

ON THE SOLUBILITY OF MANGANOUS SULPHATE

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Something over a year ago, during the discussion of some other work, Dr. Bancroft called my attention to a very interesting case of equilibrium in systems of manganous sulphate and water, studied by Linebarger,¹ among which, according to his determinations, we have several possible combinations consisting of a stable hydrate, an unstable hydrate, solution and vapor, where the stable form is the more soluble. Thus, for example, according to Linebarger, at 15° the stable form is the pentahydrate and its solubility is 72.33 parts anhydrous salt per 100 parts of water; while that of the tetrahydrate (stable from 18° to 30°) is 67.12 parts per 100 of water. Thus it seems natural to assume that if some of each hydrate were introduced into a solution, containing say 70 parts salt to 100 parts of water, the stable form would dissolve and the unstable form be precipitated; unless it be possible to form two solutions of the same concentration, but differing in their properties, depending upon which hydrate they were made up from.

It was with the hope of throwing some light on this matter that the present work was undertaken. It soon became manifest that the greater part at least of the peculiarities of these systems are to be explained by inaccuracies in Linebarger's solubility determinations, and the problem then resolved itself into a redetermination of these and this it is that forms the major part of this present paper.

The solubility of this salt has received the attention of a number of workers previous to this time. Brands² seems to be the first whose results are worthy of attention at the present day.

¹ Amer. Chem. Jour. 15, 225 (1893).

² Pogg. Ann. 20, 556 (1830).

His methods were rather crude and the data are of interest more in a qualitative than a quantitative sense. Étard¹ has also given us some values and deduced from them linear equations connecting solubility with temperature, but the experimental data presented are so meagre that it becomes practically impossible to coordinate them with later work. Mulder² determined the solubility from 0° to 102.5°, using the tetrahydrate as solid phase to start with, which is a very indefinite statement of the conditions as will be seen from what follows. His results are all somewhat higher than those here presented, and diverge more from these as the temperature rises. They are, however, all lower than those of Linebarger. I have been unable to procure Mulder's original papers and the abstracts which are available give nothing of the experimental details. Since the publication of Linebarger's papers, Stortenbeker³ has called attention to the improbable character of his curves, but seems to have made no experiments on the matter.

Linebarger's work includes the hydrates with 1, 2, 3, 4, 5, 6, and 7 molecules of water of crystallization. The only hydrates which I have been able to prepare are those with 1, 4, 5, and 7 of water, which of course need only mean that the exact conditions required for the separation of the others have not been realized; but it probably indicates that, if they are stable at any temperature, their solubility curves lie close to those of the other hydrates, and the salts have little tendency to crystallize from their supersaturated solutions.

Of these other hydrates, the one with six molecules of water was obtained by Brands⁴ on drying the heptahydrate between folds of filter-paper at 8° to 10°. As the transition point from heptahydrate to pentahydrate is about 9°, it seems quite likely that Brands was dealing with a mixture of these two. Linebarger obtained the salt as hexagonal plates by cooling a

¹ Comptes rendus, 106, 208 (1888).

² Scheik. Verhandel, Rotterdam, p. 137 (1864).

³ Stortenbeker. Zeit. phys. Chem. 17, 648 (1895).

⁴ Pogg. Ann. 20, 569 (1830).

solution "containing about 80 pct. of anhydrous salt"¹ into a temperature of 2° to 5° until crystals separated. Some of these were then sown in a solution kept at 0° and thus well-formed crystals prepared.

During the present investigation, a number of attempts were made to prepare this salt by cooling strong solutions to 0° and also a few degrees above and below, but it was always the heptahydrate that separated out. Expecting that the hexahydrate, if it existed, would probably be isomorphous with those of zinc or magnesium, crystals of these were introduced into the supercooled solutions, but they gradually dissolved and eventually a separation of heptahydrate set in (see det. 117).

As to the trihydrate, Linebarger seems to be the only one who has separated it in well-formed crystals. Brands' method for its preparation consisted in treating the higher hydrate with boiling absolute alcohol or oil of turpentine, also by allowing the anhydrous salt to absorb moisture from the air; and he sometimes found it mixed with tetrahydrate in the crystallization of the latter. Linebarger quotes Graham as the only previous investigator who has mentioned the spontaneous crystallization of the trihydrate from solution. Playfair² however obtained it as a crust on the surface of a boiling saturated solution. These crusts were removed and rapidly dried between folds of filter-paper. Linebarger himself prepared it both by the dehydration of the tetrahydrate with 98 percent of alcohol at 20° for a month, and also by crystallizing aqueous solutions at 33° to 35°. The dihydrate was obtained by Brands on melting the heptahydrate in its water of crystallization and also by heating it to about 80° with 55 percent alcohol. Linebarger found that it formed as a crust over the surface of a solution evaporated on the water-bath

¹ By this is probably meant a solution containing 80 parts of anhydrous salt to 100 parts of water, as the most concentrated solutions given by Linebarger do not exceed 88 parts of salt to 100 parts of water, and even this value is probably much too high, on account of his method of analysis, which is to be discussed later.

² Quoted by Thorpe and Watts, *Jour. Chem. Soc. (Lond.)* 37, 113 (1880) from previously unpublished manuscript.

and also secured well-formed crystals by evaporating a solution in the thermostat at 40° to 45°. He found the same salt was likewise produced when a layer of strong solution of the salt was allowed to diffuse into concentrated sulphuric acid.

The salts used in the following work were prepared by recrystallizing the manganous sulphate from three different factories, viz. : Merck and Co., New York ; Rosengarten and Sons, Philadelphia ; and Mallinckrodt Chemical Works, St. Louis. Both the Merck and Mallinckrodt were found to be the tetrahydrate, while the Rosengarten preparation was the pentahydrate. The only appreciable impurities in these appeared to be traces of calcium and aluminium sulphate which were pretty effectually removed by the recrystallization. Even in the monohydrate, where these would be most apt to put in an appearance, they did not exceed 0.1 percent.

The monohydrate used in the determinations was prepared by saturating a solution at about 30° to 40° with one of the higher hydrates and, after filtration, bringing the clear liquor to a boil with constant stirring. The monohydrate thus precipitated was rapidly filtered off with the aid of the filter-pump and most of the mother-liquor removed in the same way. It was then transferred to an air-bath at 100° to 130°, where it remained for an hour or two, being ground to fine powder a little while before the heating was concluded. For the water content and treatment of the individual samples, see Table I.

TABLE I

Det. No.	Pct. of H ₂ O	
—	10.66	Monohydrate Theoretical, calculated for MnSO ₄ + H ₂ O.
95	11.10	Crystallized slowly at 43° to 48°.
96	10.75	Same material as det. 95.
97	11.24	Thin crystalline plates, crystallized at 45 ±.
98	11.33	Made by drying tetrahydrate (det. 107) at 90° to 130° for 4 hours, weighing this as monohydrate, then heating to 280° to 300° and weighing as anhydrous.

TABLE I—(Continued)

Det. No.	Pct. of H ₂ O	
99	10.77	Made by drying det. 16 at 100° to 120° for 3 hours, and weighing as monohydrate before last heating of 2 hours at 280°.
100	10.88	Same method as 99 applied to det. 17.
101	10.81	Materials prepared by bringing clear sol. of Rosengarten and Son's pentahydrate saturated at about 40° or 50° to boil, filtering with suction, and drying 3 or 4 hours at 100° to 120°.
102	10.91	Prepared as in det. 101 except that tetrahydrate from Mallinckrodt Chem. Works was used as starting-point, and drying was effected at 100° to 150° for about an hour.
		Tetrahydrate
—	32.29	Theoretical, calculated for $\text{MnSO}_4 + 4\text{H}_2\text{O}$.
103	32.84	Merck's tetrahydrate freshly ground from large lumps. Dehydration effected at 200°.
104	31.81	Same material as det. 103 after standing in sat. sol. for a few days at 30° to 33°.
105	32.00	Crystallized at 30° to 40°.
106	32.57	Crystallized at 30° to 40°.
107	32.19	Selected crystals formed at 30° to 40°.
		Pentahydrate
—	37.36	Theoretical, calculated for $\text{MnSO}_4 + 5\text{H}_2\text{O}$.
108	37.21	Crystallized rapidly in vacuo over H_2SO_4 .
109	36.35	Rosengarten and Son's, taken directly from original package.
110	37.05	Crystallized at $13^\circ \pm$ by slow evaporation over H_2SO_4 . Large perfect crystals.
111	39.6	Started for preparation of heptahydrate. Strong solution surrounded with ice, the whole placed in sawdust, and left over night. In the morning, temperature 10°. Crystals dried quickly with filter-paper.
		Heptahydrate
—	45.70	Theoretical, calculated for $\text{MnSO}_4 + 7\text{H}_2\text{O}$.
112	46.34	Crystals slightly damp. Crystallized at 0°.
113	44.24	Crystallized by cooling strong sol. to 0°, filtered off and aspirated for 3 hours, and dried in desiccator 1 hour.

TABLE I—(Continued)

Det. No.	Pct. of H ₂ O	
114	44.17	Same material as det. 113, but not placed in desiccator. Made two days later when crystals had partly liquefied.
115	46.28	Precipitated from strong solution by cooling to -10° . Filtered and aspirated 2 hours in funnel packed in ice. Still slightly damp.
116	47.7	Another mixture treated as in det. 115. Aspirated a shorter time. Crystals still quite damp when taken for analysis.
117	49.06	Crystals prepared by cooling saturated solution of pentahydrate with ice and introducing crystal of $\text{ZnSO}_4 + 6\text{H}_2\text{O}$ (see p. 639). Crystals dried rapidly between filter-paper, but still damp.

In order to make sure that the final heating had no effect upon the solubility of the hydrate, parallel determinations were made upon some of the moist material removed from the funnel after aspirating off the mother-liquor, and also that which had been dried in the oven. Determinations Nos. 73, 77, and 78 are on the damp hydrate, while Nos. 72, 74, 75, and 76 are on the dried material and were made in the same thermostat at the same time. These two sets show as complete agreement as was to be expected.

The tetrahydrate was prepared by dissolving the commercial salt in water until a saturated solution at about 30° was formed, and after filtration placing them in a desiccator over sulphuric acid; the desiccator then being placed in a thermostat maintained at 30° to 40° . In the course of a few days, a good crop of perfectly clear and regular crystals was invariably obtained.

The pentahydrate was prepared by allowing a solution of the commercial salt to evaporate in a desiccator at the ordinary room temperature.

The heptahydrate was prepared by cooling a solution of the

commercial salt, saturated at 30° to 40°, with ice and salt until the whole was several degrees below zero. If crystallization had not already set in, it was brought about by vigorous shaking, which was continued until precipitation was complete, thus leaving the salt in a finely divided form suitable for the solubility determinations. This was then rapidly filtered off in a Gooch crucible surrounded by ice, or ice and salt, and air aspirated through until the crystals were fairly dry.

The salt whose solubility was to be determined was placed in a bottle of from 8 to 20 cc capacity, depending upon the work in hand. The liquid to be saturated was then added and the bottle clamped by copper springs to the face of a wooden wheel, wholly immersed in the water of a thermostat and rotated by a small water-wheel, or, in the later work, an electric motor. In the determinations up to 33°, a bath of about 3 liters capacity was used, but from there on one of more than double this capacity was substituted. Both were covered with asbestos and provided with a modification of the Ostwald gas regulator, capable of maintaining the temperature constant within 0.2° night and day. The main supply of gas was independent of the regulator which controlled just sufficient of it to effect the necessary regulation. It required only about 0.02° change in the temperature to turn the gas completely on or off. The temperatures were read on a thermometer which had been compared with a Reichsanstalt Standard (No. 5640-1894).

When a sample of the solution was wanted for analysis, the bottles were slipped out from under the strings, the neck brought above water, carefully dried, and the stopper removed. For drawing the sample, two forms of filtering pipette were used, and in all cases they were brought to the same temperature as the solution being introduced into it. For the lower temperatures, the pipette consisted of a straight piece of glass tube 2 or 3 mm bore and about 15 cm in length. Over one end of this was placed first a bit of well-washed muslin, and over this a piece of filter-paper. The edges of these were then pressed down about the tube and wound tightly with a narrow strip of thin sheet rubber

which was continued spirally up the tube to a small wire hook where the end was made fast. When enough of the liquid had been drawn up through the filter, the upper end was closed by the thumb, the filter removed, the lower end of the tube wiped clean, and the contents quickly transferred to the weighing bottles, which were small Erlenmeyer flasks with glass stoppers. For the higher temperatures, it was feared that the above pipette would necessitate too great a loss by evaporation, and it was therefore discarded in favor of the following. A capillary tube was bent into a siphon with arms of about 7 cm and 30 cm respectively. To the short arm was sealed a centimeter of larger tube, and over the end of this was fastened the muslin and filter-paper as in the other pipette, except that for temperatures above 75° platinum wire took the place of the rubber strip. The short end of the siphon was passed through a rubber stopper which fitted the bottle containing the liquid. A second hole in the stopper carried a tube through which air could be forced into the bottle, thus driving the liquid out through the filter and siphon, the longer end of which was surrounded by a small water jacket to reduce the danger of evaporation when the solution emerged.

After weighing, the Erlenmeyer flasks were placed in the air-bath at about 100° until the liquid was completely evaporated, when they were transferred to a second bath at a temperature of 270° to 280°, where they remained for an hour, and in many of the earlier determinations much longer.

Right here is where Linebarger's greatest inaccuracy seems to lie. He effected his drying at 160° to 170°, a temperature not sufficient to dehydrate the salt in any reasonable amount of time, as shown in the following determinations.

Three of the regular determinations, after drying at 100°, were heated to 170° to 180° for three and one-half hours, weighed, heated again for three hours at 270° to 280°, and again weighed, with the following results:

TABLE II

Weight of residue		Loss in weight	
After 1st heating Grams	After 2nd heating Grams	Grams	Percent on 1st weight
1.0987	0.9955	0.1032	9.4
0.6492	0.5790	0.0702	10.8
0.4425	0.3969	0.0456	10.3

From this, it is evident that at 170° , the tendency is to leave the monohydrate.

Linebarger assigns no reason for adopting the particular temperature that he did; nor does he speak of any work being done to test the accuracy of the method. This is the more surprising, as it is a commonplace statement in many text-books that the last molecule of water is not lost below 200° .

This explains why Linebarger's curves all lie above those here presented, but it does not furnish any clue as to why the determinations for the individual hydrates should lead to such smooth and regular curves, bearing such peculiar relations to one another. For this I have no explanation to offer. The temperature adopted in the present determinations (270° to 280°) is the same as used by Watts and Thorpe in their paper already referred to, and the accuracy of the method was tested in the following way.

A few cubic centimeters of a strong solution of manganous sulphate were placed in a long-necked flask of about 30 cc capacity and boiled down carefully to a solid with constant shaking, thus spreading it in a thin layer over the sides of the flask. This was then closed by a cork through which passed two small glass tubes, the first reaching nearly to the bottom, communicated directly with the outside air; while the second, reaching only to the junction of the neck with the body of the flask, was connected at its other end with a potash bulb filled with a solution of barium chloride plus a little free nitric acid. The potash bulb was in its turn connected to a filter pump. The flask and contents together with the six weighing bottles containing dets. Nos. 69 to 74 inclusive, were placed in the air-bath, which was then brought to 240° to 245° and maintained

between these limits for one and one-half hours, while a slow current of air was drawn through the flask. In order to settle any question as to the possibility of this air current producing a cooling great enough to invalidate the experiment, it was interrupted for intervals of about five minutes several times during the work, but no change could be detected. Considerable water was at first deposited in the tubes, but as the heating continued, this was soon carried over by the air current into the potash bulb, the solution in which remained perfectly clear. The weighing bottles were stoppered, cooled, and weighed, then returned to the bath, and the whole carried up and held at 270° to 280° for one hour, when the weighing was repeated. Finally, the whole was heated for about three-quarters of an hour by alternately running the temperature up to 350° and down to 300° , in all about three such cycles being made. No turbidity whatever was produced in the barium solution, even on standing several days. To ascertain the sensitiveness of this test a few milligrams of sulphur were burned close to the mouth of the potash bulb and the air rapidly aspirated through. On standing, a very noticeable precipitate was produced, although the quantity of sulphur entering the bulb could not have been more than a couple of milligrams. The weighings of the six Erlenmeyer flasks heated at the same time are given in the following table, only two being subjected to the final heating. The fact that the figures for the second heating are uniformly a little greater than for the first is probably due to the flasks having stood longer in the desiccator before the second weighing was made, i. e., it is an effect due to the condition of the glass surface of the weighing bottles :

TABLE III

Det. No.	Weight of flask and stopper	Weight of same plus MnSO_4		
		After 1st heating	After 2nd heating	After 3rd heating
69	11.3097	11.8706	11.8710	—
70	9.7200	10.5058	10.5060	10.5059
71	13.6030	14.1820	14.1822	14.1821
72	14.3568	14.8610	14.8614	—
73	12.1416	12.6071	12.6069	—
74	10.3347	10.9876	10.9879	—

The residues left after the heating were always found to dissolve completely in water, forming perfectly clear solutions. A few rough determinations of sulphuric acid by precipitation as barium sulphate, were made as a further assurance that this time the compound was really anhydrous normal salt. The values found were a few tenths of a percent lower than that calculated by the formula $MnSO_4$, but did not diverge sufficiently from this to be of any consequence. From the above data it is evident that the analytical method adopted here is sufficiently accurate for the purpose in hand.

From determination 58 onward, all samples were heated at 270° to 280° for one to one and one-half hours, cooled in a desiccator in stoppered flasks and weighed within an hour of the time they were removed from the air-bath. In the earlier determinations (prior to 58) the flasks were not stoppered, but were always weighed within half an hour from the time they were transferred from the air-bath to the desiccator, and successive weighings after different periods of standing in the desiccator and balance case showed that the maximum error thus introduced did not exceed a few tenths of a milligram at any time.

In order to ensure complete saturation, each mixture was stirred in the thermostat until it seemed probable that saturation was complete; a sample was drawn and the stirring then continued for some time longer and a second sample drawn. The agreement of these two samples upon analysis was found to be a safe guide in the case of all except the monohydrate. Another and more general method, of greater certainty, which was used throughout the work on the monohydrate, and often enough upon the higher hydrates to establish the validity of the previous method for them, was the approach to the same composition of two mixtures, one made up of the salt and water, and the other of the salt and supersaturated solution. The application of these may be readily seen by referring to the data given in Table IV.

In the early part of the work, experiments were made upon the solubility of one hydrate in strong solutions made up from

another hydrate. For this purpose the tetrahydrate and pentahydrate were employed; but it was found to make no difference how the solutions were prepared; the point of equilibrium depended only upon the temperature and the solid phase left at the end. This is also seen in cases where the transition of one solid phase into another occurred during the period of saturation; the solubility for the form finally left, agreeing completely with that determined in the usual way. It might have been interesting to have extended these experiments more in detail to the monohydrate, as its behavior seems to differ so from the others, but as the main reason for attempting them with the tetrahydrate and pentahydrate was to furnish the assurance that the relation of the solubility of these two salts reported by Linebarger could not be explained by such phenomena, it seemed unnecessary to proceed further at present.

The tetrahydrate, pentahydrate, and heptahydrate in themselves and in their relations to one another show no noticeable peculiarities. With the monohydrate the case is somewhat different. At moderate temperatures the systems containing it as solid phase came to equilibrium with surprising slowness. Thus at 33.7° a solution made up from water and excess of monohydrate rose during the first day to a concentration of a little more than 61 parts anhydrous salt to 100 parts of water, which during the next week gradually increased by about 1 part per 100; while during the same interval a solution saturated with respect to tetrahydrate, i. e., containing about 67.4 parts anhydrous salt per 100 of water, — to which monohydrate had been added, did not decrease in concentration by more than 0.3 parts per 100.

From the general trend of the curve, it appears probable that the solution made up from the water and monohydrate comes very much nearer to representing the true solubility of the salt than the other. This accounts for the very high values obtained by Linebarger for the solubility of the monohydrate, as his method consisted in heating up a solution of known strength until precipitation began, and taking the strength of the solution as the solubility at this temperature.

Above 40° the change is somewhat more rapid, as shown by dets. Nos. 62 to 66, while above 50° approximate equilibrium is established within a period comparable with that necessary for the other hydrates. It is in this latter region that both Mulder and Linebarger place the transition point for monohydrate, while from the present work it would appear to lie most probably quite near to that from tetrahydrate to pentahydrate. On account of the extreme slowness with which the system comes to equilibrium in this region, the position of the point could not be determined directly. The solubility curve down to 41.5° may be taken with moderate certainty. The point plotted at 33.7° represents the maximum value obtained from the solutions starting with water and monohydrates, and for the reasons already given deserves much less confidence than those at higher temperatures. The same applies in a still greater degree, of course, to the value at 18° , which is only a rough approximation. Both of these last values may be best considered as lower limits.

An inspection of the accompanying curves shows that, strictly speaking, the tetrahydrate, the commonest form on the market, is to be considered as unstable at any temperature with respect to neutral solutions or at most, stable over a very limited range of temperatures.

In preparing the tetrahydrate crystals as already described, experiments were made by varying the temperature of the thermostat containing the desiccator. For over a month one solution was kept at a temperature between 28° and 35° as extreme limits, and for the greater part of the time between 29° and 31° . In all this time, nothing but well-formed crystals of tetrahydrate separated. Similar experiments were made at temperatures up to about 48° lasting for a week or more at each temperature, with the result that up to about 40° little or no monohydrate was formed. Between 40° and 50° a mixture of monohydrate and tetrahydrate was usually obtained, and above 50° monohydrate could safely be counted on.

If pentahydrate crystals and water were placed in one of the bottles of the solubility apparatus and stirred at a temperature of 40° , within an hour the larger part of them would be converted into tetrahydrate; but it was usually necessary to continue this

for many hours before the next change, i. e., to monohydrate,—would set in; and it was a matter of days before it was complete.

The details of the solubility determinations are given in Table IV. The liberty has here been taken of omitting the earliest of the determinations, made before the method and apparatus were well in hand; also a number over the unstable parts of the curves where the transition to another hydrate had evidently set in, but had not been completed before the sample was drawn; and finally a number which from imperfections in the manipulation, such as too great variation in temperature during saturation, imperfect filtration in drawing sample and the like, while useful to some extent as rough checks and suggestions during the progress of the work, add nothing to the final results.

The determinations are here arranged in the order in which they were made. Usually two or three bottles containing different mixtures were placed on the wheel of the apparatus at one time, and thus the solubilities of different hydrates determined in exactly similar conditions.

The column headed "Mixture No." indicates which samples were drawn from the same bottle without other change in the contents of the latter than that caused by a longer period of saturation. Thus every time water, salt, or solution was added to a bottle, it was considered as a new mixture and has been so numbered. In the same column the sign ↓ indicates falling concentration, i. e., at the start the liquid phase consisted of a supersaturated solution and consequently salt would crystallize out as stirring continued. Similarly the sign ↑ indicates that to begin with, the liquid phase was either pure water or a solution weaker than the saturated solution for that temperature and hydrate, and consequently tended to dissolve the hydrate, the concentration rising until saturation was reached. The convergence of the results from such a pair of mixtures furnishes us with the best criterion to trace the approach of the system to equilibrium. The necessity of such a guide is clearly seen in the experiments on the monohydrate, particularly at moderate temperatures, which have been already referred to.

TABLE IV

Det. No.	Mixture No.	Hydrate used as solid phase	Temp. °C.	Time of saturation	Approx. weight of sample analyzed. Gms.	Parts MnSO ₄ per 100 parts H ₂ O
¹ 1	1↑	5	16.0	2.5	2.7	61.62
2	2↑	5	16.0	2	2.4	61.57
² 3	3↑	5	16.0	2.5	2.6	61.51
4	2↑	5	16.0	2.5	2.7	61.68
5	4↑	4	16.0	2	2.6	64.01
6	4↑	4	16.0	4	2.8	63.86
7	4↑	4	16.0	6	2.1	63.94
8	5↑	5	25.0	1	2.4	64.78
9	6↑	4	25.0	1.5	3.0	65.26
10	6↑	4	25.0	2	2.9	65.38
11	5↑	5	25.0	2.2	2.9	64.79
12	8↑	4	30.0	2	3.0	66.42
⁸ 13	7↑	5	30.0	2	2.7	67.76
14	8↑	4	30.0	3.5	3.6	66.37
⁴ 15	7↑	4	30.0	3.5	4.0	66.49
16	9↑	4	35.0	2	3.0	67.82
⁵ 17	10↑	4	35.0	2	2.6	67.92
18	11↑	4	18.5	2.7	2.4	64.18
19	12↑	4	18.5	2.7	2.3	64.20
20	13↑	4	39.9	1	2.5	68.83
21	13↑	4	39.9	2.2	3.7	68.79
22	14↑	4	17.7	0.5	2.7	64.22
23	15↑	4	17.7	0.5	2.4	64.20
24	14↑	4	17.7	1.5	2.5	63.94
25	15↑	4	17.7	1.5	2.4	64.10
26	14↑	4	17.7	3.7	2.1	64.17
27	15↑	4	17.7	3.7	2.6	64.17
28	16↓	5	9.0	1.2	2.5	59.14
29	17↓	7	9.0	1.2	2.4	59.34
30	16↓	5	9.0	2	2.1	59.23
31	17↓	7	9.0	2	1.3	59.25

¹ Started with a mixture of penta- and tetrahydrates, but transition to penta complete before sample was drawn.

² Mixture at first contained only tetrahydrate as solid phase, but transition to pentahydrate occurred during saturation.

³ Probably an error in det. (See det. 69 and 70.) Not plotted.

⁴ Transition to tetrahydrate has here evidently occurred.

⁵ Mixture started with pentahydrate, but transition set in during saturation.

TABLE IV—(Continued)

Det. No.	Mixture No.	Hydrate used as solid phase	Temp. °C.	Time of saturation	Approx. weight of sample analyzed. Gms.	Parts MnSO ₄ per 100 parts H ₂ O
¹ 32	18	7	-10	—	2.2	47.96
33	19	5	5.0	I	2.4	58.06
34	20	7	5.0	I	2.6	56.59
² 35	19	7	5.0	2.2	2.8	56.24
36	20	7	5.0	2.5	2.7	56.31
³ 37	21	(4)	9.0	0.7	2.3	59.31
38	20	7	9.0	1.5	2.3	59.41
⁴ 39	22	7	0.0	0.7	2.3	53.35
⁵ 40	23	7	0.0	1.5	2.5	53.18
41	24	7	0.0	1.5	2.7	53.15
42	25	5	35.5	0.3	2.6	71.61
43	26	4	35.5	0.7	2.6	68.02
44	26	4	35.5	2	2.7	68.14
45	27	4	32.2	1.7	2.5	66.82
46	27	4	32.2	3.2	2.3	66.83
47	27	4	49.9	I	1.9	72.54
48	27	4	49.9	2.5	2.4	72.42
⁶ 49	28	4	50.0	I	1.9	72.83
50	29	5	12.0	1.2	2.3	60.15
51	30	5	12.0	1.2	2.2	60.20
52	30	5	12.3	2.2	2.6	60.13
53	29	5	12.3	2.2	2.6	60.19
54	31	5	15.0	1.5	2.5	61.08
55	32	7	12.0	I	3.0	61.87
56	32	7	12.0	1.5	2.9	61.68
57	33	7	14.3	I	2.7	63.93
58	34	I	41.4	47.5	1.4	61.21
59	34	I	41.4	90.2	1.4	60.94
⁷ 60	34	I	41.6	156	1.2	61.23

¹ Rough determination made by analyzing mother-liquor from preparation of heptahydrate.

² Transition from pentahydrate set in spontaneously (Cf. det. 33).

³ Tetrahydrate evidently transformed to one of the higher hydrates.

⁴ Det. started with tetrahydrate, but evidently heptahydrate formed during saturation.

⁵ Det. started with pentahydrate, but evidently heptahydrate formed during saturation.

⁶ Det. started with pentahydrate. Evidently transition to tetrahydrate set in.

⁷ The time here includes the 90.2 hours at 41.4°.

TABLE IV—(Continued)

Def. No.	Mixture No.	Hydrate used as solid phase	Temp. °C.	Time of saturation	Approx. weight of sample analyzed. Gms.	Parts MnSO ₄ per 100 parts H ₂ O
61	35 ¹	I	41.6	65.5	1.4	62.14
62	34 ¹	I	41.6	198.5	1.2	60.87
¹ 63	35 ¹	I	41.6	119.5	1.3	60.97
² 64	35 ¹	I	41.7	137.5	1.4	60.82
² 65	35 ¹	I	41.5	167.5	1.1	60.77
² 66	35 ¹	I	41.5	189.5	1.0	60.59
³ 67	36 ¹	4	50.0	I	0.7	72.4
⁴ 68	37 ¹	I	18	(?)	1.1	68.3
⁵ 69	38 ¹	5	31.1	I	1.4	67.94
⁵ 70	38 ¹	5	31.1	1.5	1.9	67.90
⁶ 71	39 ¹	I	50.0	0	1.4	72.53
⁷ 72	40 ¹	I	50.0	3	1.4	58.14
⁸ 73	41 ¹	I	50.0	2	1.3	57.41
⁹ 74	39 ¹	I	50.0	4	1.7	62.32
⁹ 75	39 ¹	I	50.3	28.5	1.7	58.31
⁹ 76	40 ¹	I	50.3	27.5	1.5	57.89
⁹ 77	41 ¹	I	50.3	26.5	1.5	58.32
⁹ 78	41 ¹	I	67.5	16.5	1.2	52.10
⁹ 79	42 ¹	I	67.5	48	1.7	51.60
80	43 ¹	I	75.0	2	1.7	51.42
81	44 ¹	I	75.0	1.2	1.1	47.48
82	45 ¹	I	95.0	0.7	1.7	38.71
83	46 ¹	I	84.8	2.5	1.2	45.12
84	47 ¹	I	84.8	3	1.4	43.63
85	46 ¹	I	84.8	3.5	2.1	45.04
86	47 ¹	I	84.8	4.2	1.2	45.69
87	48 ¹	I	67.0	17.5	2.0	51.50
88	49 ¹	I	67.0	17.5	1.6	50.43
89	49 ¹	I	67.0	23	2.1	51.19
90	48 ¹	I	67.0	23.5	1.0	51.42
91	50 ¹	I	99.6	4	2.4	35.63
92	51 ¹	I	99.6	4.2	2.7	34.11
93	50 ¹	I	99.6	8.7	1.1	34.49
94	51 ¹	I	99.6	8.2	0.8	33.24

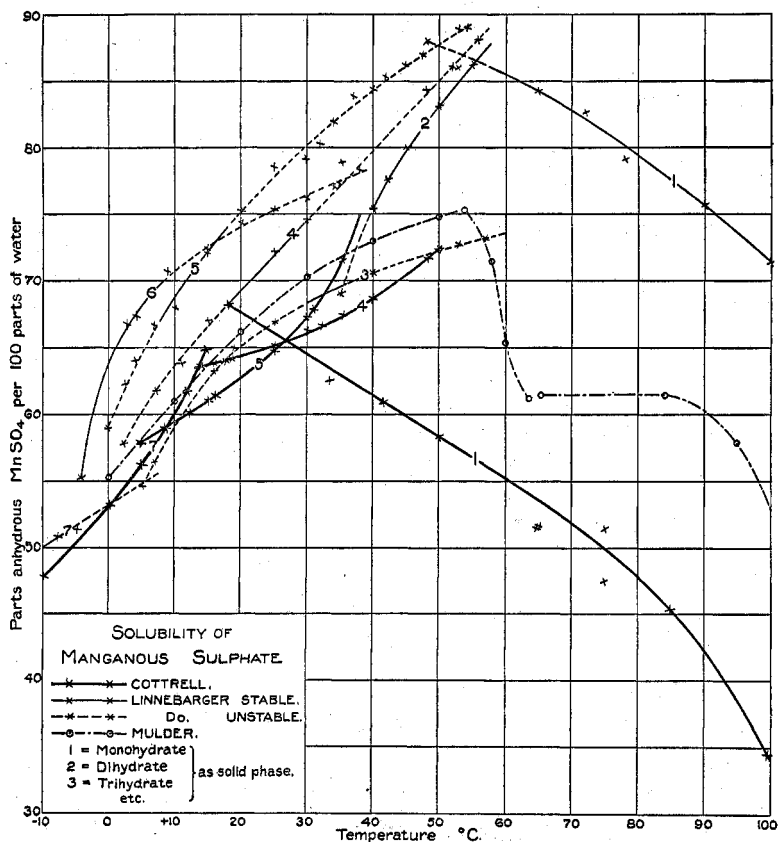
¹ The time here includes that at 41.6°.

² The time here includes that at 41.6° and 41.7°.

³ Made by placing powdered pentahydrate in water and bringing up to temperature when transition sets in. Only intended as rough approximation.

⁴ Started as a determination of monohydrate at 50° about 5 p.m., but

The data given in this table are also embodied in the accompanying set of curves, where for the sake of comparison have been added those of Linebarger and Mulder. In Linebarger's curves, the parts given by him as stable are represented



gas went out during the night and bath was found next morning at 18° (motor still running) and sample taken.

⁵ Taken with particular pains to verify or correct det. 13.

⁶ Solution made by saturating water at 50° with tetrahydrate and then adding monohydrate and drawing sample within a few minutes.

⁷ Solution made by adding monohydrate dried at 130° ± to water.

⁸ Sample slightly cloudy. Solution prepared by adding freshly precipitated monohydrate, which had not been dried in oven, to water.

⁹ Time here includes that at 50°.

by continuous lines and the unstable portions by dotted lines. The abscissæ represent temperature in °C and the ordinates are parts of anhydrous salt per 100 parts of water.

My warmest thanks are due to my good friends of the Chemical Department for the kindly interest and help they have extended during this work. In particular I wish to acknowledge my indebtedness to Dr. W. C. Blasdale for carrying out check analyses on a portion of the work and to Mr. G. W. Beattie, who in the early stages of the problem, kindly undertook some experiments on the electrical conductivity of solutions of the salt that had been kept at different temperatures for some time, in order to determine, if possible, whether any change in the constitution of the solution occurred. No appreciable differences were noted between solutions kept at room temperature and the same solution which had been heated for a week or more at 30° to 40°. This work was carried out before the errors in Linebarger's values were discovered, and, after these had come to light, the explanation of the phenomena naturally took an easier channel and the resistance measurements were discontinued.

The main results of the present paper may be summed up as follows :

1. The solubility of the hydrates of manganous sulphate with 1, 4, 5, and 7 molecules of water of crystallization have been determined for temperatures between -10° and +100° C.
2. Contrary to the results of Linebarger, there appears to be nothing peculiar in the behavior of the last three, but systems containing the monohydrate as solid phase reach equilibrium very slowly, this effect being greatest at the lower temperatures.
3. The temperature of 170° C is not sufficient to expel the last molecule of water from manganous sulphate as assumed by Linebarger and his results are consequently too high.
4. A temperature of 250° is sufficient to dehydrate manganous sulphate completely, and there is no appreciable decomposition of the anhydrous salt up to temperatures considerably above 300°.
5. In the case of the three higher hydrates at least it makes

no difference from which of them the solution is prepared ; at a given temperature if it is finally saturated with either one of the hydrates, its concentration will depend only upon this latter.

6. Incidentally, a few simple devices which have been found of use in the solubility determinations have been described.

*University of California,
June, 1900.*