

CLII.—*The Ternary System Ammonium Chloride-Manganous Chloride-Water.*By FREDERICK WILLIAM JEFFREY CLENDINNEN and
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THE system ammonium chloride-manganous chloride-water has received a great amount of attention, probably because it is typical of a large number of cases in which mixed-crystal formation occurs between ammonium chloride and a hydrated chloride of a multi-valent metal. There remain, however, some points worth further consideration.

Three double salts have been described, the respective molecular proportions of the components, in the order named in the title, being 1 : 1 : 2 (Hautz, *Annalen*, 1848, **66**, 285), 2 : 1 : 1 (Rammelsberg, *Pogg. Annalen*, 1855, **94**, 507; Pickering, T., 1879, **35**, 654) and 2 : 1 : 2 (Hauer, *J. pr. Chem.*, 1854, **63**, 436). Lehmann (*Zeitsch. Kryst. Min.*, 1883, **8**, 445) evidently recognised mixed-crystal formation. Saunders (*Amer. Chem. J.*, 1892, **14**, 127) endeavoured to prepare double salts and concluded that only the 2 : 1 : 2-compound was a definite substance. Various solids that he obtained he regarded as mechanical mixtures and, curiously enough, he did not consider the possibility of mixed-crystal formation. Johnsen (*Jahrb. Min.*, 1903, **2**, 93) studied the crystallography of the mixed crystals. The most systematic investigation so far carried out is by Foote and Saxton (*J. Amer. Chem. Soc.*, 1914, **36**, 1695). They worked only at 25° and claimed to have proved the existence of the double salt 2 : 1 : 2 and to have shown that this and ammonium chloride form two series of mixed crystals, there being a gap between the limiting compositions of each series.

It is unlikely that work at 25° will show the exact type of the system, since at this temperature $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, which is obviously the important hydrate of manganous chloride in this connexion, is not a stable phase in pure water or in dilute solutions of ammonium chloride. The consequence is that, at one end, the mixed-crystal system is obscured by the appearance of the stable tetrahydrate, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, which does not enter into the formation of any compound or mixed crystal. As the invariant point, dihydrate-tetrahydrate-water, in the (condensed) binary system manganous chloride-water, is 57·85°, we have chosen to work at 60° and to apply the results obtained there to explain the 25° isotherm.

The experimental procedure is simple, including direct estimation of ammonium and chloride radicles by familiar methods and, in a few cases, of the manganese radicle as pyrophosphate.

Table I gives the figures obtained at 60° and these are shown plotted in the usual triangular method in Fig. 1.

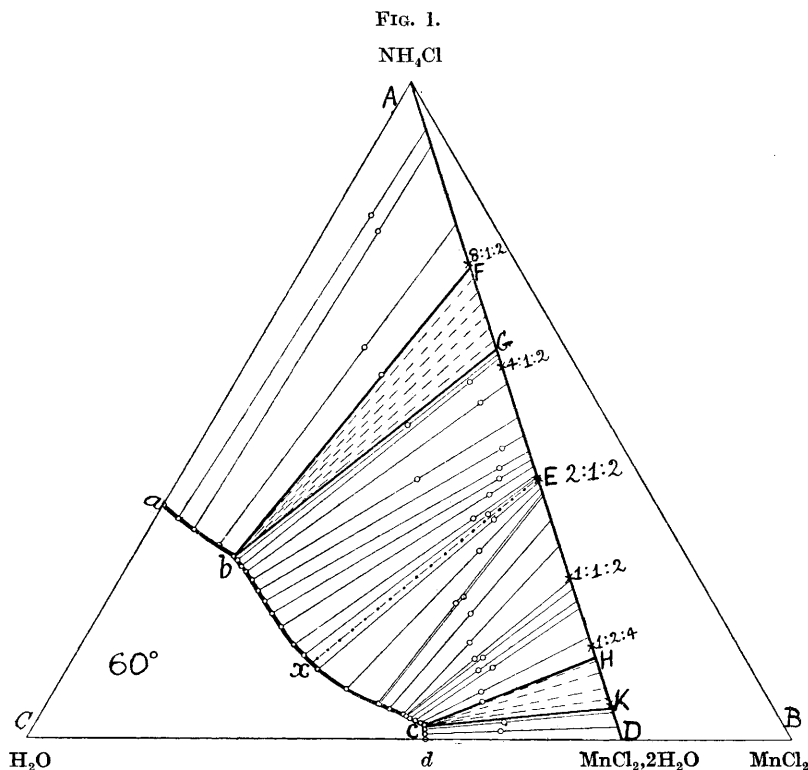
TABLE I.
System at 60°.

No.	Density.	Percentage composition.			
		Solution.		Residue.	
		NH ₄ Cl.	MnCl ₂ .	NH ₄ Cl.	MnCl ₂ .
1	1.105	33.52	2.91	79.77	5.04
2	1.129	31.93	5.84	77.37	7.03
3	1.183	29.50	10.16	59.70	14.10
4	1.192	27.81	12.95	55.53	18.32
5	1.200	27.07	13.79	47.90	25.68
6	1.214	25.94	15.16	—	—
7	1.210	25.28	15.91	51.30	33.37
8	1.225	24.11	17.19	39.70	31.01
9	1.239	22.51	18.86	44.36	39.71
10	1.255	20.93	20.51	41.41	40.86
11	1.267	19.04	22.42	39.80	41.74
12	1.288	16.98	24.65	37.22	41.65
13	1.317	14.33	27.74	33.64	41.34
14	1.339	12.61	29.87	34.18	43.04
15	1.365	10.52	32.80	33.45	44.06
16	1.426	7.55	38.02	28.56	44.63
17	1.482	5.44	43.10	20.70	45.67
18	1.486	5.33	43.27	21.70	46.15
19	1.523	4.64	45.00	19.12	48.34
20	1.543	3.93	47.20	14.76	50.39
21	—	3.47	47.84	12.48	53.37
22	—	3.11	48.50	10.46	53.74
23	1.575	2.94	49.33	11.00	55.23
24	1.581	2.45	50.22	7.23	55.67
25	1.583	2.21	50.68	5.83	56.58
26	1.592	1.61	51.16	2.69	61.00
27	1.619	0.91	51.47	1.20	62.20

The residue method (Schreinemakers, *Zeitsch. physikal. Chem.*, 1893, 11, 81) has been adopted in determining the compositions of solids in equilibrium with particular solutions. It has been taken as fully proved by previous workers that the solid phases lie on the line *AD* connecting the compositions of pure ammonium chloride and the dihydrate of manganous chloride.

It is clear from the figure that the system is one of a somewhat uncommon type of mixed crystals. Fixing attention first on the solid phases, one sees that there are three very well-defined series of mixed crystals, namely, *AF*, *GH*, and *KD*, with two gaps, *FG* and *HK*. The three curves *ab*, *bc*, and *cd* correspond with the

series, respectively, and the intersections b and c with the gaps. The composition of the alleged compound 2:1:2 is at E , well within the second series GH . The line AD is, of course, simply a section across the temperature-concentration diagram of the binary system ammonium chloride-manganous chloride dihydrate at a temperature, 60° , which is below that at which any liquid phase may be formed.



The first interpretation suggesting itself is that there are here two binary systems linked together. The first is that extending from A to E , the components being ammonium chloride and 2:1:2; the second from E to D , the components being 2:1:2 and the dihydrate. Each of these will correspond with either the fourth or fifth of Roozeboom's (*Zeitsch. physikal. Chem.*, 1889, **30**, 384) types of mixed crystal formation in binary systems. Foote and Saxton (*loc. cit.*), working only at 25° , recognised only the portion AE . We have supplemented their work and very com-

TABLE II.
System at 25°.

No.	Density.	Percentage composition.			
		Solution.		Residue.	
		NH ₄ Cl.	MnCl ₂ .	NH ₄ Cl.	MnCl ₂ .
1	1.077	28.33	—	—	—
2	1.101	26.47	3.01	68.97	3.92
3	1.119	25.11	5.37	83.37	5.76
4	1.140	23.71	7.89	73.57	8.74
5	1.164	22.35	10.70	72.44	13.19
6	1.181	21.12	13.00	71.43	15.36
7	1.200	20.30	14.62	68.16	17.89
8	1.209	19.48	16.04	65.54	19.70
9	1.215	19.09	16.78	64.60	22.91
10	1.216	19.07	16.57	63.32	22.36
11	1.222	18.37	17.54	57.87	26.54
12	1.227	17.77	18.16	56.67	27.79
13	1.230	17.40	18.71	58.44	28.66
14	1.237	16.90	19.39	55.72	30.35
15	1.245	16.35	20.14	54.44	32.40
16	—	15.76	20.92	46.95	30.97
17	1.255	15.41	21.42	—	—
18	1.263	14.84	22.17	41.02	33.64
19	1.265	14.54	22.58	36.40	33.11
20	1.268	14.26	23.02	45.54	38.19
21	1.270	14.13	22.98	44.70	37.91
22	1.273	13.82	23.43	38.59	37.88
23	1.286	12.69	24.83	42.80	41.64
24	1.292	12.22	25.33	31.33	36.87
25	1.297	11.77	25.98	37.66	41.23
26	1.317	10.00	28.07	37.30	44.16
27	1.338	8.56	30.16	32.00	41.55
28	1.362	7.05	32.65	35.96	44.68
29	1.396	5.53	35.42	28.97	42.93
30	1.413	4.86	37.02	30.65	44.90
31	1.448	3.85	39.53	35.73	46.66
32	1.494	2.95	43.11	23.55	46.39
33	1.494	2.95	43.22	2.18	54.34
34	1.492	2.26	43.28	1.08	53.97
35	1.490	1.31	43.31	0.63	54.18
36	1.485	—	43.45	—	—

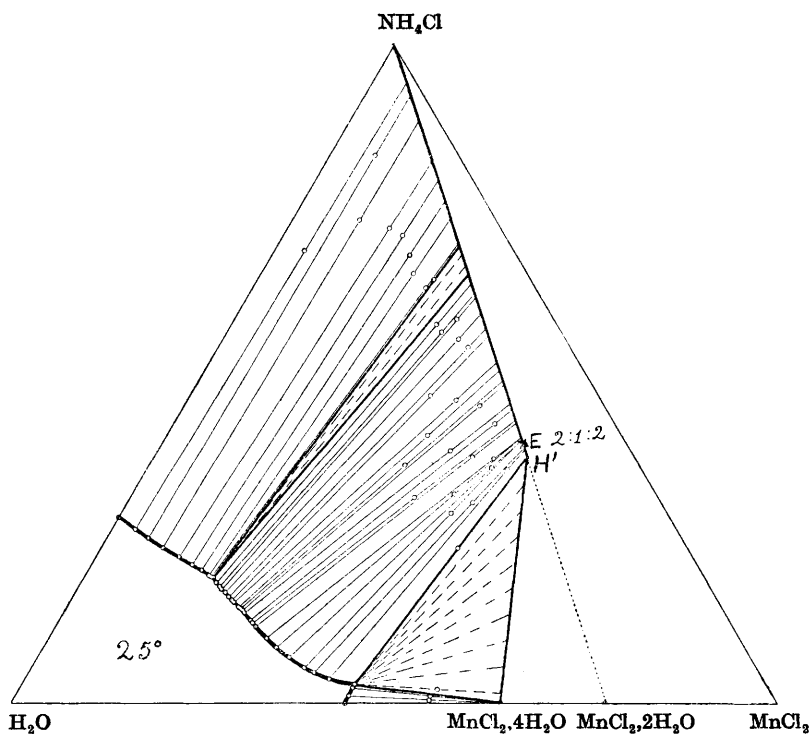
pletely determined the 25° isotherm. The results are given in Table II and plotted in Fig. 2.

There can be no doubt whatever that even here mixed crystals of composition richer in MnCl₂·2H₂O than 2 : 1 : 2 do exist, extending, however, over only the comparatively small range *EH'*. The series ends at *H'* since thereafter the solid phase, MnCl₂·4H₂O, enters, a complication not showing itself at 60°. As a matter of fact, the figures of Foote and Saxton themselves clearly demonstrate this extension beyond 2 : 1 : 2, but these authors, who did not use the residue method but endeavoured always to obtain pure solid free from mother-liquor, failed to trust their own work sufficiently and suggested that the solids in equilibrium with the solutions

at the latter part of the curve were really 2 : 1 : 2 from which they had only incompletely removed adhering liquor rich in manganese chloride.

The 60° work definitely establishes the conclusion that the second series of mixed crystals does not stop at 2 : 1 : 2 (*E*) and the question arises as to whether even this last of the various alleged double salts may justly be called a compound. While it is true that there

FIG. 2.

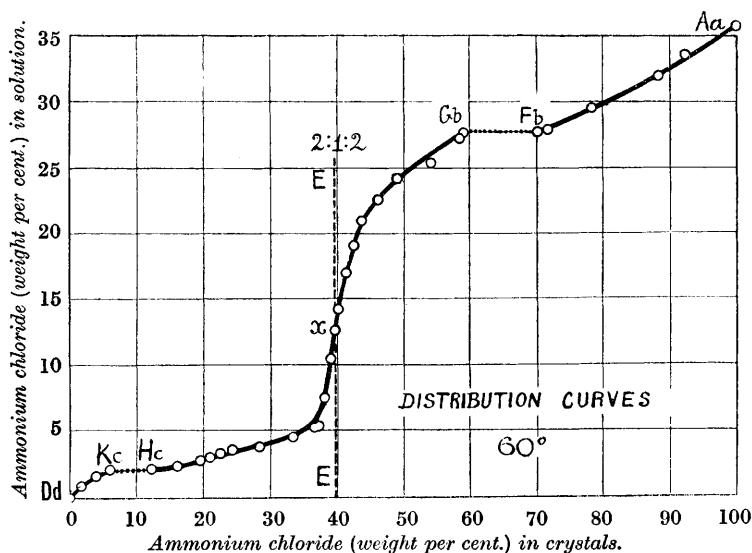


is a tendency for solutions over quite a considerable range about the middle of the curve to be in equilibrium with solids tending towards, or grouping themselves around, 2 : 1 : 2, yet, as can be seen from Fig. 1, there is no evidence at all that 2 : 1 : 2 exists as the stable solid phase with more than a single solution. This solution has a composition represented by a point at or near *x* in Fig. 1. If, however, it were a compound in the usual, although ill-defined, sense of the term, one would expect it to exist in equilibrium with a series of solutions, however small; not to change its composition with an infinitesimal change in the solution. One might indeed almost

Z Z*

as reasonably claim that 1 : 2 : 4, 1 : 1 : 2, 3 : 1 : 2, and 4 : 1 : 2 are definite compounds, since all fall along the line GH , and similarly other molecular proportions falling along FA or KD . The difference in the case of 2 : 1 : 2 is only that somewhere about this proportion does seem to be a more favoured grouping in the mixed crystals as shown by the spread of the tie-lines in its neighbourhood. This difference (which is only a difference of degree) appears perhaps more clearly when another method is adopted for plotting results, namely, that represented in Fig. 3 showing the distribution of ammonium chloride in co-existing phases.

FIG. 3.



Along rectangular axes are plotted percentages of ammonium chloride in solution and in the corresponding crystals, respectively. The horizontal dotted lines, Kc , Hc , and Gb , Fb , represent the gaps of Fig. 1. The existence of any particular solid with a series of solutions would show itself as a vertical line. There is no such line in the figure. The nearest approach to it is in the neighbourhood of the line EE , corresponding with the composition of 2 : 1 : 2; but it is quite clear that the experimental curve does not coincide with the vertical line at more than the single intersection point x .

If, now, one restricts the term compound to a solid which may exist in equilibrium with a series of solutions, then clearly there is no justification for supposing a compound 2 : 1 : 2 to exist.

The question of the criteria of a definite solid compound is one

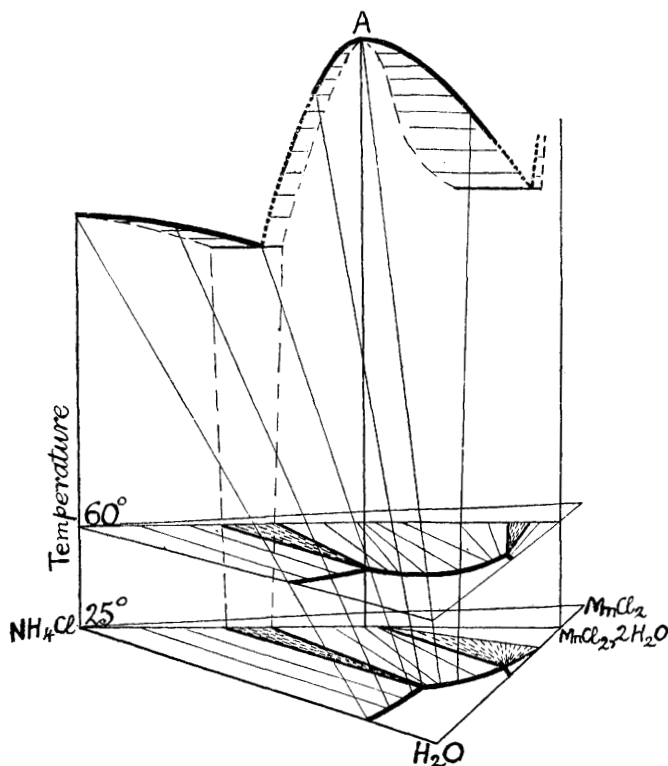
of much interest from the point of view of the Phase Rule, and is perhaps best studied in a binary system. The line AD , as already stated, is an isothermal section of a binary system in which the two components are ammonium chloride and manganous chloride dihydrate, a system in which there are three series of mixed crystals and two gaps. It is easy to deduce from Roozeboom's (*loc. cit.*) types with a single gap, or from isothermals of thermodynamic potential (ζ -function) and composition of solid and liquid, typical diagrams for temperature-composition relations in which two gaps exist between series of mixed crystals. At the changes of curvature in the liquidus curve there may be two transition or two eutectic points, or one of each. Owing to the instability of the components, the binary system ammonium chloride-dihydrate, cannot be investigated at temperatures at which liquid phases appear. It is thus not possible to ascertain directly the type of the system. One may, however, obtain some clue from a consideration of the ternary isotherms if one admits that the addition of water to the binary system of solids has an effect closely analogous to that of the addition of heat. In each case liquefaction is brought about as a main result. There are also other changes effected, such as ionic dissociation, which will differ more or less in the two cases, but consequent differences in other respects due to this may be qualitatively allowed for. Thus in the ternary concentration-temperature prism one may carry out an extrapolation from the 25° and 60° isotherms on to the temperature-composition plane of the binary system, ammonium chloride-manganous chloride dihydrate, in the manner represented quite diagrammatically in Fig. 4.

The portion at the dihydrate end cannot be traced below the entry of the tetrahydrate at 25° , nor can one be certain of other parts shown by dots where the extrapolation line falls on different curves at the respective temperatures. An extrapolation to the binary solidus curves offers difficulties, but making allowances as far as possible one may conclude that the binary system, if obtainable, would be one of two eutectics, with the corresponding solids somewhat as shown by the interrupted curves. The intermediate curve passes through a maximum. The maximum, as it happens, is as nearly as possible at 60.2 per cent. of manganous chloride dihydrate, which is the composition of 2:1:2. This might scarcely have been expected in such an extrapolation. The general type is quite a familiar one in metallography, although not so common in salt work.

Now the two-phase maximum point A is, from a phase-theory point of view, a one-component system, hence univariant. In the present case, the system is invariant because regarded as con-

densed. But this single degree of freedom might also be exercised in arbitrary selection (within limits) of a composition for the solid, or one for the liquid, phase, these being the other two variables. The pressure would then require to be adjusted to maintain the system. Putting this conversely, the composition at the maximum point might vary with the pressure, although no doubt such variation would be exceedingly slight. The case is indeed similar to that

FIG. 4.

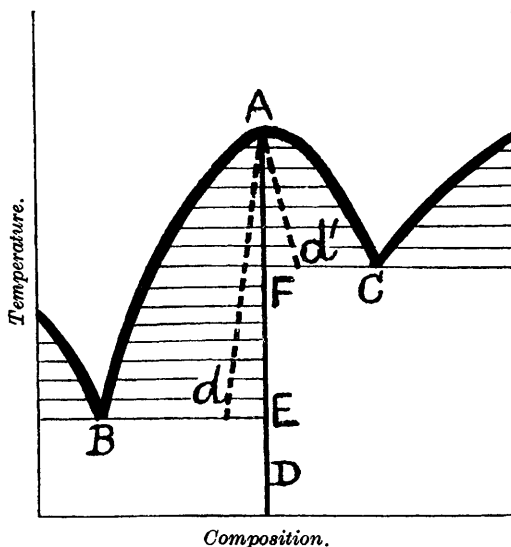


of a constant-boiling (maximum temperature) binary liquid mixture such as is obtainable from hydrogen chloride and water, although here the dependence on temperature is so marked that the term compound would never be applied even if the components were present in integral molecular proportions.

The question now arises as to whether a maximum ever does indicate a compound. The claim that it does so is made in those cases usually represented by a diagram such as Fig. 5.

The curve BAC gives solutions any one of which may be in equilibrium with solid of composition represented by the vertical line AD . Such a case, however, is theoretically impossible. The areas ABE and AFC are two-phase univariant (condensed) systems. Therefore if the composition of one phase, the solid, be fixed, both temperature and composition of the liquid are fixed. If AE and AF are vertical, this certainly cannot be the case. Hence each must have some inclination, however small, to the vertical, as shown by Ad and Ad' . A is thus always just a special member of a series of mixed crystals, and if a mixed crystal be something quite

FIG. 5.



distinct from a compound, the latter term can never, strictly speaking be applied to the solid of composition of the maximum point. This is precisely the same point as that raised by Alkins (*Trans. Inst. Metals*, 1921, 25, 209) in another connexion. He used it to conclude that any two metals cannot be perfectly immiscible in the solid state.

The whole question becomes merely one of definition of terms and amounts simply to asking how near Ad and Ad' need approach to the vertical AD to justify the application of the term compound to the composition of A . Only an arbitrary answer is possible, but whatever it may be it is unlikely to allow so much deviation as to permit $2\text{NH}_4\text{Cl}, \text{MnCl}_2, 2\text{H}_2\text{O}$ to be classed as a compound or double salt.

A few remarks may be made in conclusion regarding the formation of mixed crystals in these ternary solutions. It is obvious that only when the amount of solid formed is very small is the composition of the whole solid likely to be exactly that in equilibrium with the liquid. Otherwise the solid may be a succession of layers of different compositions, of which only the outer is in equilibrium with the liquid. We have always worked with complexes calculated to give only a small proportion of solid. Nevertheless, the limits of the gaps between series cannot be considered to have been exactly determined : nor are our tie-lines always identical with those of Foote and Saxton (*loc. cit.*), doubtless partly for the same reason. In addition, however, it has been proved that the composition of the mixed crystal varies for some hours with the time for which it has been in contact with the solution. It would seem as though a supersaturated solid solution, or mixed crystal, were at first formed, and that this then steadily rejected one of its constituents, the crystals undergoing fracture in the process. The following figures give an example at 60°.

Time of shaking.	Percentage composition.			
	Solution.		Solid (by extrapolation from solution and residue).	
	NH ₄ Cl	MnCl ₂	NH ₄ Cl	MnCl ₂
1 hour	29·8	9·7	77·3	17·5
24 and				
96 hours	29·5	10·2	78·4	16·6

This is a fairly common phenomenon and will be mentioned again in the more striking case of the ternary system, ammonium chloride–ferric chloride–water, about which some considerations will be advanced in a subsequent paper.

Summary.

1. The 60° isotherm of the ternary system ammonium chloride–manganous chloride–water, shows three distinct curves in equilibrium respectively with three sets of mixed crystals, there being two gaps in the series of solids ranging from pure ammonium chloride to pure manganous chloride dihydrate.

2. The composition of the hitherto accepted compound $2\text{NH}_4\text{Cl}, \text{MnCl}_2, 2\text{H}_2\text{O}$ occurs in the second or intermediate series of mixed crystals. At any selected temperature a solid of this composition can exist in equilibrium with one solution only. It is suggested that there is no justification for applying the term compound in such a case.

3. The 25° isotherm has been worked out and explained in accordance with deductions from that at 60°.

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4. The probable type of the binary system ammonium chloride-manganous chloride dihydrate, is discussed and some considerations are advanced regarding the significance of maxima on concentration-composition curves.

5. Some observations on the behaviour of mixed crystals are recorded.

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