138. *Acid Salts in Systems of the Type Monobasic Acid–Alkaline-earth Salt–Water.*

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IN continuation of earlier work from this laboratory (Sandved, J., 1927, 2967), a number of ternary systems of the type described in the title have been studied. Some corresponding binary systems (*i.e.*, acid + salt) have been systematically examined by Kendall and his collaborators, who found that the tendency of a given acid to form anhydrous acid salts diminished as the electropositive character of the metal in the salt became less marked. With the introduction of water as a third component, the conditions governing the formation and stability of acid salts naturally become more complex, and the present investigation is a contribution to the experimental exploration of these conditions. Reference should be made in this connexion to a recent paper by Ross and Morrison (J., 1933, 1016), who review earlier work and present an experimental study of the systems mandelic acid–metal mandelate–water.

EXPERIMENTAL.

The procedure followed was that customary in phase-rule studies of ternary systems, involving the attainment of equilibrium at a constant temperature (25° + 0·01°) and the subsequent analysis of the saturated solution and the corresponding wet solid. From the data so obtained graphical methods, as shown by Schreinemakers, gave not only the course of the saturation curves but also the composition of the corresponding solid phases.

The materials used were the best obtainable commercially and were further purified when considered necessary. Many of the salts were prepared from the pure acid and the hydroxide or carbonate of the base. For the determination of acidity, carefully standardised baryta solution was employed, and appropriate gravimetric methods were used for the estimation of the metals, except occasionally in the case of calcium. All percentage compositions quoted in the tables and diagrams below refer to 100 g. of mixture.

Results.

A. *Systems in which Formic Acid is the Acid Constituent.*—(1) *Formic acid–barium formate–water.* The saturated solution of barium formate in water at 25° contains 23·51 g. of anhydrous salt per 100 g. of the solution, in agreement with the value interpolated from Stanley's results (*Chem. News*, 1904, **89**, 193). According to Krasnicki (*Sitzungsber. K. Akad. Wiss. Wien*, 1887, **96**, 736), barium formate crystallises from water as the dihydrate, but no evidence of this was found in the present investigation. The experimental data in Table I—set out graphically in Fig. 1*—show that the solid phase in equilibrium with saturated solutions containing up to about 20% of formic acid is the anhydrous salt.

FIG. 1.

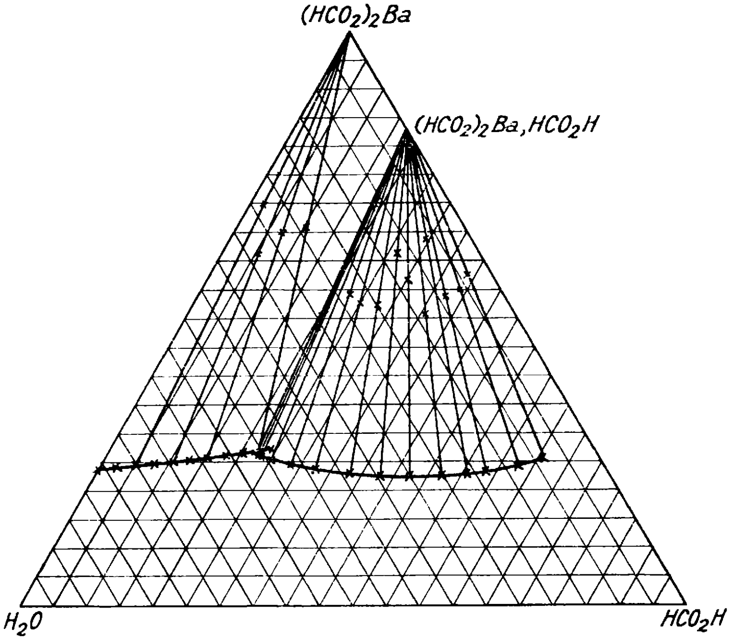

TABLE I.

Saturated solution.		Moist solid.		
$H\cdot CO_2H$.	$Ba(HCO_2)_2$.	$H\cdot CO_2H$.	$Ba(HCO_2)_2$.	Solid phase.
0·00	23·51	—	—	$(H\cdot CO_2)_2Ba$
5·39	24·25	2·16	69·8	,,
10·57	25·03	5·46	61·2	,,
15·41	25·72	7·27	64·9	,,
22·43	26·87	10·50	65·9	,,
23·38	26·09	20·45	51·7	$(H\cdot CO_2)_2Ba,H\cdot CO_2H$
28·49	24·71	22·62	54·3	,,
38·07	23·11	27·77	52·5	,,
47·5	22·56	30·16	56·9	,,
58·4	23·45	37·34	54·0	,,
65·8	25·72	38·7	57·7	,,

The acid salt $H\cdot CO_2H,Ba(H\cdot CO_2)_2$, recorded by Kendall and Adler (*J. Amer. Chem. Soc.*, 1921, **43**, 1474) in their investigation of the binary system acid + salt, is now shown to be the stable solid phase in contact with solutions containing as much as 50% of water. It can be obtained in well-formed crystals which, if exposed to air, lose half their acid content in about 8 days.

The composition of the solution at the point where the two saturation curves intersect is

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* This figure, as also some of the later ones, includes results which, from considerations of space, have been omitted from the tables.

21·8% $H{\cdot}CO_2H$, 26·7% $Ba(H{\cdot}CO_2)_2$, 51·5% H_2O. Metastable conditions were realised in one case, where the anhydrous salt was the solid phase in a solution containing 24·5% $H{\cdot}CO_2H$. Extrapolation of the saturation curve for the acid salt to the adjacent side of the triangle in Fig. 1 indicates a value for the point of section in agreement with Kendall and Adler's measurements (*loc. cit.*, p. 1476).

(2) *Formic acid–strontium formate–water.*—The saturated solution of strontium formate in water at 25°—the dihydrate being the solid phase—contains 12·52 g. of the anhydrous salt per 100 g. of solution, in agreement with the value interpolated from Stanley's measurements (*loc. cit.*).* The results for the ternary system are set out in Table II and Fig. 2.

Fig. 2.

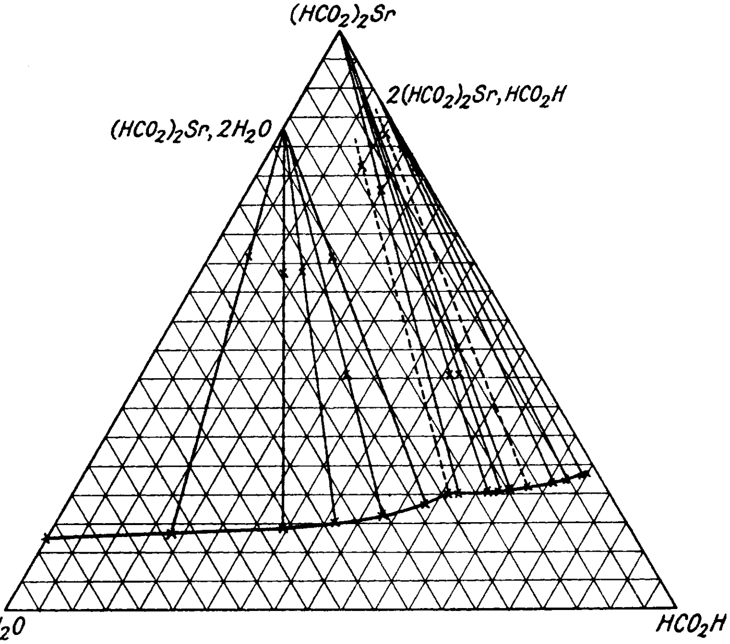

Table II.

Saturated solution.		Moist solid.		
$H{\cdot}CO_2H$.	$Sr(H{\cdot}CO_2)_2$.	$H{\cdot}CO_2H$.	$Sr(H{\cdot}CO_2)_2$.	Solid phase.
0·00	12·52	—	—	$(H{\cdot}CO_2)_2Sr,2H_2O$
18·01	13·30	5·75	61·2	,,
34·24	14·17	12·51	58·4	,,
41·5	15·28	15·18	58·8	,,
48·0	16·40	30·52	40·8	,,
53·4	18·27	18·59	61·2	,,
57·3	20·07	19·80	72·8	$(H{\cdot}CO_2)_2Sr$
61·5	20·51	45·9	40·7	,,
63·3	20·74	47·3	40·7	,,
64·7	20·94	44·8	45·3	,,
70·5	22·04	19·38	79·8	$2(H{\cdot}CO_2)_2Sr,H{\cdot}CO_2H$
72·3	22·54	20·49	78·7	,,
74·3	23·03	23·06	76·6	,,

A first inspection of Fig. 2 would suggest that there are only two saturation curves, but careful examination of the wet solids showed clearly that there must be three, though the point of intersection of two of these [estimated to be at 68·7% $H{\cdot}CO_2H$, 21·3% $Sr(H{\cdot}CO_2)_2$, and 10·0% H_2O] is not very definite. The dihydrate, the anhydrous salt, and the acid salt, $H{\cdot}CO_2H,2Sr(H{\cdot}CO_2)_2$, are the solid phases successively in equilibrium with solutions of diminish-

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* The figures given for the solubility in Stanley's paper are in error, and were recalculated from his analytical data.

ing water content. The composition of the solution which is in equilibrium with both dihydrate and anhydrous salt is 55·9% $H{\cdot}CO_2H$, 20·0% $Sr(H{\cdot}CO_2)_2$, and 24·1% H_2O.

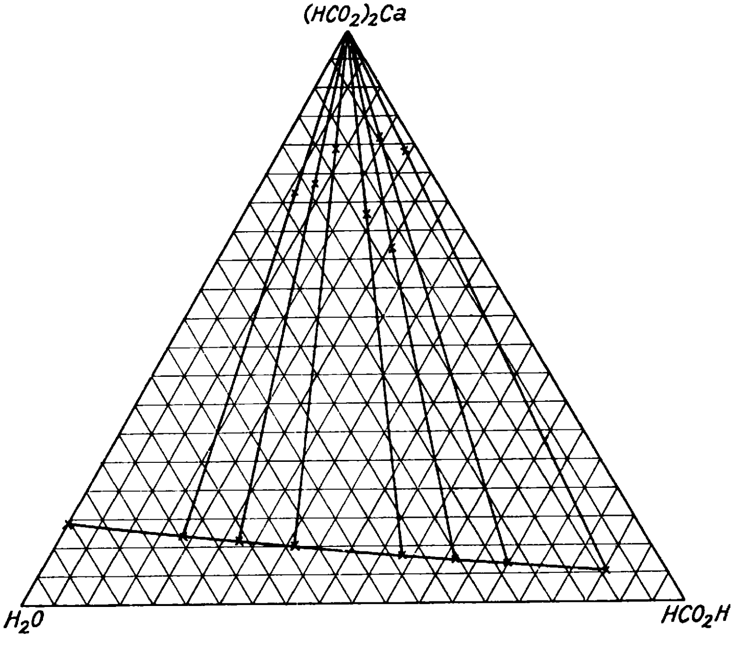
(3) *Formic acid–calcium formate–water.* The calcium formate in the solutions of this system was estimated by evaporation and subsequent drying at a gentle heat. Special experiments showed that this method was accurate. The weighed wet solids were dissolved in excess water, and an aliquot portion of the resulting solution was taken for the estimation of the calcium formate content.

The value obtained for the solubility of calcium formate in water at 25°—**14·43** g. of anhydrous salt per 100 g. of saturated solution—is in good agreement with those interpolated from the results of Lumsden (J., 1902, **81**, 355) and of Krasnicki (*loc. cit.*). As appears from the data set out in Table III and Fig. 3, anhydrous calcium formate is the only stable solid phase throughout the whole range of solutions investigated, *i.e.*, up to 90% formic acid content.

TABLE III.

Saturated solution.		Moist solid.		
$H{\cdot}CO_2H$.	$Ca(H{\cdot}CO_2)_2$.	$H{\cdot}CO_2H$.	$Ca(H{\cdot}CO_2)_2$.	Solid phase.
0·00	14·43	—	—	$(H{\cdot}CO_2)_2Ca$
18·48	12·11	5·97	71·8	,,
27·41	11·16	8·33	73·2	,,
36·31	10·20	8·41	79·2	,,
53·3	8·42	18·74	67·9	,,
61·6	7·60	25·55	61·9	,,
69·9	6·86	14·15	81·1	,,
85·4	5·43	19·16	78·7	,,

FIG. 3.



(4) *Formic acid–magnesium formate–water.* In contrast with the behaviour of the barium and strontium salts, but in agreement with that of calcium formate, the solubility of magnesium formate in water is lowered by the addition of formic acid. The saturated solution of magnesium formate in water at 25°—the dihydrate being the solid phase—contains 12·23 g. of anhydrous salt per 100 g. of solution. As shown by the data of Table IV and the graphical representation of Fig. 4, there is only one saturation curve and one stable solid phase, the dihydrate, over the range of solutions investigated, which extended to over 90% formic acid content. It is clear from this that magnesium formate must have a considerable affinity for

water. Indeed, it was observed that if excess of the powdered anhydrous salt were stirred with 90% formic acid, the full quantity of water of crystallisation was taken up by the solid phase.

FIG. 4.

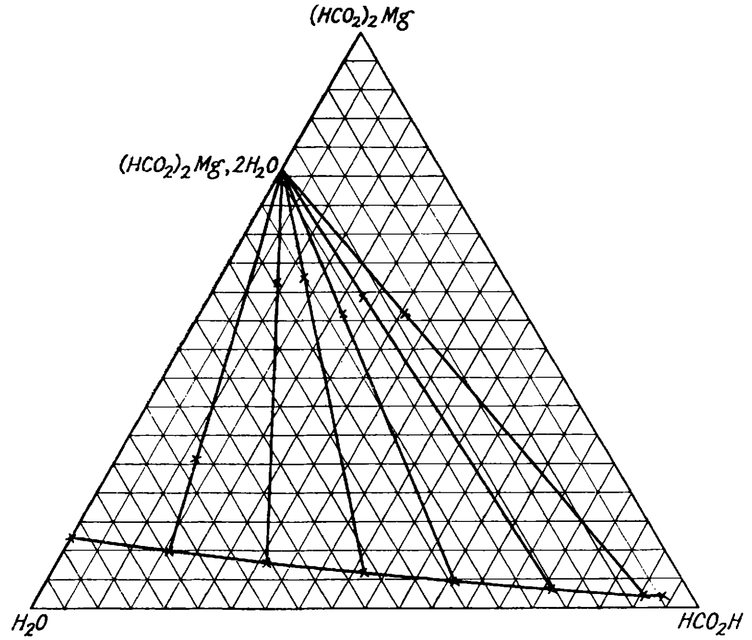


TABLE IV.

Saturated solution.		Moist solid.		
$H\cdot CO_2H$.	$Mg(H\cdot CO_2)_2$.	$H\cdot CO_2H$.	$Mg(H\cdot CO_2)_2$.	Solid phase.
0·00	12·23	—	—	$(H\cdot CO_2)_2Mg,2H_2O$
15·73	10·10	12·09	25·77	,,
31·28	8·01	9·08	56·7	,,
46·7	6·22	12·47	57·6	,,
60·9	4·68	21·53	51·3	,,
76·2	3·19	22·84	54·3	,,
90·8	2·15	30·51	51·3	,,

B. *Systems in which Acetic Acid is the Acid Constituent.*—(1) *Acetic acid–barium acetate–water.* According to Iwaki (*Mem. Coll. Sci., Kyoto,* 1914, **1**, 81), the three solid phases successively in equilibrium with solutions of increasing acid content are $Ba(CH_3\cdot CO_2)_2,3H_2O$, $3Ba(CH_3\cdot CO_2)_2,3CH_3\cdot CO_2H,11H_2O$, and $Ba(CH_3\cdot CO_2)_2,2CH_3\cdot CO_2H$. (For the examination of the binary system barium acetate–acetic acid, see Davidson and McAllister, *J. Amer. Chem. Soc.,* 1930, **52**, 514.)

The present investigation of this system was limited to a confirmation of the hydrated acid salt recorded by Iwaki; the results obtained were in better agreement with his formulation than with the simpler $Ba(CH_3\cdot CO_2)_2,CH_3\cdot CO_2H,4H_2O$. The latter requires 65·9% salt, 15·5% acid, and 18·6% water, while Schreinemakers's method applied to the experimental data indicates a solid phase containing 66·7% salt, 15·9% acid, and 17·4% water, much closer to the composition of Iwaki's compound.

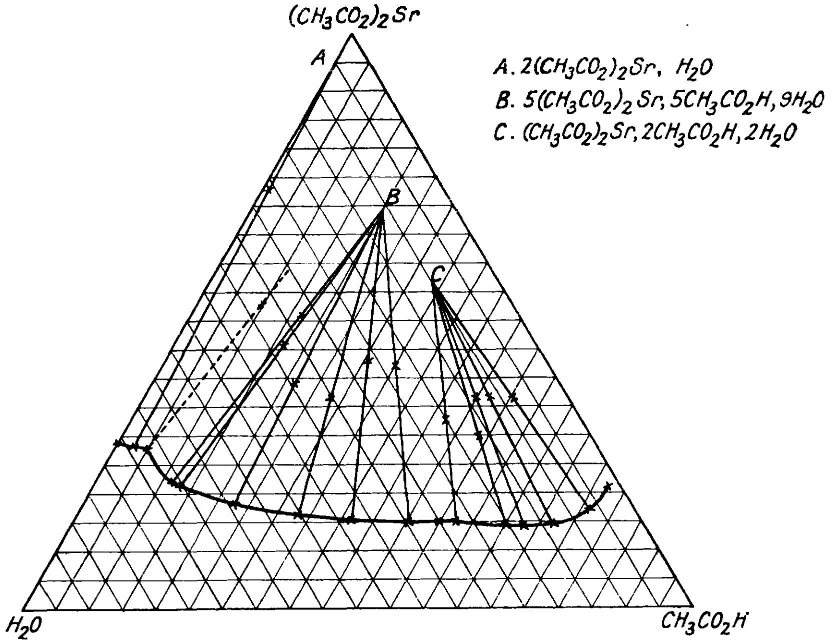
(2) *Acetic acid–strontium acetate–water.* The saturated solution of strontium acetate in water at 25°, the solid phase being $2Sr(CH_3\cdot CO_2)_2,H_2O$, was found to contain 28·79 g. of anhydrous salt per 100 g. of solution, in good agreement with Osaka and Abe (*Mem. Coll. Eng., Kyoto,* 1911—12, **3**, 51). The experimental data for the ternary system are set out in Table V and the corresponding graphical representation in Fig. 5.

The solid phases successively in equilibrium with solutions of increasing acid content are $2Sr(CH_3\cdot CO_2)_2,H_2O$, $5Sr(CH_3\cdot CO_2)_2,5CH_3\cdot CO_2H,9H_2O$, and $Sr(CH_3\cdot CO_2)_2,2CH_3\cdot CO_2H,2H_2O$. The formulation of the second of these phases was deduced by careful graphical treatment of

TABLE V.

Saturated solution.		Moist solid.		
$CH_3 \cdot CO_2H$.	$Sr(CH_3 \cdot CO_2)_2$.	$CH_3 \cdot CO_2H$.	$Sr(CH_3 \cdot CO_2)_2$.	Solid phase.
0·00	28·79	—	—	$2(CH_3 \cdot CO_2)_2Sr,H_2O$
2·75	28·20	0·97	73·0	,,
11·62	22·09	16·57	51·0	$5(CH_3 \cdot CO_2)_2Sr,5CH_3 \cdot CO_2H,9H_2O$
22·63	18·27	21·49	39·22	,,
33·10	16·49	28·09	36·52	,,
41·6	15·56	30·44	43·1	,,
50·4	15·21	34·97	42·2	,,
57·3	15·25	47·4	32·64	$(CH_3 \cdot CO_2)_2Sr,2CH_3 \cdot CO_2H,2H_2O$
65·2	14·32	53·6	29·77	,,
71·9	14·42	51·9	36·75	,,
76·1	16·90	55·5	36·54	,,

FIG. 5.



the data on large-scale co-ordinate paper, and is definitely in better agreement with these data than the simpler, and not very different, formula $Sr(CH_3 \cdot CO_2)_2,CH_3 \cdot CO_2H,2H_2O$ (see Villiers, *Compt. rend.*, 1877, **85**, 1234). The second acid salt, $Sr(CH_3 \cdot CO_2)_2,2CH_3 \cdot CO_2H,2H_2O$, has not been described previously. Both acid salts are produced in well-formed crystals from acetic acid solutions of appropriate concentration, but lose acid rapidly when removed from their mother-liquors and exposed to air.

It is obvious that, in addition to the saturation curves shown in Fig. 5, there must be a fourth, corresponding with either anhydrous strontium acetate or an anhydrous acid salt as the solid phase. This fourth saturation curve must be very short, since the compound $Sr(CH_3 \cdot CO_2)_2,2CH_3 \cdot CO_2H,2H_2O$ was shown to be the stable solid phase even in a solution containing only 7% water. The separation and identification of the solid phase from still more concentrated acid solutions presented considerable difficulties and could not be satisfactorily achieved.

(3) *Acetic acid–calcium acetate–water.* The saturated solution of calcium acetate in water at 25°—the solid phase being $Ca(CH_3 \cdot CO_2)_2,H_2O$—was found to contain 26·10 g. of anhydrous salt per 100 g. of solution. Lumsden (J., 1902, **81**, 355) found the value 25·5, with the dihydrate as the solid phase.

The experimental data for the ternary system * are set out in Table VI, and the corresponding

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* This system had already been studied in this laboratory by Miss J. L. Philip and the data in Table VI are mainly her results.

graphical representation in Fig. 6. Apart from the short saturation curve for the hydrate of calcium acetate, there is an extensive saturation curve corresponding to the hydrated acid salt $Ca(CH_3{\cdot}CO_2)_2,CH_3{\cdot}CO_2H,H_2O$ as the stable solid phase—a compound already recorded by Villiers (*loc. cit.*, p. 756). The composition of the solution saturated with both the hydrated calcium acetate and the hydrated double salt is 7·6% acetic acid, 25·1% calcium acetate, and 67·3% water.

FIG. 6.

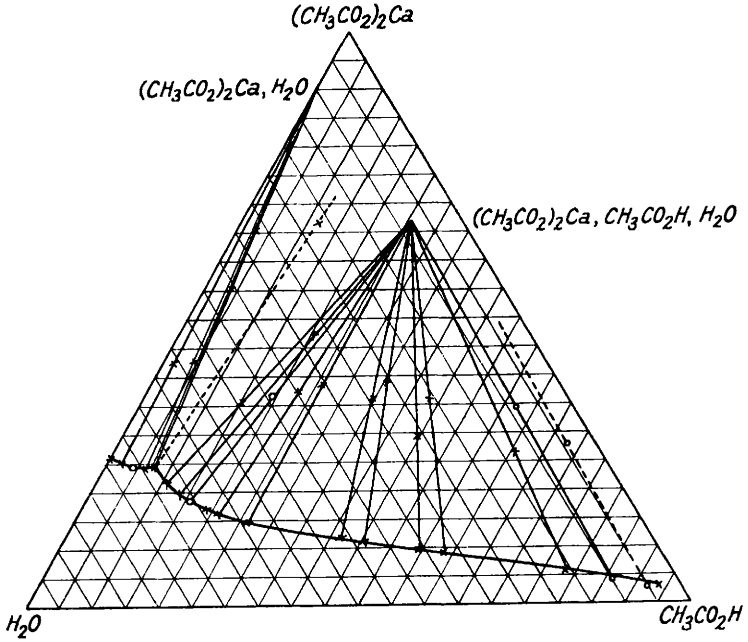

TABLE VI.

Saturated solution.		Moist solid.		
$CH_3{\cdot}CO_2H$.	$Ca(CH_3{\cdot}CO_2)_2$.	$CH_3{\cdot}CO_2H$.	$Ca(CH_3{\cdot}CO_2)_2$.	Solid phase.
0·00	26·10	—	—	$(CH_3{\cdot}CO_2)_2Ca,H_2O$
2·1	25·4	1·5	42·6	,,
6·4	24·3	4·6	42·8	,,
7·5	24·7	4·0	55·3	,,
10·8	21·7	15·2	35·5	$(CH_3{\cdot}CO_2)_2Ca,CH_3{\cdot}CO_2H,H_2O$
15·75	18·73	19·36	36·58	,,
26·3	14·7	25·9	38·5	,,
41·6	11·7	34·45	36·2	,,
58·6	9·2	43·15	36·0	,,
78·4	6·0	60·5	26·5	,,
86·2	4·12	57·3	34·21	,,

Accurate investigation of the solid phase in equilibrium with solutions containing over 90% acetic acid is not possible, but somewhere in that region the saturation curve for the hydrated acid salt must be cut by another curve corresponding presumably with the compound $Ca(CH_3{\cdot}CO_2)_2,CH_3{\cdot}CO_2H$ as solid phase, the existence of this compound having been established by a study of the binary system calcium acetate–acetic acid (Davidson and McAllister, *loc. cit.*). As shown by these authors, the solubility of calcium acetate in anhydrous acid at 25° is extremely small.

(4) *Acetic acid–magnesium acetate–water.* This system has been examined by Iwaki (*loc. cit.*), whose results pointed to the existence of the double salts $2Mg(CH_3{\cdot}CO_2)_2,3CH_3{\cdot}CO_2H,3H_2O$ and $5Mg(CH_3{\cdot}CO_2)_2,10CH_3{\cdot}CO_2H,7H_2O$. Satisfactory quantitative results are, however, not easily obtained because of the exceptional viscosity of the solutions (compare Rivett, J., 1926, 1065) and the difficulty of securing an adequate separation of the solid phase.

C. *Systems in which Benzenesulphonic Acid is the Acid Constituent.*—The four ternary systems of this type which have been examined—containing the barium, strontium, calcium, and magnesium salt respectively—are remarkably similar. In all cases there is only one saturation curve within the range of concentrations used (up to about 50% acid), and this curve corresponds in each case with a hydrate of the salt as the solid phase—the same hydrate as is in equilibrium with the saturated aqueous solution in the absence of acid. The solubility of the salt in all four cases is rapidly reduced with progressive increase of the acid concentration until, in 50% acid solution, the solubility is exceedingly small. This will be evident on inspection of the experimental data set out in Table VII, and of Fig. 7. This figure, which is the graphical representation of the data for the barium salt, will serve as typical of the other cases in which benzenesulphonic acid is the acid constituent. It is clear that in none of these cases is there any tendency to form acid salts—a result in harmony with the observations of Bassett and Taylor on the system $Ca(NO_3)_2$–HNO_3–H_2O (J., 1912, **101**, 581).

Fig. 7.

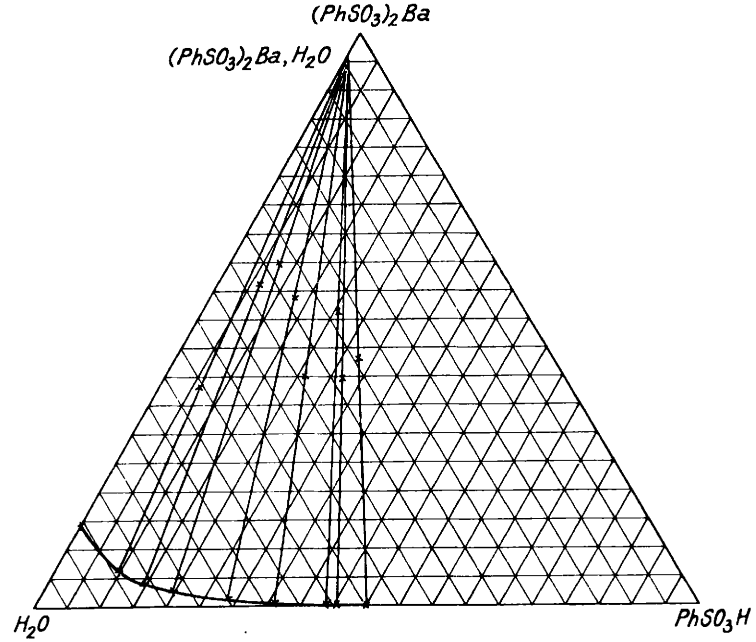

TABLE VII.

Saturated solution.		Moist solid.		Saturated solution.		Moist solid.	
$Ph{\cdot}SO_3H$.	$Ba(Ph{\cdot}SO_3)_2$.	$Ph{\cdot}SO_3H$.	$Ba(Ph{\cdot}SO_3)_2$.	$Ph{\cdot}SO_3H$.	$Sr(Ph{\cdot}SO_3)_2$.	$Ph{\cdot}SO_3H$.	$Sr(Ph{\cdot}SO_3)_2$.
0·00	14·33	—	—	0·00	15·37	—	—
9·71	6·20	6·24	38·2	7·93	8·51	6·38	26·43
14·60	3·92	6·35	56·2	10·56	6·43	8·90	22·84
19·62	2·65	7·56	59·8	14·12	5·10	10·59	28·66
28·67	1·10	12·97	53·8	19·29	3·26	17·10	13·79
35·96	0·37	21·21	40·2	28·49	2·39	19·02	33·71
43·8	0·23	20·64	51·6	41·8	0·31	29·32	28·09
50·0	0·12	27·61	43·4	44·7	0·16	38·84	12·67
				49·6	0·07	43·0	12·59
$Ph{\cdot}SO_3H$.	$Ca(Ph{\cdot}SO_3)_2$.	$Ph{\cdot}SO_3H$.	$Ca(Ph{\cdot}SO_3)_2$.	$Ph{\cdot}SO_3H$.	$Mg(Ph{\cdot}SO_3)_2$.	$Ph{\cdot}SO_3H$.	$Mg(Ph{\cdot}SO_3)_2$.
0·00	28·07	—	—	0·00	8·26	—	—
15·01	15·78	—	—	5·27	5·41	—	—
27·30	8·18	18·03	37·32	13·88	2·36	—	—
36·12	4·09	25·13	31·04	16·78	2·02	6·15	50·3
37·33	3·48	26·26	30·33	28·81	2·01	10·28	51·1
64·00	0·07	—	—	40·2	1·20	—	—
				47·0	0·92	29·18	30·29
				62·5	0·14	—	—

With the barium, strontium, and calcium benzenesulphonates the stable solid phase was the monohydrate in each case, although for the strontium salt the application of Schreinemakers's method to the data for the most dilute acid solutions left a little doubt as to whether the solid phase was the monohydrate or the anhydrous salt. The data for the more concentrated acid solutions, however, pointed quite definitely to the monohydrate as the stable solid phase at 25°. With the magnesium salt the evidence is on the whole in favour of the hexahydrate being the stable solid phase, although the results obtained by Schreinemakers's method indicated a hydrate of somewhat lower water content.

DISCUSSION.

The present paper is mainly a record of experimental work, and accordingly attention will be directed only to certain general relationships which have emerged. A comprehensive theoretical treatment of this field cannot profitably be undertaken until many more data are available.

A comparison of the three acids which have been employed shows that with acetic acid there is extensive formation of acid salts, with formic acid this tendency is much less, and with benzenesulphonic acid it appears to be entirely absent (cf. Bassett and Taylor, *loc. cit.*). It is noteworthy also that the concentration of acid required to permit the formation of an acid barium salt is distinctly smaller with acetic acid (4%) than with formic acid (22%).*

So far as the different metals are concerned, it would appear that the tendency to form acid salts falls off in the order barium, strontium, calcium : this at least is the case with formic acid. A barium acid formate is stable in a solution containing a minimum of 22% acid, the strontium acid formate is not stable below about 68% acid, while no calcium acid salt is formed even in an 85% formic acid solution. The position with acetic acid, however, is not so clear cut.

It has often been remarked that an increase in the solubility of a salt on the addition of the corresponding acid foreshadows a change in the solid phase. This rule is verified in the case of barium and strontium formates; further, the definite *decrease* of solubility observed with calcium and magnesium formates, and, more strikingly, with all the benzenesulphonates, in none of which cases has any change of solid phase been observed, is noteworthy. With acetic acid, however, there is a decrease of solubility of the alkaline-earth salt on the first addition of acid, and yet in the majority of cases an acid salt is formed on further addition : this appears from Tables V and VI and Figs. 5 and 6 (see also Sandved, *loc. cit.*; Iwaki, *loc. cit.*).

SUMMARY.

The equilibria prevailing at 25° in systems of the type monobasic acid–alkaline-earth salt–water have been determined experimentally with formic, acetic, and benzenesulphonic acids, the compositions of the solid phases present being deduced by Schreinemakers's method.

Of the three acids examined, acetic acid exhibits the greatest, and benzenesulphonic acid the least, tendency to the formation of acid salts. For a given acid, barium appears to form acid salts most readily, followed in order by strontium and calcium.

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