. The weight of the salt was known within one part in 3,000. The sum of these errors is about 0.004 in each case. The actual probable error for the experiments as conducted was calculated from the customary formula, $^2/_3\sqrt{\Sigma d^2/n(n-1)}$ and is quoted below the average found in each case.

In this way the specific heat of $CuSO_4.5H_2O$ was determined. Twenty-three and six-tenths grams of the salt after heating to 250° for 7 hours weighed 15.13 grams, while the calculated weight of the anhydrous salt is 15.09 grams. The specific heat was found to be:

	—78.4° to +22°.	—190° to +22°.
	0.237	0.197
	0.236	0.201
	0.236	0.207
Average	0.236	0.202
Probable error	0.001	0.006

Copper sulfate anhydrous was found to contain 39.06% Cu, calculated, 39.91%. The specific heat was:

	—78.4° to +22°.	—190° to +22°.
	0.134	0.118
	0.120	0.122
	0.128	0.119
Average	0.127	0.120
Probable error	0.008	0.003

Copper ammonium sulfate hexahydrate was found to have 15.77% and 15.78% Cu, calculated, 15.91%. The specific heat was:

	—78.4° to +22°.	—190° to +22°.
	0.242	0.226
	0.250	0.233
	0.255	0.231
Average	0.249	0.230
Probable error	0.008	0.004

Copper sodium sulfate hexahydrate was found to have 15.60% Cu, calculated, 15.55%. The specific heat was:

	—78.4° to +22°.	—190° to +22°.
	0.184	0.151
	0.179	0.155
	0.194	0.154
Average	1.086	0.153
Probable error	0.010	0.003

Copper potassium sulfate hexahydrate was found to have 14.35% Cu, calculated, 14.39%. The specific heat was:

	—78.4° to +22°.	—190° to +22°.
	0.217	0.171
	0.220	0.171
	0.217	0.181
Average	0.218	0.174
Probable error	0.001	0.007

Ammonium sulfate dried at 110° for 4 hours lost 0.04%. The specific heat was:

	—78.4° to +22°.	—190° to +22°.
	0.331	0.282
	0.330	0.281
	...	0.286
Average	0.330	0.283
Probable error	0.001	0.003

Sodium sulfate dried for 4 hours at 110° lost 0.02%. The specific heat was:

	—78.4° to +22°.	—190° to +22°.
	0.201	0.169
	0.200	0.162
	0.191	0.171
Average	0.197	0.167
Probable error	0.006	0.002

Potassium sulfate, dried at 110° for 4 hours lost 0.20%. The specific heat was:

	—78.4° to +22°.	—190° to +22°.
	0.173	0.154
	0.171	0.141
	0.168	0.147
Average	0.171	0.147
Probable error	0.003	0.008

Zinc sulfate, heptahydrate heated to 250° for 10 hours lost 43.70%, calculated, 43.90%. The specific heat was:

	—78.4° to +22°.	—190° to +22°.
	0.287	0.212
	0.288	0.216
	0.285	0.216
Average	0.287	0.215
Probable error	0.001	0.003

These measurements were made as an independent research. In connection with a previous problem, the following two salts were determined; high quality chemicals were used, but they were not analyzed:

Cadmium sulfate ($3CdSO_4.8H_2O$).

	—78.4° to +22°.	—190° to +22°.
	0.167	0.135
	0.166	0.134
	0.170	0.133
	0.171	0.138
Average	0.168	0.135
Probable error	0.001	0.001

Ferrous sulfate heptahydrate.

	—78.4° to +22°.	—190° to +22°.
	0.283	0.242
	0.296	0.236
	0.297	0.229
	0.293	0.229
Average	0.292	0.234
Probable error	0.002	0.002

By simple arithmetic the specific heats of these salts may be found for the range —190° to —78.4° and the results may be tabulated, as follows:

Salt.	—78.4° to +22°.	—190° to +22°.	—190° to —78.4°.
$CuSO_4.5H_2O$	0.236±0.001	0.202±0.006	0.169±0.007
$CuSO_4$	0.127±0.008	0.120±0.003	0.114±0.010
$Cu(NH_4)_2(SO_4)_2.6H_2O$	0.249±0.008	0.230±0.004	0.212±0.012
$CuNa_2(SO_4)_2.6H_2O$	0.186±0.010	0.153±0.003	0.121±0.013
$CuK_2(SO_4)_2.6H_2O$	0.218±0.001	0.174±0.007	0.135±0.008
$(NH_4)_2SO_4$	0.330±0.001	0.283±0.003	0.241±0.004
Na_2SO_4	0.197±0.006	0.167±0.002	0.140±0.008
K_2SO_4	0.171±0.003	0.147±0.008	0.125±0.011
$ZnSO_4.7H_2O$	0.287±0.001	0.215±0.003	0.150±0.004
$CdSO_4.8/3H_2O$	0.168±0.001	0.135±0.001	0.105±0.002
$FeSO_4.7H_2O$	0.292±0.002	0.234±0.002	0.182±0.004

The Specific Heat of Ice.

Person[1] began this interesting study in 1847 by cooling ice with salt and ice to —20°. He found the value 0.5017 as the average of five determinations.

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[1] Person, *Ann. chim.*, [3] 21, 295 (1847).

Regnault[1] in 1849, had solid carbon dioxide at his disposal, and, in connection with other work, found the value 0.474 for the range of —78.4° to 0°.

The subject does not seem to have been touched on again until 1905 when Dewar,[2] made determinations through various ranges with his "Liquid Air and Hydrogen Calorimeter." He gives some interesting figures, but no data in regard to their accuracy, merely saying that "with precautions it is easy to get results within 2%." His figures were:

—252.5° to —188°	0.146
—188° to —78.4°	0.285
—188° to —18°	0.348

Nordmeyer and Bernoulli with their apparatus found the specific heat of ice from —185° to 0° to be 0.345.

For this work we used a J. Lawrence Smith platinum crucible full of carefully distilled water. In cooling it, it was necessary to cool only the bottom of the tube containing the crucible until the water was frozen. In this way, the expansion of the ice was all directed upward, otherwise the crucible could not stand the strain. The latent heat of melting, 78.8 calories, and the specific heat of liquid water had to be considered in calculating. The results were as follows:

	—78.4° to 0°.	—188° to 0°.	—188° to —78.4°.
	0.428	0.343	...
	0.428	0.337	...
	0.422	0.335	calculated
	0.431	0.332	...
	0.413	...	...
Average	0.424	0.337	0.277
Probable error	0.002	0.001	0.003

The specific heats of almost all of the single salts studied here have been determined at higher ranges by other investigators. These values are given in Landolt and Börnstein's tables. If they were more reliable, an interesting study of the change of molecular heat with change of temperature could be made, but this must wait for more accurate data at the higher ranges. In a previous paper[3] on the specific heats of the elements at low temperatures, a graphic method was outlined for showing the change of atomic heat with change of temperature. In our experience with thirty elements we found that the atomic heat of nearly every one decreased at an increasing rate with decreasing temperature. This seems also to be true of the molecular heats of the sulfates, except

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[1] Regnault, *Ann. chim. phys.*, [3] 26, 261 (1849).

[2] Dewar, *Proc. Roy. Soc.*, (*A*) 76, 325 (1905).

[3] Richards and Jackson, *loc. cit.*

copper sulfate pentahydrate and anhydrous, although metallic copper shows a marked decrease. The molecular heats of the salts are shown in the following table:

MOLECULAR HEATS.

Salt.	—190° to —78.4°.	—68.4° to +22°.	Approximately +22° to +45°.
$CuSO_4.5H_2O$	42.2 ± 1.7	58.4 ± 0.3	71.2
$CuSO_4H_2O$	18.2 ± 1.8	20.3 ± 1.2	29.4
$Cu(NH_4)_2(SO_4)_2.6H_2O$	84.7 ± 4.8	99.5 ± 3.2	..
$CuNa_2(SO_4)_2.6H_2O$	49.6 ± 5.2	76.2 ± 4.0	..
$CuK_2(SO_4)_2.6H_2O$	59.6 ± 3.2	96.2 ± 0.4	..
$(NH_4)_2SO_4$	31.8 ± 0.6	43.6 ± 0.2	46.2
Na_2SO_4	19.9 ± 1.2	28.0 ± 0.8	32.5
K_2SO_4	21.8 ± 2.0	28.8 ± 0.5	34.1
$ZnSO_4.7H_2O$	43.1 ± 1.2	82.5 ± 0.3	99.7
$CdSO_4.8/3H_2O$	26.9 ± 0.4	43.1 ± 0.3	..
$FeSO_4.7H_2O$	50.6 ± 1.0	81.2 ± 0.5	96.2

Some interesting conclusions can be drawn from these figures. The molecular heat of anhydrous copper sulfate from —190° to —78.4° is 18.2 ± 1.8, and that of the salt with five molecules of water of crystallization is 42.2 ± 1.7. Then the difference, 24.0 ± 3.5, is five times the molecular heat of water of crystallization, plus any loss in internal heat capacity that the copper sulfate molecule may have suffered in taking on water of crystallization. The molecular heat of free ice for this range was found to be 4.99 ± 0.6. Five times this is 24.95 ± 3.0.

Comparisons at the range —78.4° to +22° are more complicated. In practice, the ice would melt with a latent heat of melting of 78.8 calories per gram. This would throw the calculation out, because the water of crystallization does not melt. But, if we could superheat the ice to 22° without melting it, we could make the comparison. By extrapolating the curve of the specific heat of ice, we find a specific heat of about 0.5 for the range 0° to +22°, giving a specific heat for the range, —78.4° to +22° of 0.441, or a molecular heat for this range of 7.93, estimated probable error ±0.2.

Making this assumption, we can repeat the above calculation for this range. The hydrated salt has a heat of 58.4 ± 0.3 and the anhydrous salt a heat of 20.3 ± 1.2, difference, 38.1 ± 1.5. Five molecules of ice need 39.65 ± 1.0. In both of these cases it is evident that there may well have been no loss in internal heat energy, and that water of crystallization has the same specific heat as that of ice.

Turning now to the double salts of copper, we find that copper ammonium sulfate hexahydrate has a molecular heat at the range —190° to —78.4° of 84.7 ± 4.8, copper sulfate pentahydrate, 42.2 ± 1.7, ammonium sulfate 31.8 ± 0.6, ice 4.99 ± 0.6. These factors add up to 79.0 ± 2.9. At the higher range the molecular heat of the product is 99.5 ± 3.2, while the molecular heats of the factors are 58.4 ± 0.3, 43.6 ± 0.2, and 7.9 ± 0.2, total, 109.9 ± 0.7.

In the same way, copper sodium sulfate hexahydrate at the low range has a molecular heat of 49.6 ± 5.2, while the factors are 42.2 ± 1.7, 19.9 ± 1.2, and 4.99 ± 0.6, total, 67.1 ± 3.5. At the high range the product has a molecular heat of 76.2 ± 4.0 and the factors are 58.4 ± 0.3, 28.0 ± 0.8, and 7.9 ± 0.6, total, 94.3 ± 1.7.

Copper potassium sulfate hexahydrate at the low range has a molecular heat of 59.6 ± 3.2. Its factors are 42.2 ± 1.7, 21.8 ± 2.0, and 4.99 ± 0.6, total, 69.0 ± 4.3. At the high range the molecular heat of the product is 96.2 ± 0.4 and of the factors is 58.4 ± 0.3, 28.8 ± 0.8, and 7.9 ± 0.6, total, 95.1 ± 1.7.

These results are compiled in the following table:

Salt.	Products.	Factors.	Difference.
	—190° TO —78.4°.		
$CuSO_4.5H_2O$	42.2±1.7	43.1±4.8	— 5.6 to + 7.4
$Cu(NH_4)_2(SO_4)_2.6H_2O$	84.7±4.8	79.0±2.9	—13.4 to + 2.0
$CuNa_2(SO_4)_2.6H_2O$	49.6±5.2	67.1±3.5	+ 7.8 to +26.2
$CuK_2(SO_4)_2.6H_2O$	59.6±3.2	69.0±4.3	+ 2.5 to +16.9
	—78.4° TO +22°.		
$CuSO_4.5H_2O$	58.4±0.3	59.9±2.2	— 1.0 to + 4.0
$Cu(NH_4)_2(SO_4)_2.6H_2O$	99.5±3.2	109.9±0.7	+ 6.4 to +14.3
$CuNa_2(SO_4)_2.6H_2O$	76.2±4.0	94.3±1.7	+12.4 to +23.8
$CuK_2(SO_4)_2.6H_2O$	96.2±0.4	95.1±1.7	— 3.2 to + 1.0

Conclusions.

From this table, it can be seen that the sum of the molecular heats of the factors agrees within the limits of error with the molecular heat of the product in the case of $CuSO_4.5H_2O$. With the double potassium salt, the agreement is excellent at one range, and close to the limit in the other. With the double ammonium salt, the agreement is within the limit in one case, and 10% out in the other. With the double sodium salt, however, the factors consistently have a greater heat energy content than the product. This shows a loss of internal heat capacity on the formation of the double salt of 20 to 25%.

It remains to be shown whether there is any connection between this and the fact that sodium sulfate will crystallize with water of crystallization, while potassium and ammonium sulfates will not. Another method of attack is through the heats of solution of these double salts and their factors. It is hoped that this work can soon be undertaken. A revision is also planned of the specific heats of these salts between +22° and +45°, giving a third range for comparison and an opportunity to study the change of molecular heat with change of temperature.

At the suggestion of Professor T. W. Richards, this investigation was begun several years ago. Practically all of the work was, however, executed in the summer during his absence. It is a pleasure to express my thanks to Professor G. P. Baxter for having put the facilities of the Harvard laboratory at my disposal.

Summary.

The specific heats of eleven salts and of ice between —190° and +22°, and —78.4° and +22° are determined adiabatically.

From these figures the molecular heats are calculated between —190° and —78.4°, and —78.4° and +22°

Comparisons are made at both ranges between the molecular heats of hydrated and double salts and those of their factors.

It is shown that these are almost the same except in the case of copper sodium sulfate.

An outline of further work on the subject is given.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE PREPARATION OF PERCHLORIC ACID.

BY H. H. WILLARD.

Received August 30, 1912.

Among the various methods used for preparing perchloric acid only two deserve serious consideration. The first is that of Kreider,[1] which consists in treating sodium perchlorate with concentrated hydrochloric acid, filtering off the sodium chloride formed, and evaporating to expel all hydrochloric acid. The details of this method have been carefully worked out by Mathers.[2] The acid thus obtained is contaminated with sodium perchlorate, together with impurities present in the materials. To obtain a pure product, the crude acid must be distilled under diminished pressure. The second method is that of Mathers,[3] which consists in the distillation of potassium perchlorate with concentrated sulfuric acid in a current of steam under diminished pressure. The only advantage of this method over the preceding is in the use of the cheaper potassium salt, but this is more than counterbalanced by its disadvantages. Only comparatively small quantities can be used at a time, the distillation is rather troublesome, and the acid obtained contains 20–25% of sulfuric acid, so that, if a reasonably pure acid is required, it must be redistilled or the sulfuric acid precipitated by barium carbonate.

In trying to find a cheaper method of preparing perchloric acid, attention was directed to the ammonium salt, which is not much more expensive than the potassium salt, and considerably cheaper than the sodium

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[1] *Z. anorg. Chem.*, **9**, 343; *Am. J. Sci.*, [3] **49**, 443.

[2] THIS JOURNAL, **32**, 66.

[3] *Indiana University Studies*, **9**, 173; *Trans. Am. Electrochem. Soc.*, **21**, 331.