STUDIES IN THREE COMPONENT SYSTEMS.

Part I. Systems Composed of Sulphuric Acid, Water and either Zinc Sulphate or Magnesium Sulphate.

BY N. K. JOSHI AND S. C. DEVADATTA.

(From the Chemistry Laboratories, Wilson College, Bombay.)

Received September 9, 1937.

THE results of the solubility measurements of zinc sulphate hepta-hydrate at various temperatures up to 100° C. showed that on raising the temperature, the hepta-hydrate progressively turned into the lower hydrates—the hexa and the mono. The transition temperatures are: $ZnSO_4, 7H_2O$ to $ZnSO_4 \cdot 6H_2O$, 39° C. and $ZnSO_4 \cdot 6H_2O$ to $ZnSO_4 \cdot H_2O$, 70° C. The presence of these hydrates could be established as they are stable over a wide range of temperatures. These results, however, cannot be taken to exclude the possibility of the formation of intermediate hydrates between the hexa-hydrate and the mono-hydrate which might be stable over a narrow range of temperature.

Similarly the solubility measurements of magnesium sulphate in water at different temperatures showed the presence of three stable hydrates—the hepta, the hexa and the mono with transition points at 48° C. and 68° C. Various other hydrates like the penta, the tetra and the five-fourths are claimed by several investigators.[1]

It is known that the addition of sulphuric acid in sufficient quantity to the saturated solution of a hydrated salt, with which the acid does not react, will cause the salt to crystallise, either as a lower hydrate or in the anhydrous condition. This property of sulphuric acid of producing lower hydrates of different salts has been used by Tabonry[2], D'Ans,[3] Van Dorp,[4] H. W. Foote[5] and others. Sulphuric acid being soluble in water in all proportions, it is possible to increase the concentration of the acid to any desired extent. But this method is applicable only in the case of sulphates, as the sulphuric acid will react chemically with other salts.

---

1 *Cf.* T. E. Rozbiersky, *Sitzler. Akad., Berlin*, 1899, 340 ; Takegami, *Mem. Coll. Sci. Kyoto Imp. Uni.*, 1921, 4, 317.

2 *Compt. rend.*, 1914, 159, 180.

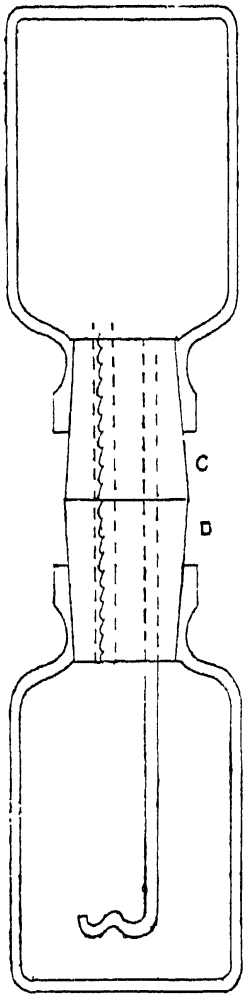
3 *Z. Anorg. Chem.*, 1906, 49, 356 ; 1909, 61, 91.

4 *Z. Physik. Chem.*, 1910, 73, 289.

5 *J. Amer. Chem. Soc.*, 1915, 37, 290.

In order to detect the presence of intermediate hydrates of zinc sulphate and of magnesium sulphate, the study of the systems composed of sulphuric acid, water and zinc sulphate (or magnesium sulphate) was undertaken.

On applying the Phase Rule $-F = n + 2 - r$ to the systems of three components, *viz.*, zinc sulphate (or magnesium sulphate), sulphuric acid and water and of three phases, *viz.*, solid hydrate, solution and vapour, we see that these systems are divariant. It means that *even though the temperature is arbitrarily fixed* (*within certain limits*), the hydrate can exist in contact with solutions of varying composition. If two hydrates are present, the system becomes univariant and the hydrates would be in equilibrium with a solution of definite composition at any arbitrarily fixed temperature. The relative proportions of the solid hydrates, however, can change and hence the composition of the solid residue as a whole will vary.



Solubility Bottle.

In a series of solubility determinations of a salt in presence of different concentrations of sulphuric acid, the existence of pure hydrate is indicated, if the composition of the solution varies while that of the residue remains constant. On the other hand, if the solubility remains constant, but the residue varies in composition, it follows that there must be two hydrates in equilibrium. It is possible, therefore, to detect by this method all the stable hydrates of normal sulphates at any convenient temperature.

The apparatus for solubility measurements was a pair of bottles joined to each other by a rubber stopper and two glass tubes as shown in the diagram. This apparatus was designed by N. Campbell.[6] It possesses the advantage of compactness, simplicity and of filtering the solution from the solid residue dy merely inverting it in the thermostat. This apparatus works well and is found suitable for Phase Rule studies involving the analysis of a solid phase. Actual procedure is to take 5 c.c. of distilled water and excess of salt hydrate in one of the bottles and then to add increasing amounts of sulphuric acid. These bottles were fixed to a stirrer of an electrically regulated water thermostat and were rotated till equilibrium was attained (*i.e.*, for about 12 hours). On inverting these bottles in the

[6] *J. Chem. Soc.*, 1930, 179.

thermostat, the solution filtered through glass wool into the lower empty bottle. The solid residue and the solution were then analysed.

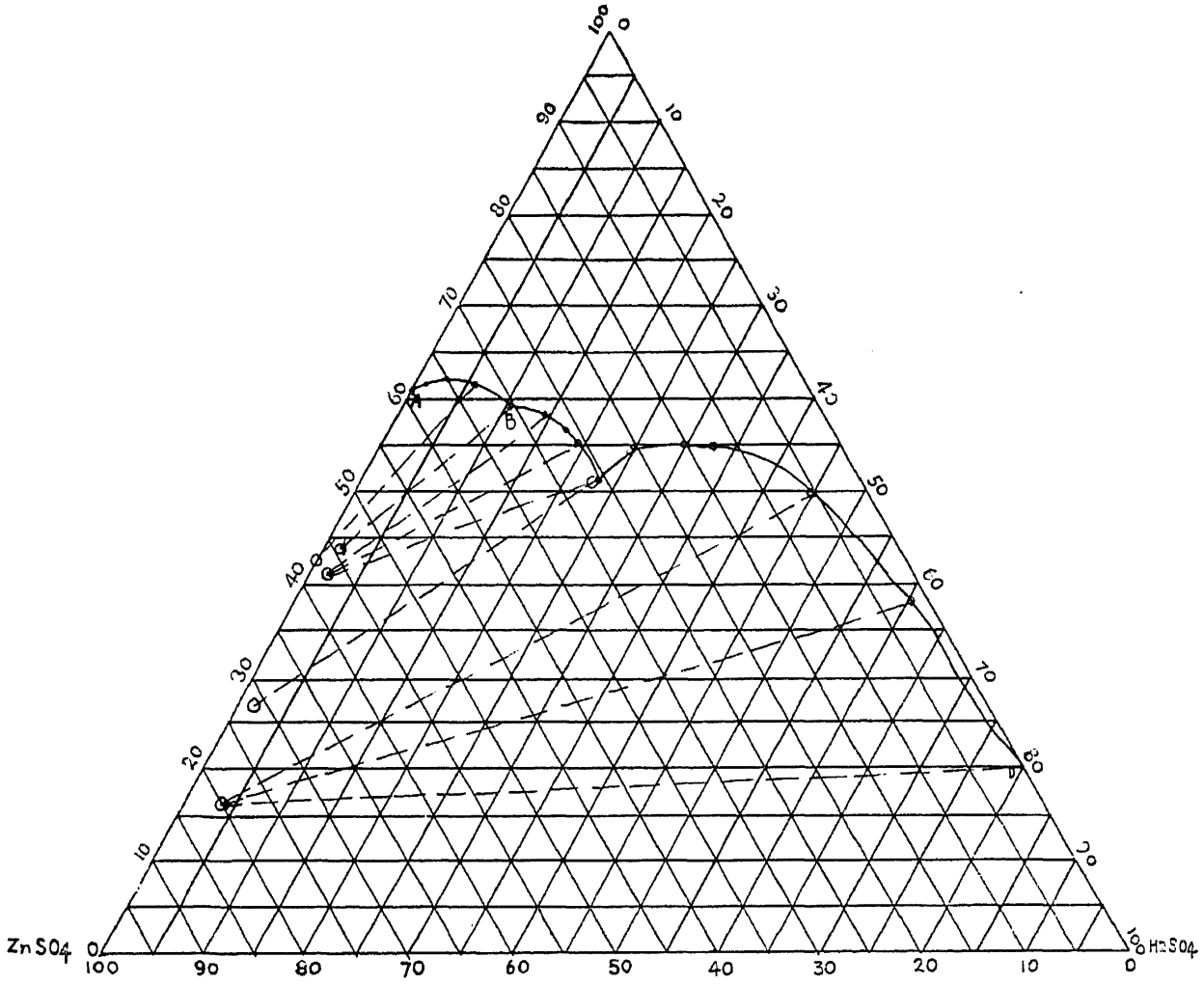
Zinc was estimated volumetrically by titrating it against standard sodium sulphide solution using sodium nitroprusside as an external indicator and magnesium was estimated gravimetrically as magnesium pyrophosphate. The total sulphate was determined by the usual method of weighing the barium sulphate formed. By subtracting the weight of sulphate corresponding to zinc or magnesium, the weight of free sulphuric acid was determined. Water was always determined by difference.

Two methods were adopted for determining the composition of the solid phase. The " Dry residue " method of H. W. Foote[7] and the " Residue method " of Schreinemakers.[8] Both these methods were tried and were found to give identical results. The results obtained with Schreinemakers' method only are given here. This method is based on the principle that the composition of the solid with adhering mother-liquor when plotted on a triangular graph lies on a straight line joining the points representing the compositions of the solution and the dry solid phase. Thus when at least two different solutions are analysed together with their residues, the composition of the pure solid is found by extrapolation. This method of extrapolation is only useful when the solid consists of one phase of constant composition.

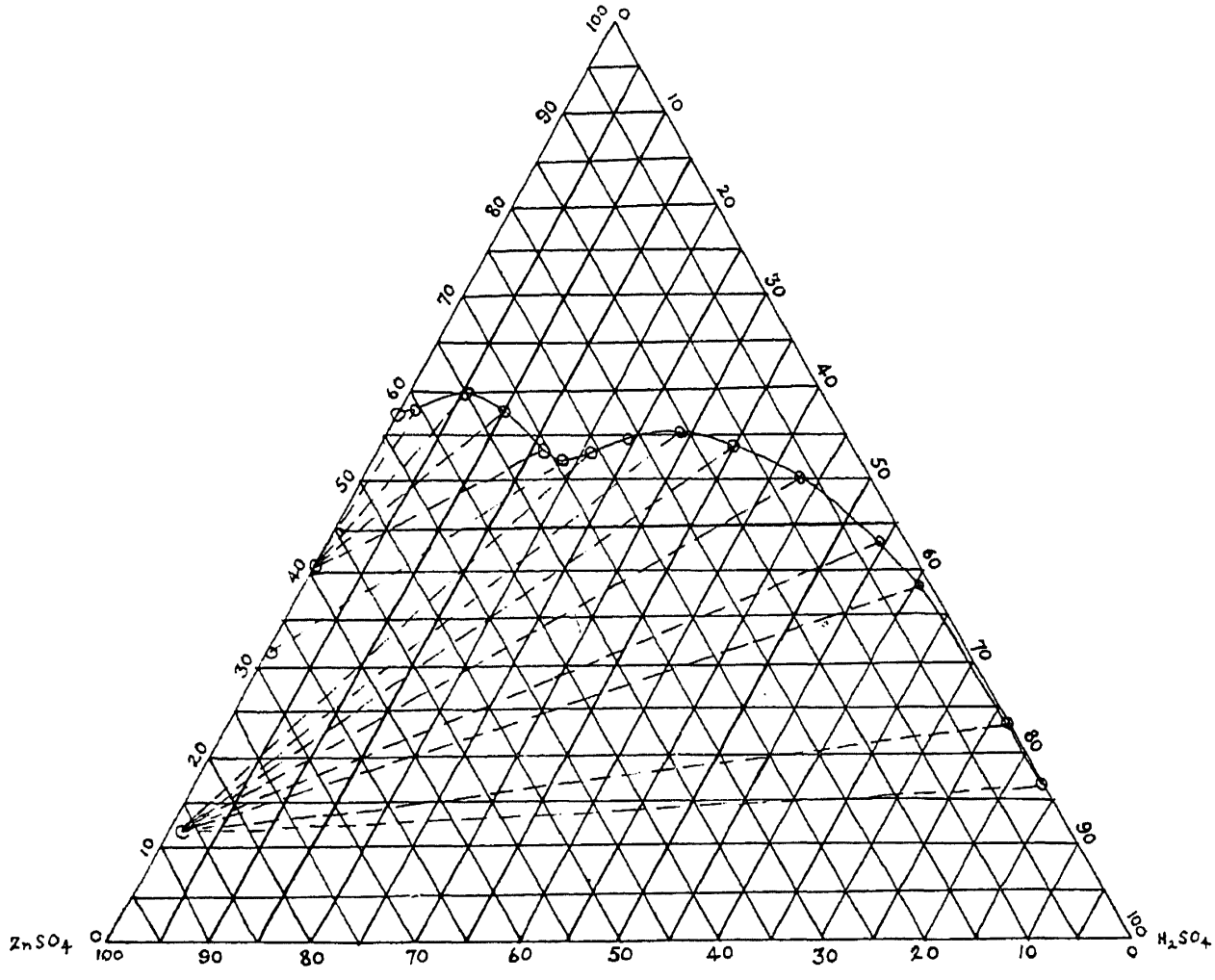
The results obtained with zinc sulphate at 30° C. and at 45° C. and with magnesium sulphate at 30° C. are given in Tables I, II and III respectively. Out of several readings only significant and necessary ones are given. Results of the systems zinc sulphate, or magnesium sulphate, sulphuric acid and water are plotdte on the triangular graphs.

[7] *J. Amer. Chem. Soc.*, 1912, **34**, 880 ; 1914, **36**, 1695.

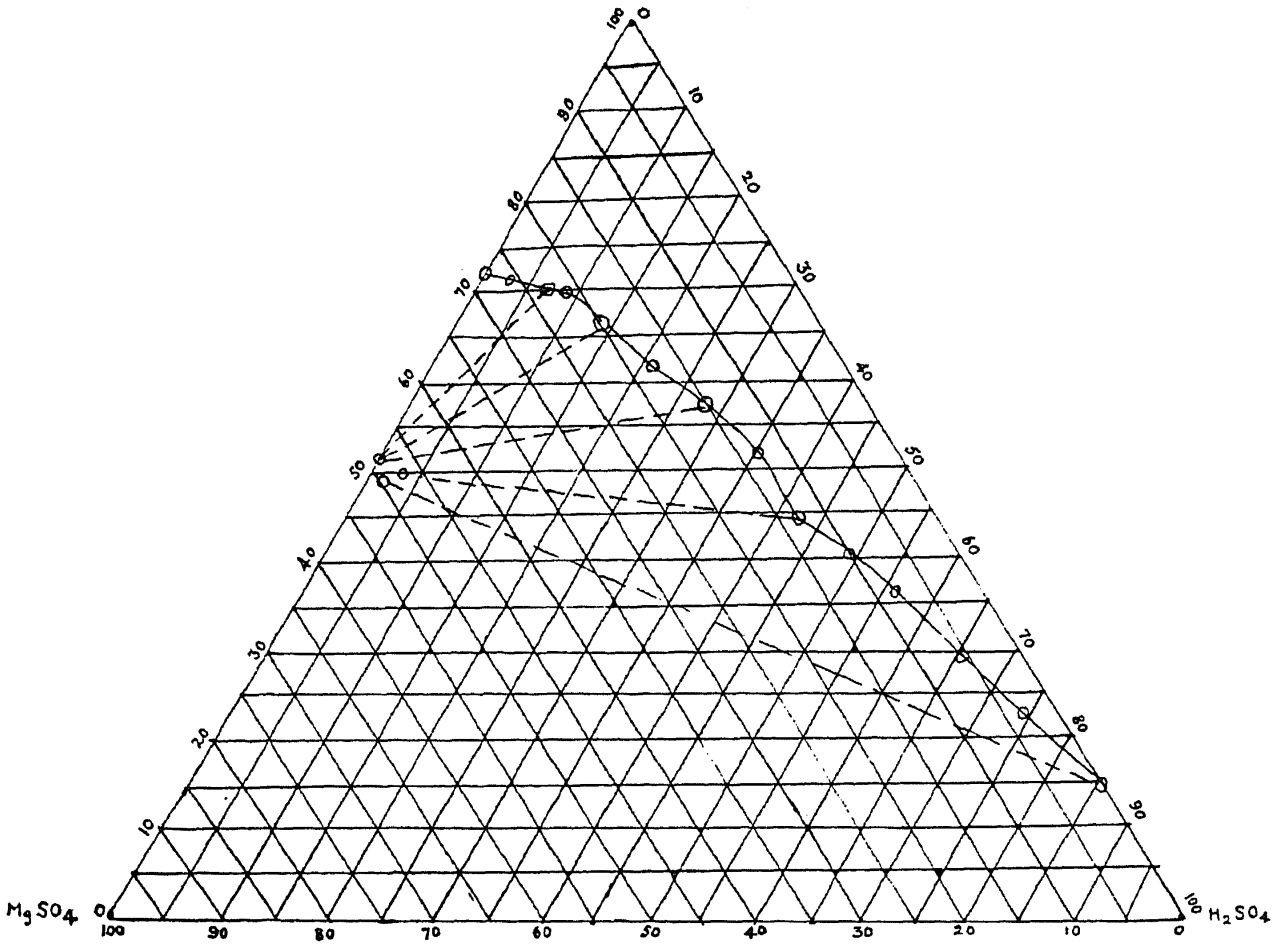
[8] *Ibid.*, 1924, **46**, 1766.



GRAPH 1. $ZnSO_4$—HSO_4—H_2O at 30° C.



GRAPH 2. $ZnSO_4 - H_2SO_4 - H_2O$ at 45° C.



GRAPH 3. $MgSO_4 - H_2SO_4 - H_2O$ at 30° C.

In these cases there are three components, zinc sulphate (or magnesium sulphate), sulphuric acid and water, and three phases solid, solution and vapour, the system, therefore, is divariant. With the temperature arbitrarily fixed the system has only one degree of freedom and the *solution in equilibrium, can vary in composition*. If there are two hydrates, the system becomes univariant, *i.e.*, the solid composed of two hydrates can be in equilibrium with a solution of definite composition at any arbitrarily fixed temperature as could be seen from Tables I, II and III.

Graph 1 shows that the solid has a constant composition as required by the formula $ZnSO_4 \cdot 7H_2O$ whereas the composition of the solution varies from 0 gm. of sulphuric acid and 38·88 gm. of zinc sulphate to 9·64 gm. of sulphuric acid and 30·34 gm. of zinc sulphate per 100 gm. of solution. But when the composition of the residue changes from that required by the formula $ZnSO_4 \cdot 7H_2O$ to give a mixture of two hydrates, the solution has only one composition, *viz.*, 10·43 gm. of sulphuric acid and 30·52 gm. of zinc sulphate. Any attempt to change the composition of the solution even slightly by the addition of more sulphuric acid invariably results in the formation of lower hydrate, having the composition expressed by the formula $ZnSO_4 \cdot 6H_2O$. The solid phase again shows a constant composition of

TABLE I.

Zinc Sulphate—Sulphuric Acid—Water at 30° C.

"Wet Residue Method."

Grams per 100 grams of solution			Grams per 100 grams of wet residue			Solid phase
H_2SO_4	$ZnSO_4$	H_2O	H_2SO_4	$ZnSO_4$	H_2O	
0·00	38·88	61·12	0·00	58·66	43·34	$ZnSO_4 \cdot 7H_2O$
1·98	36·47	61·55	0·98	50·65	48·37	,,
4·05	34·78	61·17	1·56	47·32	51·12	,,
7·23	31·89	60·38	1·12	52·09	48·79	,,
10·43	30·52	59·05	1·42	54·61	43·77	$ZnSO_4 \cdot 7_2HO$ & $ZnSO_4 \cdot 6H_2O$
12·41	29·12	58·47	1·23	56·78	41·99	$ZnSO_4 \cdot 6H_2O$
17·27	26·98	55·75	0·87	58·19	40·94	,,
21·15	26·02	52·83	2·06	56·69	41·25	,,
22·89	25·72	51·39	1·77	71·35	26·88	$ZnSO_4 \cdot 6H_2O$ & $ZnSO_4 \cdot H_2O$
27·13	18·04	54·83	3·65	80·21	16·14	$ZnSO_4 \cdot H_2O$
32·31	12·11	55·58	5·16	77·35	17·49	,,
42·23	7·15	50·62	2·10	85·56	12·34	,,
50·52	3·86	45·62	2·99	84·45	12·56	,,
63·61	1·04	35·36	3·18	85·29	11·53	,,
81·10	0·00	18·90	6·33	82·52	11·15	,,

TABLE II.

Zinc Sulphate—Sulphuric Acid—Water at 45° C.

"Wet Residue Method."

Grams per 100 grams of solution			Grams per 100 grams of wet residue			Solid phase
H_2SO_4	$ZnSO_4$	H_2O	H_2SO_4	$ZnSO_4$	H_2O	
0·00	42·35	57·65	0·00	59·62	40·38	$ZnSO_4 \cdot 6H_2O$
1·23	40·31	58·46	0·34	55·67	43·99	,,
5·81	34·88	59·31	1·32	55·56	43·12	,,
9·98	32·46	57·56	1·01	57·48	41·51	,,
16·37	30·21	53·42	1·53	57·58	40·80	,,
18·48	29·51	52·01	1·23	67·31	31·46	$ZnSO_4 \cdot 6H_2O$ & $ZnSO_4 \cdot H_2O$
21·29	25·35	53·36	1·57	85·45	12·98	$ZnSO_4 \cdot H_2O$
24·34	21·03	54·63	2·82	83·91	13·27	,,
29·36	15·44	55·20	2·84	83·72	13·44	,,
34·86	10·95	54·19	2·33	84·97	12·70	,,
42·89	6·55	50·56	3·98	82·64	13·38	,,
54·27	2·08	43·65	3·29	84·38	11·33	,,
60·73	1·00	38·27	5·71	81·27	13·02	,,
75·97	0·56	23·47	3·01	86·20	10·79	,,
82·92	0·00	17·08	4·32	85·46	10·22	,,

TABLE III.

Magnesium Sulphate—Sulphuric Acid—Water at 30° C.

"Wet Residue Method."

Grams per 100 grams of solution			Grams per 100 grams of wet residue			Solid phase
H_2SO_4	$MgSO_4$	H_2O	H_2SO_4	$MgSO_4$	H_2O	
0·00	28·12	71·88	0·00	48·20	51·80	$MgSO_4 \cdot 7H_2O$
1·94	26·89	71·17	0·45	46·24	53·51	,,
3·49	25·54	70·97	0·76	45·38	53·86	,,
6·82	23·11	70·07	1·00	44·68	54·32	,,
9·24	21·79	68·97	2·31	42·91	54·78	,,
14·78	19·23	65·99	2·09	44·18	53·73	,,
19·98	17·59	62·43	3·23	43·76	53·01	,,
21·58	16·97	61·45	2·15	45·67	52·18	,,
28·42	14·99	56·59	2·37	45·71	51·92	,,
35·28	13·40	51·32	2·79	45·73	51·48	,,
39·09	12·86	48·05	1·32	47·51	51·17	,,
43·18	12·82	44·00	3·58	46·36	50·06	$MgSO_4 \cdot 7H_2O$ & $MgSO_4 \cdot 6H_2O$
49·38	9·95	40·67	1·63	49·34	49·03	$MgSO_4 \cdot 6H_2O$
56·21	7·92	35·87	1·55	49·57	48·88	,,
65·34	4·87	29·79	2·11	49·05	48·84	,,
74·01	2·96	23·03	2·05	49·12	48·83	,,
84·33	0·00	15·67	8·56	78·45	12·99	$MgSO_4 \cdot H_2O$
85·82	0·00	14·18	9·32	77·81	12·87	,,

60·20 gm. per 100 gm. of the residue even though the composition of the solution changes considerably. On further addition of sulphuric acid we get a mixture of two hydrates—the hexa and the mono, which are in equilibrium with a solution of a definite composition, *viz.*, 23·00 gm. of sulphuric acid and 25·89 gm. of zinc sulphate per 100 gm. of the solution. Further addition of sulphuric acid changes the hexa hydrate into mono hydrate completely. The stable hydrates of zinc sulphate are the hepta, the hexa and the mono. It may be noted that anhydrous zinc sulphate was not formed by heating the hydrate with water even to 100° C. nor by adding excess of sulphuric acid. The solubility of zinc sulphate decreases from 38·86 gm. to 0 gm. per 100 gm. of solution when the amount of sulphuric acid increases from 0 gm. to 81·10 gm. per 100 gm. of the same solution.

Exactly similar information is gathered from Table II where the first stable hydrate is the hexahydrate instead of the hepta as the temperature of the experiment was 45° C.

The results obtained with system magnesium sulphate, sulphuric acid and water at 30° C. are embodied in Table III. By applying Phase Rule to the study of the system, we get the hepta, the hexa and the mono as the stable hydrates of magnesium sulphate. In this case also the anhydrous magnesium sulphate was not obtained by adding even 85·82 gm. of sulphuric acid nor by raising the temperature of a mixture of magnesium sulphate and water upto 100° C.

In conclusion, it can be stated that the addition of sulphuric acid to a higher hydrate in order to study its lower hydrates at room temperature is a very convenient method, though rather limited in its application. In the two cases considered we have not been able to substantiate the claims of various workers for hydrates intermediate between the hexa and the mono.

We are grateful to Prof. P. M. Barve for his helpful suggestions.

REFERENCES.

N. Campbell, *J. Chem. Soc.*, 1930, **179.**

D'Ans, *Z. Anorg. Chem.*, 1906, **49**, 356 ; 1909, **61**, 91.

H. W. Foote, *J. Amer. Chem. Soc.*, 1915, **37**, 290; *ibid.*, 1912, **34**, 880; *ibid.*, 1914, **36**, 1695.

T. E. Rozbiersky, *Sitzber. Akad., Berlin*, 1899, **340.**

Schreinemakers, *J. Amer. Chem. Soc.*, 1924, **46**, 1766.

Taboury, *Compt. rend.*, 1914, **159**, 180.

Takegami, *Mem. Coll. Sci. Kyoto. Imp. Uni.*, 1921, **4**, 317.

Van Drop, *Z. physik. Chem.*, 1910, **73**, 289.