On the Systems: Barium Oxide—Acetic Acid—Water and Magnesium Oxide—Acetic Acid—Water.

By

Junichi Iwaki.

(Received October 10, 1914.)

The equilibrium of the systems consisting of barium or magnesium oxide, acetic acid and water at $25 \cdot 0°$C. has been studied; and the present article is an account of the results.

I. The System: Barium Oxide, Acetic Acid and Water.

The materials used were barium hydroxide, barium acetate, acetic acid and water. They were mixed in different proportions, the free base and acid not being used at the same time; and each mixture was put in an Erlenmeyer flask of a capacity of about 50 cc. The flasks were made to rotate in a thermostat at $25 \cdot 0°$ for at least one day; then the solution was separated from the residue, and both, the latter still wet with the former, were analysed for barium and acetic acid.
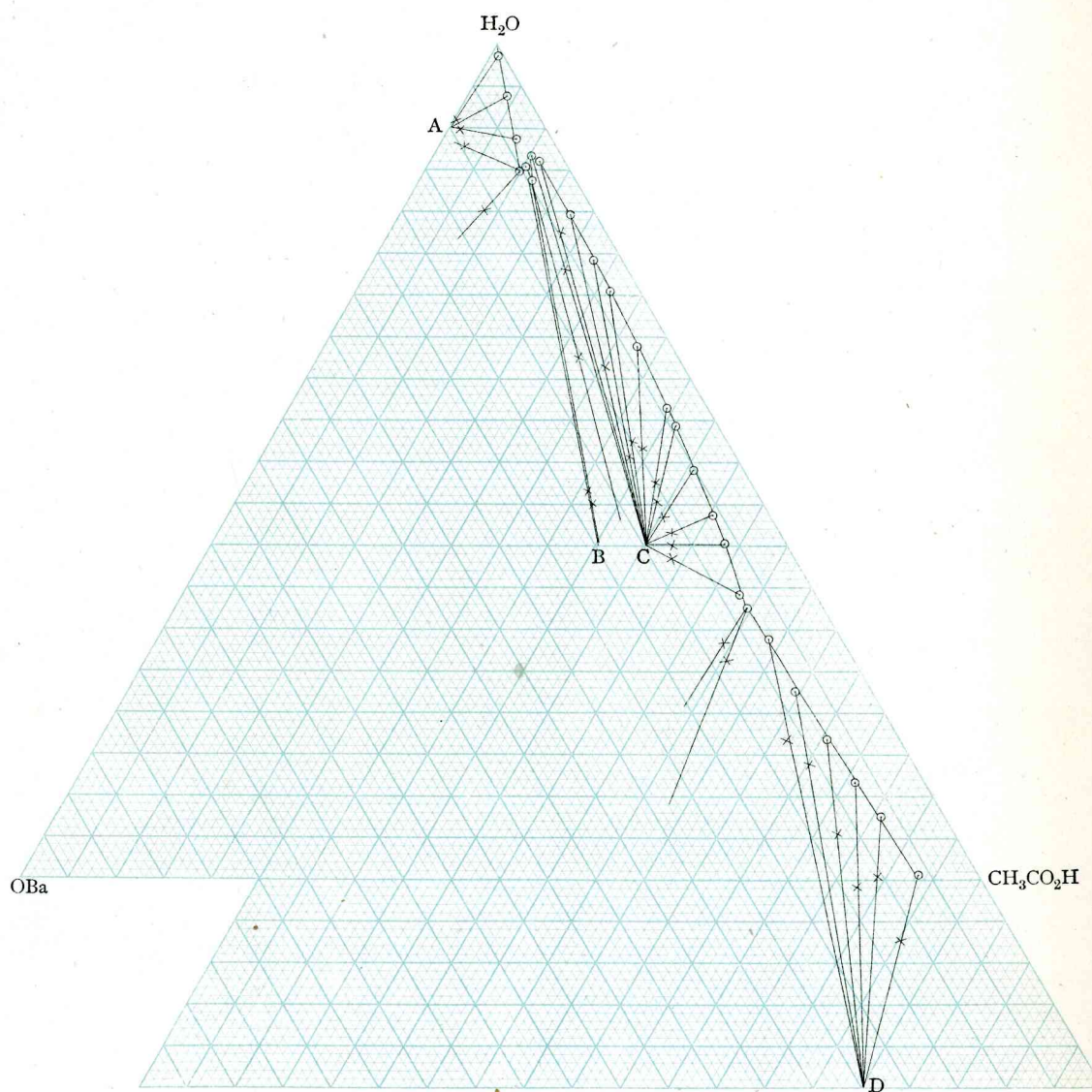
The analysis was carried out in the following way. A given quantity of a sample, mixed with some water and phosphoric acid, was subjected to distillation; and when the liquid in the distillation flask was reduced to a small quantity, the distillation was continued by passing steam through, until the distillate ceased to react acid to a litmus paper. Of this distillate, acetic acid was titrated with a decinormal solution of sodium hydroxide, using phenolphthalein as indicator. Barium was determined as the sulphate in the residue in the distillation flask in the usual way. The amount of water was found by noting the difference.

The results are given in Table 1 and graphically represented in Fig. 1.

Junichi Iwaki.

TABLE I.

No.	Solution.			Residue, wet with the solution.			Residue.
	OBa	CH₃CO₂H	H₂O	OBa	CH₃CO₂H	H₂O	
1	0·39	0	99·61	—	—	—	$(HO)_2Ba.8H_2O$.
2	1·06	0·56	98·31	9·10	0·26	90·63	„
3	2·30	4·06	93 64	8·25	1·04	90·72	„
4	4·06	7·49	88·45	9·22	1·09	89·71	„
5	5·22	9·80	84·94	9·82	2·73	87·71	$\{(HO)_2Ba.8H_2O$; $(CH_3CO_2)_2Ba.3H_2O$.
6	5·24	9·87	84·89	11·36	8·64	80·00	$(CH_3CO_2)_2Ba\ 3H_2O$.
7	4·92	10 04	85 06	17 76	35·91	46·31	„
8.	5·10	11·53	83·37	18·00	37 00	45·02	$\{(CH_3CO_2)_2Ba.3H_2O$; $3(CH_3CO_2)_2Ba;3CH_3CO_2H.11H_2O$.
9	5·05	11·49	83·52	10·76	26 85	62·38	$3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$.
10	3·88	10 09	86·30	6 86	20 21	72·98	„
11	2·95	11·35	85·72	5·10	17·37	77·52	„
12	2·94	17·58	79 49	8·51	30 21	61·32	„
13	3·21	22·76	74 03	9 30	34·30	56·37	„
14	3·44	26·21	70·36	10·34	37·32	52·35	„
15	3·91	32·17	63·92	9·80	·38·91	51·29	„
16	4·53	9·04	56·44	10·25	42·52	47·23	„
17	4·89	41·07	54·05	11·37	43·64	44·98	„
18	5·62	45·53	48·84	11·82	45·08	43·10	„
19	6·29	50·03	43·63	11·78	47·09	41·15	„
20	6·80	53·15	40 05	12·28	47·87	39·84	„
21	8·10	57·80	36·09	12·97	48·53	38·50	„
	8·23	59·13	32 63	12·80	59·00	28·20	$\{3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$; $(CH_3CO_2)_2Ba.2CH_3CO_2H$.
23	8·22	59·41	32·36	13·53	60·12	26·35	$(CH_3CO_2)_2Ba.2CH_3CO_2H$.
24	7·94	63·77	28 31	12·06	71·58	16·36	„
25	8·02	69·71	22·27	11·14	75·54	13·32	„
26	7·88	75·70	16·43	12·72	82·12	5·16	„
27	7·62	81·16	11·24	13·69	87·66	−1·33	„
28	7·23	85·96	6·82	11 09	88·90	0	„
29	6·85	93·11	0 03	12·28	95·15	−7·43	„

Fig. 1.

A. $(HO)_2$ Ba. $8H_2O$.
B. $(CH_3CO_2)_2$ Ba. $3H_2O$.
C. $3(CH_3CO_2)_2$ Ba. $3CH_3CO_2H$. $11H_2O$.
D. $(CH_3CO_2)_2$ Ba. $2CH_3CO_2H$.

In Fig. 1, triangular coordinates are used, barium oxide, acetic acid and water, as the components, being represented by the angular points. The compositions of the residues were estimated in the usual way, as seen from the figure, and are given in formulas in the last column of the table.

Of the normal salt, two hydrates, $(CH_3CO_2)_2Ba.3H_2O$ and $(CH_3CO_2)_2Ba.H_2O$, are known and their transition point has been determined to be $24.7°$.[1] The temperature of the present investigation was only $0.3°$ higher than that transition point, and moreover it was not an easy matter to obtain a system with the normal salt as the residue, as its solubility attains maximum at about $25°$. If we take these facts into consideration, it is not improbable that the trihydrate here obtained at $25°$ was a metastable state.

Two acid salts have been found, namely $3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$ and $(CH_3CO_2)_2Ba\ 2CH_3CO_2H$. The former is in prismatic or, needle-shaped crystals and seems to be identical with that represented as $(CH_3CO_2)_2Ba.CH_3CO_2H.4H_2O$ by Villiers.[2] The difference in composition according to these two formulas is slight, and might be caused by a minute quantity of adhering mother liquor. In the present method of investigation, the adhering mother liquor does not affect the result.

To verify the Villiers's result the crystals were pressed between folded filter paper to remove as much of the mother liquor as possible, and then exposed to a current of dry air. They were analysed in different stages of the procedure. The results, in the order of the analysis, together with those of Villiers are given in the following table.

TABLE II.

	Bariumacetate	Excessive acid
Villiers	65.53	15.85
Iwaki 1.	65.54	16.39
2.	66.28	16.14
3.	66.42	15.79
4.	68.32	15.37
Calc. for $3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$	66.94	15.73
„ „ $(CH_3CO_2)_2Ba\ CH_3CO_2H.4H_2O$	65.91	15.49

---

[1] Walker and Fyffe, J. chem. Soc., **83**, 173 (1903).

[2] C. R., **85**, 1235 (1877).

As may be seen from the table, it is quite difficult or almost impossible to determine the composition of the crystals by obtaining them pure enough for analysis in the usual way.

To make sure, another method of analysis was adopted. The mother liquor and the wet residue were diluted or dissolved respectively to a given volume; and an aliquot part was titrated for the free acid, while in another portion barium was determined. From this data the percentage composition of the sample was calculated, and the results are given in the following table.
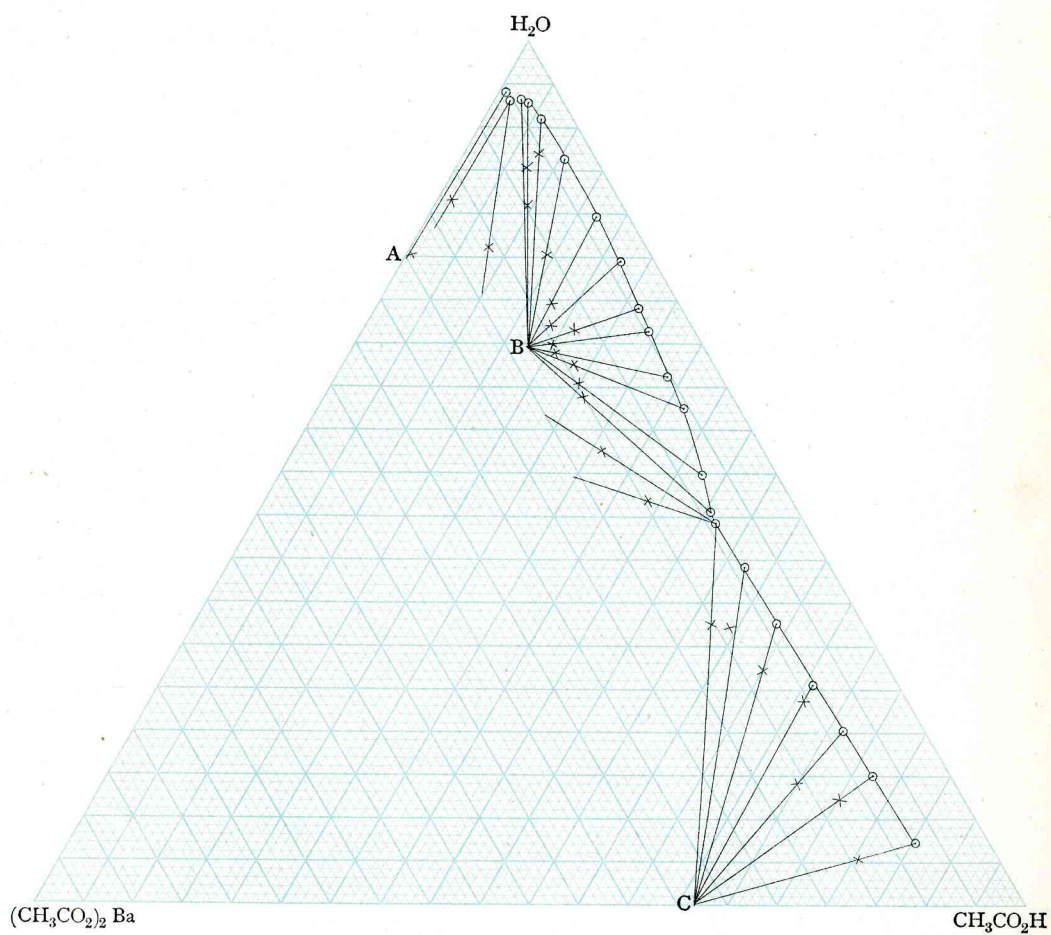
TABLE III.

No.	Solution.			Residue, wet with the solution.			Residue.
	CH_3CO_2H	$(CH_3CO_2)_2Ba$	H_2O	CH_3CO_2H	$(CH_3CO_2)_2Ba$	H_2O	
1	3·30	3 48	93·22	9·81	9·85	80·35	$3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O.$
2	10·23	3·14	86 64	14·04	10·40	75·56	,,
3	16 92	3·24	79 84	17·46	12·77	69 68	,,
4	20 60	3 62	75·77	18·77	14·19	67·04	,,
5	26·48	4·41	69·10	21·04	12·11	66·86	,,
6	28·72	4·52	66·77	19 87	15·12	64·95	,,
7	33·14	5·23	61·62	20·67	15·30	64·04	,,
8	36·54	5·60	57·86	23·18	14 00	62·82	,,
9	42·08	7·85	50 05	24·87	14·52	60 60	,,
10	45·28	8·82	45·93	25·95	14·90	59·14	,,
11	46 90	8·92	44·17	23·54	15·92	60·57	,,

From this data is derived the same conclusion as before as to the composition of the residue, as seen in Fig. 2; and Villiers's formula is very improbable.

Villiers[1] obtained another acid salt from a glacial acetic acid solution of barium acetate. It was so unstable that its formula could not be determined definitely; but he suggested from anaytical results, that it might have the formula $(CH_3CO_2)_2Ba.2CH_3CO_2H.2H_2O$. In the present investigation, the crystals obtained from solutions, comparatively concentrated for acetic acid, were silky, as those described by Villiers, and had the composition, $(CH_3CO_2)_2Ba.2CH_3CO_2H$, as graphically estimated in Fig. 1.

[1] *Loc. cit.*

Fig. 2.

A. (CH_3CO_2) Ba. $3H_2O$.

B. $3(CH_3CO_2)_2$ Ba. $3CH_3CO_2H$. $11H_2O$.

C. $(CH_3CO_2)_2$ Ba. $2CH_3CO_2H$.

Experiments were begun for the study of the normal, acid and basic acetates of barium, and barium oxide, acetic acid and water were considered to be the components as in Table 1 and Fig. 1. The non-existence of any basic salt being ascertained, it became convenient to take acetic acid, barium acetate and water as the components; and to make the equilibrium state more intelligible, the following table was derived from the foregoing, supplemented by some new experiments. It is graphicplly represented in Fig. 2.

TABLE IV.

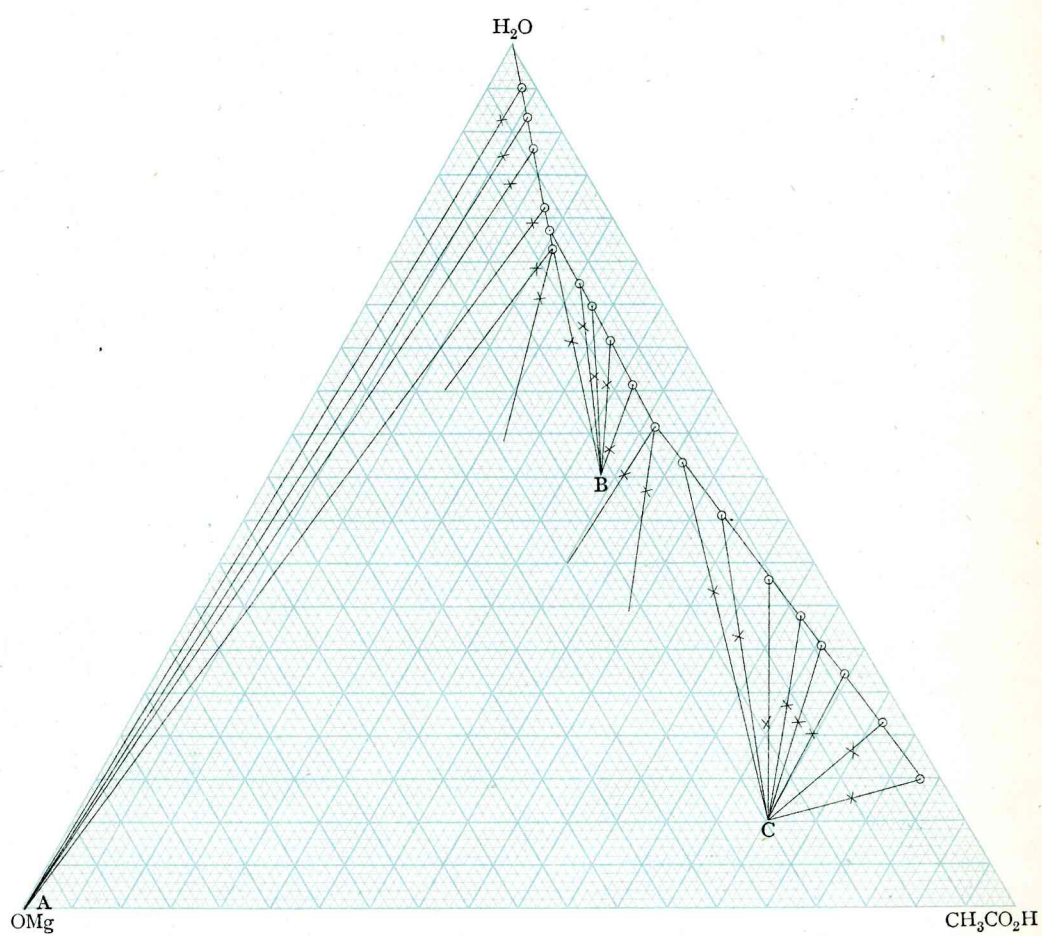| No	Solution.			Residue, wet with the solution			Residue.
	CH_3CO_2H	$(CH_3CO_2)_2Ba$	H_2O	CH_3CO_2H	$(CH_3CO_2)_2Ba$	H_2O	
1	0	5·18	94·80	—	—	—	$(CH_3CO_2)_2Ba.3H_2O$.
2	0·41	5·21	94·36	0·30	24·11	75·59	„
3	1·40	5·34	93·22	1·22	21·94	76·84	$(CH_3CO_2)Ba.3H_2O$, $3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$.
4	1·46	5·32	63·22	7 87	15 89	76 23	$3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$.
5	2·42	4·03	93·56	6 96	7·36	85·69	„
6	3·30	3·48	93·22	9 81	9 85	80·35	„
7	5 61	3·04	91·35	7·56	5·38	87·12	„
8	10 23	3·14	86·64	14·04	10·40	75·56	„
9	16 92	3·24	79·84	17·46	12·77	69 68	„
10	20 60	3·62	75·77	18·77	14·19	67·04	„
11	26·48	4·41	69·10	21 04	12·11	66 86	„
12	28·72	4·52	66·77	19 87	15·12	64 95	„
13	33·14	5·23	61 62	20 67	15·30	64·04	„
14	36·54	5.60	57·86	23·18	14 00	62·82	„
15	42 08	7·85	50 05	24·87	14 52	66·60	„
16	45·28	8·82	45·93	25 95	14·90	59·14	„
17	46 51	8·87	44·61	30·85	16 19	52 93	$3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$, $(CH_3CO_2)_2Ba.2CH_3CO_2H$
18	46·50	8 97	44·52	38·30	14·68	47 02	$(CH_3CO_2)_2Ba.2CH_3CO_2H$
19	46 49	9·10	44·40	51·78	15·49	32·71	„
20	51·98	8·62	39 37	53·96	13·71	32·32	„
21	58·35	8·72	32 93	59·94	12·54	27·53	„
22	65·77	8·40	25·80	65 66	10·31	24·02	„
23	71·34	8·25	20 41	69·83	15·85	14·32	„
24	77·06	7 79	15·14	75·06	12·47	12·47	„
25	85·27	7·36	7·39	90·46	14·00	5·53	„

II. The System: Magnesium Oxide, Acetic Acid and Water.

The materials used were magnesium · oxide (magnesia usta), acetic acid and water, in some cases magnesium acetate instead of magnesium oxide was used. The experiments were carried out as in the case of barium, except that the rotation in the thermostat was continued for at least two days instead of one. The solution was freed from the residue by a centrifugal filter apparatus. Acetic acid was determined by distillation in the same way as before, and magnesium as the pyrophosphate in the usual way. The results are given in Table 5.
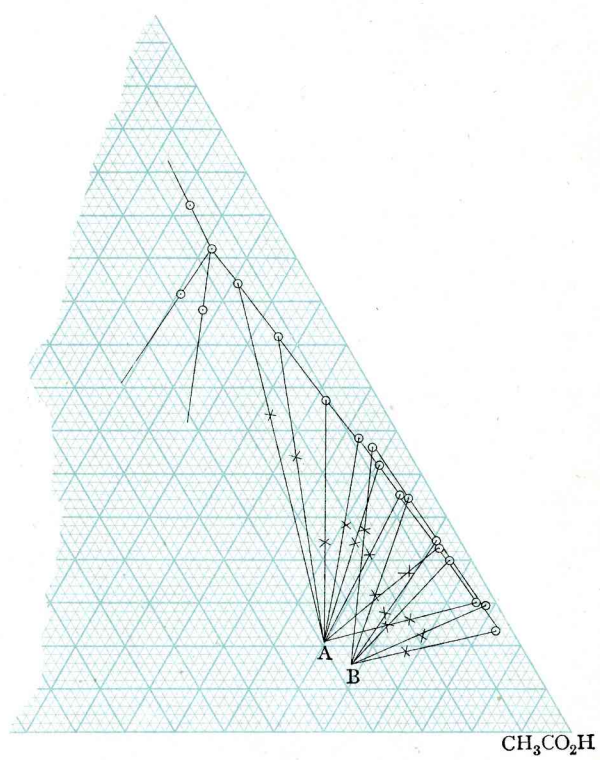
TABLE V.

No.	Solution.			Residue, wet with the solution.			Residue.
	CH_3CO_2H	OMg	H_2O	CH_3CO_2H	OMg	H_2O	
1	3·36	1·73	94·91	3·32	5·53	91·14	OMg
2	5·65	2·93	91·41	5·35	7·66	86 99	„
3	8·06	4·21	87·73	7·80	8·43	83·77	„
4	12·46	6 54	80 99	12·23	8·50	79·27	„
5	15·46	8·24	76·30	15·09	10 92	73 99	{OMg; {$(CH_3CO_2)_2Mg.4H_2O$,
6	15·38	8·31	76·30	17·29	12·20	70·49	$(CH_3CO_2)_2Mg$ $4H_2O$.
7	14·25	7·24	78·51	22·85	11·76	65·39	„
8	20·19	7·47	72·32	23·14	9·63	67·22	„
9	22·93	7·60	69·47	26·93	11·37	61·69	„
10	26·61	7·74	65·65	28·69	10·71	60 61	„
11	31·37	7·99	60·64	32·51	14·20	53·29	„
12	36·23	8·18	55·59	35·80	14·06	50·13	{$(CH_3CO_2)_2Mg$ $4H_2O$; {$2(CH_3CO_2)_2Mg.3CH_3CO_2H.3H_2O$.
13	35·77	8·17	56·06	38·93	12·88	48·18	$2(CH_3CO_2)_2Mg.3CH_3CO^2H.3H_2O$.
14	40·87	7·42	51·71	51·31	11 95	36·74	„
15	47·86	6·74	45·39	56·30	12·00	31·71	„
16	56·16	5·81	38·04	64·28	14·21	21·53	„
17	61·59	4·68	33·75	65·25	11.13	23·64	„
18	65·19	4·36	30·46	67·41	11·11	21 48	„
19	69·13	3·75	27·11	69·26	10 60	20·15	„
20	75·93	2·85	21·21	74·64	7·32	18·02	„
21	82·90	2·23	14·87	77·14	10 04	12·81	„

Fig. 3.

A.   OMg.
B. $(CH_3CO_2)_2$ Mg. $4H_2O$.
C. $2(CH_3CO_2)_2$ Mg. CH_3CO_2H. $3H_2O$.

Fig. 4.

A. $2(CH_3CO_2)_2$ Mg. $3CH_3CO_2H$. $3H_2O$.

B. $5(CH_3CO_2)_2$ Mg. $10CH_3CO_2H$. $7H_2O$.

The data in Table 5 are graphically iepresented in Fig. 3, referring to triangular cooidinates; and the chemical formulas of the residues, estimated from the figure in the usual way, are given in the last column of the table.

The normal salt with four molecules of water of crystallization is one well known in the liteiature of the subject.

No acid salt has yet been described in the literature. When magnesium acetate was dissolved in hot acetic acid and shaken in a thermostat at $25 \cdot 0°$ for .several days, an acid salt crystallised out. Again, magnesium oxide was dissolved in glacial acetic acid, the solution was evaporated to a certain extent; and when the cooled solution was rubbed by a glass rod against the side of the vessel, the syrupy solution solidified to a mass, due to the formation of an acid salt. Thus having obtained some evidence of the existence of an acid salt, a systematic study for it was undertaken; and the results are to be found in Table 5. The composition of the acid salt was estimated graphically to be $2(CH_3CO_2)_2Mg.3CH_3CO_2H.3H_2O$. It is a precipitate of microscopic rhombic plates.

When the experiments were nearly closed, another kind of acid salt was found from a solution in concentrated acetic acid. The crystalline form was almost like that of the other. The expeiimental data for that acid salt are given in Table 6.

TABLE 6.

No	Solution.			Residue, wet with the solution.			Residue.
	CH_3CO_2H	OMg	H_2O	CH_3CO_2H	OMg	H_2O	
1	63·50	3 91	32·59	67·38	9 49	23·12	$5(CH_3CO_2)_2Mg.10CH_3CO_2H.7H_2O$
2	70 09	3·17	26·73	72·23	12·19	15·59	,,
3	75·39	2·87	21·73	74·32	12·31	13·39	,,
4	77·84	2·83	19·33	74·91	12 66	12·45	,,
5	84·05	1·61	14·35	79·53	9 77	10·65	,,
6	86·50	2·19	11·31	78·72	12·46	8·82	,,

These data together with those in Table 5 relating to the acid salt are graphically represented in Fig. 4. The new data led to the formula $5(CH_3CO_2)_2Mg.10CH_3CO_2H.7H_2O$. This was almost always produced from solutions in concentrated acetic acid and the other from such
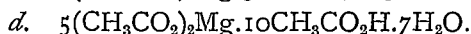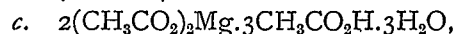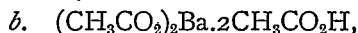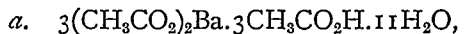
solutions only when induced by the presence of the same kind of crystals. These facts, together with the relative position of the solubility curves, seem to evidence that the heptahydrated acid salt is a stable one at least in concentrated acetic acid solutions; but time did not allow further study of the acid salts.

Lastly, as to the basic salt; the problem has been studied by Kubel.[1] From very slight differences in the density of solutions differently treated, he concluded that there exits an insoluble basic salt. His method of investigation and his conclusion, however, seem to me not free from objections.

In the present investigation the existence of the basic salt was sought by adding acetic acid in different proportions to mixtures of magnesium oxide and water. The mixtures were boiled for ten minutes and then rotated in a thermostat for more than two days. The solutions being syrupy, the separation of the residue from the mother liquor was very difficult; and, since the solution and the wet residue were very like in composition, it was almost impossible to estimate graphically the composition of the residue. But the residue was only the oxide, and there was no sign of the existrence of any basic salt in a solid state.

Summary.

1. The equilibrium of the systems: barium oxide, acetic acid and water, and magnesium oxide (magnesia usta), acetic acid and water, has been studied at $25 \cdot 0°$.

2. The following acid salts, hitherto unknown, have been found:

$a.$ $3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O,$
$b.$ $(CH_3CO_2)_2Ba.2CH_3CO_2H,$
$c.$ $2(CH_3CO_2)_2Mg.3CH_3CO_2H.3H_2O,$
$d.$ $5(CH_3CO_2)_2Mg.10CH_3CO_2H.7H_2O.$

3. The acid salts described by Villiers, as having the composition respectively of $(CH_3CO_2)_2Ba.CH_3CO_2H.4H_2O$ and $(CH_3CO_2)_2Ba.2CH_3CO_2H.2H_2O(?)$, seem to be nothing others than those here given.

4. No basic salt in a solid state exists in either case.

---

1 Arch. Pharm. [3] **230**, 173 (1892.)