STUDIES IN THREE COMPONENT SYSTEMS.

Part II. The System Composed of Zinc Sulphate, Magnesium Sulphate and Water.

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DOUBLE salts of zinc sulphate and magnesium sulphate with varying amounts of water of crystallisation are reported. J. I. Pierre[1] reported the formation of double salt having the formula $ZnSO_4$, $MgSO_4$, $14H_2O$. R. Hollmann[2] reported a double salt having the formula $ZnSO_4$, $2MgSO_4$, $21H_2O$. The existence of these salts was contradicted by E. Barchet[3] and by H. G. K. Westenbrink.[4]

With the idea of studying the suitable conditions for the formation of double salts of zinc sulphate and magnesium sulphate, the system zinc sulphate, magnesium sulphate and water was investigated at 30° C. and at 45° C. Experimental procedure was the same as that adopted in Part I.[5] The solubility of zinc sulphate, in aqueous solutions of magnesium sulphate, was determined by adding excess of zinc sulphate to 5 c.c. of an aqueous solution of magnesium sulphate of different concentrations in a solubility bottle. The bottle was shaken for three days to ensure the attainment of complete equilibrium. In a similar way, the solubility of magnesium sulphate in aqueous solutions of zinc sulphate of different strengths was determined. The solubility of a mixture of zinc sulphate and of magnesium sulphate, when both were in excess, was also determined. Zinc, magnesium and water were estimated by methods indicated in Part I (*loc. cit.*).

The results obtained at 30° C. are given in Table I and plotted on a triangular graph. The results obtained at 45° C. are given in Table II.

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[1] *Ann. Chim. Phys.*, 1846, **16**, 244.

[2] *Zeit. Phys. Chem.*, 1901, **37**, 204 ; 1902, **40**, 578.

[3] *Neues. Jahrb. Nin. B. B.*, 1904, **18**, 399.

[4] *Proc. K. Acad. Wetenskap. Amsterdam*, 1926, **29**, 1374.

[5] *Proc. Ind. Acad. Sci.*, (A), 1938, **7**, 130.

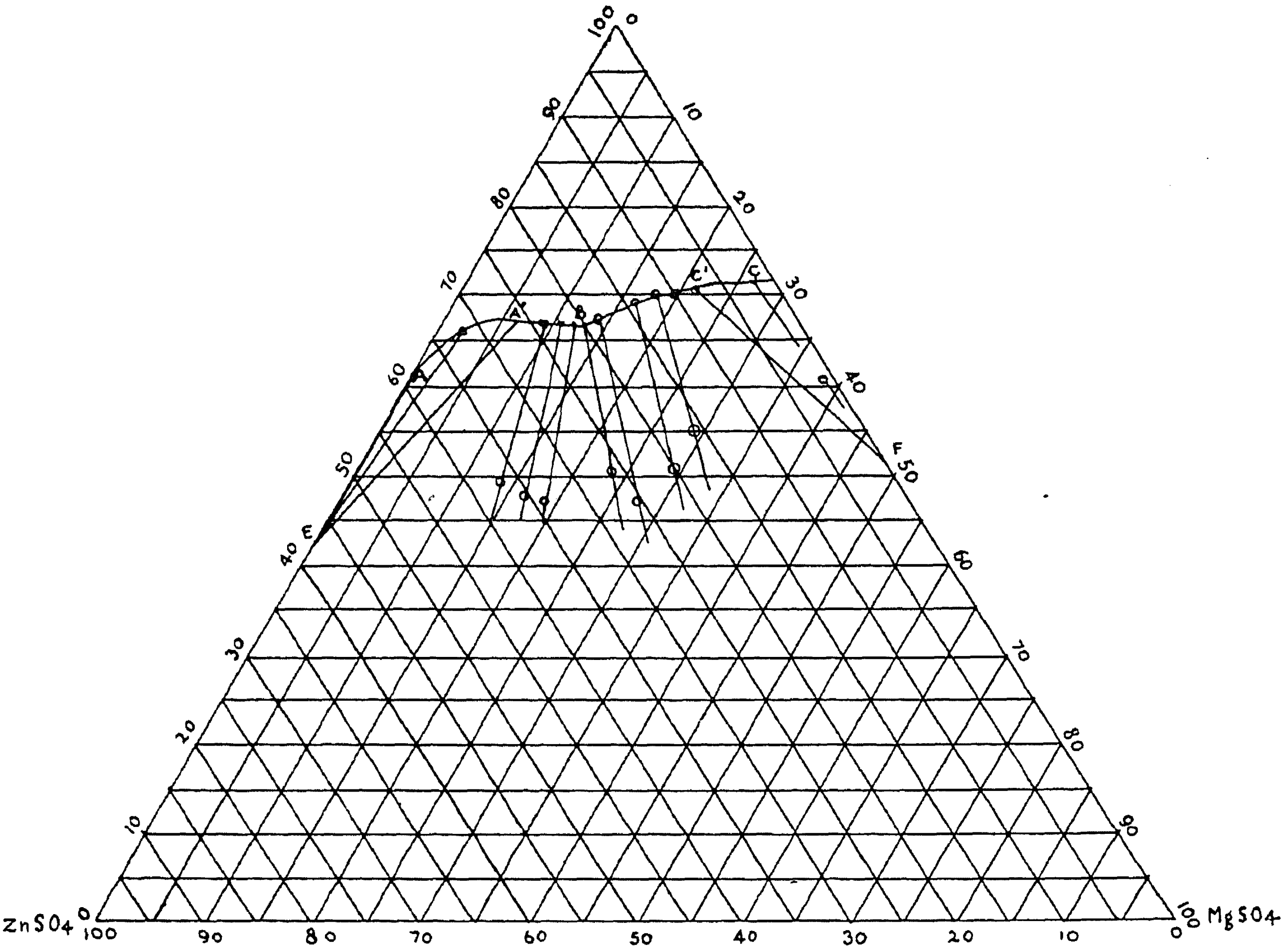

Fig. 1.

$ZnSO_4 - MgSO_4 - H_2O$ at 30° C.

It is seen from Table I that when the concentration of magnesium sulphate increases from 0 gm. to 11·99 gm. the solubility of zinc sulphate decreases from 38·88 gm. to 21·60 gm. per 100 gm. of solution. When both magnesium sulphate and zinc sulphate are added in excess, their solubilities per 100 gm. of the solution are 13·33 gm. and 20·56 gm. respectively. Similarly, the solubility of magnesium sulphate decreases from 28·12 gm. to 14·26 gm. when the concentration of zinc sulphate increases from 0 gm. to 18·57 gm. per 100 gm. of solution.

When the results of the solubility measurements are plotted on a triangular graph, we get a simple two-branched curve ABC (Fig. 1) made up of two parts AB and BC. This shows that there is no possibility of a double salt because when a double salt is formed a three-branched curve is obtained. The lines joining the points for the composition of the solution and of the wet residue for each equilibrium mixture, when extended, should meet at a point giving the composition of the solid phase in equilibrium. It is seen that for mixtures Nos. 1 to 6 (Table I) the solid residue is practically pure zinc sulphate hepta-hydrate, whereas for mixtures Nos. 14 to 17, it is practically pure magnesium sulphate hepta-hydrate. For intermediate

TABLE I.

Zinc Sulphate—Magnesium Sulphate—Water at 30° C.

Equilibrium mixture No.	Grams per 100 grams of solution			Grams per 100 grams of wet residue		
	$MgSO_4$	$ZnSO_4$	H_2O	$MgSO_4$	$ZnSO_4$	H_2O
1	0·00	38·88	61·12	0·00	56·66	43·34
2	0·58	35·65	63·77	0·38	50·56	49·06
3	1·67	32·68	65·65	0·29	51·78	47·93
4	1·96	32·06	65·98	0·54	49·42	50·04
5	4·12	29·20	66·68	0·88	51·19	47·93
6	7·02	26·09	66·89	1·32	50·47	48·21
7	9·54	23·68	66·78	13·92	41·87	44·21
8	10·41	22·94	66·65	17·48	35·73	46·79
9	11·99	21·60	66·41	19·01	34·30	46·69
10	13·33	20·56	66·11	23·60	26·58	49·82
11	14·26	18·57	67·17	27·24	25·76	47·00
12	16·38	14·37	69·25	28·89	20·84	50·27
13	18·76	11·89	69·35	29·90	15·89	45·21
14	21·23	7·98	70·79	43·26	1·69	55·05
15	23·56	5·18	71·26	44·19	0·99	54·82
16	26·31	2·67	71·02	43·46	0·63	55·91
17	28·12	0·00	71·88	48·20	0·00	51·80

TABLE II.

Zinc Sulphate—Magnesium Sulphate—Water at 45° C.

Equilibrium mixture No.	Grams per 100 grams of solution			Grams per 100 grams of wet residue		
	$MgSO_4$	$ZnSO_4$	H_2O	$MgSO_4$	$ZnSO_4$	H_2O
1	0·00	42·35	57·65	0·00	59·62	40·38
2	1·03	38·96	60·01	0·36	55·62	44·02
3	2·27	35·38	62·35	0·85	51·22	47·92
4	4·67	32·10	63·23	0·75	56·18	43·07
5	5·90	30·73	63·37	1·18	53·03	45·79
6	7·38	28·55	64·07	1·74	51·65	46·61
7	9·97	26·44	63·59	13·13	39·75	47·12
8	12·86	24·28	62·86	20·72	37·86	41·42
9	14·17	23·88	62·00	25·45	29·01	45·54
10	16·14	19·59	64·27	29·49	19·72	50·79
11	18·11	16·24	65·65	34·65	15·85	49·50
12	20·08	13·13	66·79	43·32	2·69	53·99
13	23·07	10·09	66·84	45·21	1·72	53·01
14	25·81	6·32	67·87	44·29	1·36	54·35
15	28·56	3·35	68·09	45·78	0·68	53·54
16	30·18	1·63	68·19	45·63	0·45	53·92
17	32·25	0·00	67·75	48·20	0·00	51·80

mixtures Nos. 7 to 13, the lines referred to above do not meet at a point, showing that the solid residue is not a pure substance but is a mixture. The curve definitely shows that at 30° C. there is no possibility of the formation of a double salt.

It may be pointed out that the form of the *iso*thermal solubility curve at 30° C. does not preclude the formation of double salts at some other temperature. It is known (Findlay) that a double salt breaks up into its constituent salts above the transition temperature if the double salt formation is exothermic and below the transition temperature if it is endothermic. For want of sufficient information regarding the solubility, the transition point and the heat changes involved in the formation of the reported double salts, it is difficult to state what conditions will be suitable for their formation.

Results obtained at 45° C. also do not indicate any double salt formation at that temperature. The question of suitable conditions for the formation of double salts will be satisfactorily settled after working at various temperatures and allowing sufficient time for the mixture to attain equilibrium.

The equilibrium mixtures Nos. 7–13 reveal an interesting fact that the solid residue is not a pure substance but a mixture. If the solid consists of two phases, the system must become univariant, *i.e.*, the composition of the solution should not change once the temperature is fixed. But it is actually found that the solution varies widely in composition and is yet in equilibrium with the solid. The results therefore lead to the conclusion that mixed crystals are formed.

This case corresponds to that of partial miscibility of two liquids. Zinc sulphate dissolves magnesium sulphate until the concentration of the latter in the mixed crystals reaches a certain value. Further addition of magnesium sulphate does not alter the composition of the mixed crystals, but leads to the formation of a second solid phase consisting of a solution of zinc sulphate in magnesium sulphate. At this point, there being two solid phases—a solution of magnesium sulphate in zinc sulphate and *vice versa*—the system is univariant and is represented by the break at B in the *iso*therm ABC. Three transition points appear to be indicated in the curve ABC. Of them A′ and C′ are fictitious and are probably due to the fact that under the experimental conditions there was no attainment of equilibrium owing to the fact that diffusion of ions into the crystal lattice (*e.g.*, magnesium ion into the crystal lattice of zinc sulphate) is a slow process.

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