

is  $7.1 \times 10^{-4}$ . The Joule-Thomson coefficient itself at 1 atmosphere as given by Vogel and Noell is  $0.277^\circ$  and from Bradley's work  $0.268^\circ$ . The equation gives  $0.261^\circ$ .

4. An explanation of the discrepancies in the observed Joule-Thomson numbers is suggested which assumes that at the low-pressure surface of the plug a temperature drop is superposed on the Joule-Thomson temperature change due to the momentary persistence of the fine gas streams issuing from the pores of the plug and their subsequent expansion. It is shown that this effect would produce a large apparent pressure coefficient since the specific effect of the velocity-persistence-effect is shown to vary inversely as the pressure. The value of the measured Joule-Thomson effect at  $0^\circ$  and one atmosphere pressure is given as  $0.303$  by Hoxton, while that deduced from the high-pressure measurements of Bradley and Hale is  $0.268$ , as compared with  $0.261$  calculated by the equation of state.

5. The Joly constant-volume specific heats of air are considered, and it is shown that a correction is required to compensate for the increased specific heat of the copper sphere used by Joly to contain the air. The corrected Joly values are shown to be independent of pressure, which fact confirms the validity of the form of the air equation of state employed. As a further consequence, it is pointed out that at low pressures the Joule-Thomson effect must vary inversely with the absolute temperature. Another important consequence is that the constant-volume air-thermometer scale reads directly on the absolute scale and therefore requires no correction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 363.]

## COMPOUND FORMATION AND SOLUBILITY IN SYSTEMS OF THE TYPE, FORMIC ACID:METAL FORMATE.

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The experimental work presented in the following pages has been carried out with the object of determining how far the conclusions arrived at in a similar study of systems of the type sulfuric acid: metal sulfate<sup>1</sup> may be considered as generally valid for systems HX : RX. In order to make the test as rigorous as possible, a careful selection of an acid diverse in all properties from sulfuric acid was necessary. Formic acid was finally chosen as a typical weak monobasic organic acid, contrasting strikingly with sulfuric acid, a typical strong dibasic inorganic acid. It

<sup>1</sup> Kendall and Landon, *THIS JOURNAL*, **42**, 2131 (1920); Kendall and Davidson, *ibid.*, **43**, 979 (1921).

is true that a still weaker acid might have been selected to obtain a more extreme contrast, but when it is noted that previous investigations on systems of the type ROH : HOH already furnish us with considerable data for the case of an exceedingly weak acid, the desirability of choosing an example of an intermediate type (such as formic acid) to complete the field becomes obvious. The instability of the formates of the more noble metals prevents a full survey of the series being made, but against this disadvantage is to be placed the convenience of the melting points of formic acid and its derivatives, which facilitates the experimental procedure and allows the various systems to be investigated through much larger concentration ranges than would otherwise be possible.<sup>2</sup> Furthermore, careful determinations of the conductivities of several formates in formic acid have been made by Schlesinger<sup>3</sup> and his co-workers, providing material for the future correlation of the results here obtained with ionization relationships, the final object of this work.<sup>4</sup> Nevertheless, in order that no gaps should be left in the series, a few systems of the type acetic-acid: metal-acetate have also been included in this investigation.

Practically no previous work of value has been done upon acid formates and acetates. Although Groschuff<sup>5</sup> employed the freezing-point method to examine certain of the formates with formic acid, the majority of the results obtained by him are considerably in error. A few acid acetates have been reported in isolated investigations, usually of great age and of doubtful accuracy, but no systematic study such as is here attempted has hitherto been undertaken.

In the present work the following systems have been examined: (a) with formic acid; potassium, ammonium, sodium, lithium, barium, calcium, magnesium, zinc, nickel, lead and copper formates: (b) with acetic acid; sodium, calcium, zinc, ferric and silver acetates.

### Experimental.

The freezing-point method described in previous articles<sup>6</sup> has again been utilized for the determination of compound formation and solubility relationships. The work at lower temperatures was carried out

<sup>2</sup> With acids of lower melting point (*e. g.*, propionic acid), supercooling of the solutions would render the isolation of compounds much more uncertain. With acids of higher melting point (*e. g.*, benzoic acid), the curves could not be carried very far before decomposition of the material would prevent their continuance.

<sup>3</sup> Schlesinger, *et al.*, THIS JOURNAL, 33, 1924 (1911); 36, 1589 (1914); 38, 271 (1916); 41, 72, 1921 (1919).

<sup>4</sup> See Kendall, *Proc. Nat. Acad. Sci.*, 7, 56 (1921).

<sup>5</sup> Groschuff, *Ber.*, 36, 1783 (1903).

<sup>6</sup> For details of the experimental procedure and of the theoretical principles involved, these earlier papers should be consulted.

in a modified Beckmann apparatus, the work at higher temperatures in sealed bulbs.

The more accurate freezing-point tube method could be employed only for temperatures below 60°, owing to the volatility of the acids at higher temperatures. In the sealed bulbs the air space was made as small as possible to reduce concentration changes in the solutions due to this cause. Fortunately, secondary disturbing factors such as were met with in the case of the sulfates<sup>7</sup> were here absent, so that the curves could be carried to much higher concentrations of salt than was there found feasible. A limit was set in most cases, however, by the decomposition temperature of the acid or of the neutral salt.<sup>8</sup> Only for potassium and ammonium formates, which are stable beyond their relatively low melting points, could the determinations be extended right through the complete system.

Formic acid was prepared from a standard c. p. product by treatment with boron trioxide for the removal of final traces of water.<sup>9</sup> Distillation *in vacuo* under anhydrous conditions was continued until a product melting at over 8.4° was obtained.<sup>10</sup> Acetic acid melting at 16.5°+ was prepared by addition of acetic anhydride to glacial acid, as described by Kendall and Gross.<sup>11</sup> The preparation of the various metallic formates and acetates is given under their particular systems below.

Every possible precaution was taken to prevent entrance of moisture during determinations or contamination of materials with moisture before use. The extremely hygroscopic nature of certain of the salts restricted work on systems in which they formed one component to dry, cold days.

In some cases the compounds isolated were stable in the region of their melting points, and their compositions were consequently obtained immediately from the curves. When transition to another phase occurred before the melting point of a compound was approached, it was necessary to determine its composition by direct analysis. This was carried out as described by Kendall and Landon, the stability of the compounds being sufficient to permit air drying without appreciable decomposition.

The results for the various systems are presented in order below; the

<sup>7</sup> See Kendall and Davidson, *op. cit.*, Ref. 1, p. 980.

<sup>8</sup> The decomposition temperatures of the formates vary regularly with the position of the positive radical in the electromotive series, the salts of the most electropositive metals being the most stable. See Hofmann and Schibsted, *Ber.*, 51, 1398 (1918).

<sup>9</sup> The apparatus of Schlesinger and Martin (*THIS JOURNAL*, 36, 1589 (1914)) was employed and their procedure followed.

<sup>10</sup> The most recent values for the m. p. of the pure acid approximate to 8.5°; the highest value recorded is that of Schlesinger and Calvert (*THIS JOURNAL*, 33, 1924 (1911)), 8.6°.

<sup>11</sup> Kendall and Gross, *ibid.*, 43, 1426 (1921).

more interesting curves are also given in the accompanying diagrams. Compositions are expressed in molecular percentages throughout;  $T$  denotes the temperature of initial solidification.

### Results. (A) Formic Acid Systems.

**Potassium formate:Formic acid.**—The potassium salt was prepared by dissolving a pure sample of potassium carbonate in 90% formic acid. After all of the carbon dioxide had been expelled by heating, the hydrated salt was crystallized from the solution. This compound (which is exceedingly hygroscopic) was dried as completely as possible by prolonged heating just below its melting point; the last traces of moisture were removed by recrystallization from absolute ethyl alcohol and desiccation over 99% sulfuric acid *in vacuo*. The final product melted at  $167.5 \pm 0.5^\circ$ , which compares very favorably with the previously recorded value of Groschuff,<sup>12</sup>  $157^\circ$ .

#### (a) Solid phase H.COOH.

% H.COOK	0.0	0.97	3.02	4.73	6.36	8.43	10.74	12.63	13.88	15.57
$T$ .....	8.4	7.4	4.9	2.2	-0.9	-5.7	-12.6	-18.7	-23.8	-31.5

#### (b) Solid phase H. COOK, 3H.COOH (?).

% H.COOK.....	16.32	16.62	17.44	18.10	18.88
$T$ .....	-29.0	-27.3	-23.5	-21.7	-19.5

#### (c) Solid phase H.COOK, 2H.COOH.

% H.COOK.....	19.48	19.91	21.21	22.79
$T$ .....	-19.0	-16.0	-8.0	-0.6

#### (d) Solid phase H.COOK, H.COOH.

% H.COOK	23.04	24.14	25.98	28.56	30.41	31.97	33.74	37.29	38.34	
$T$ .. ..	-10.1	7.3	29.9	53.0	65.1	72.9	80.6	93.0	96.1	
% H.COOK	41.68	42.63	42.91	45.95	50.25	51.49	54.24	58.47	61.14	63.14
$T$ .....	103.2	104.3	104.6	107.5	108.6	108.2	107.2	103.4	100.6	98.7

#### (e) Solid phase H.COOK.

% H.COOK..	66.45	68.71	71.24	75.18	77.75	82.41	86.68	91.24	100.0
$T$ .....	108.1	114.5	122.3	130.7	135.8	143.6	150.0	157.3	167.5

The above results are reproduced graphically in Fig. 1. Three acid salts have been isolated, of which one (the equimolecular compound H.COOK, H.COOH) is stable right up to its melting point,  $108.6^\circ$ . This salt has been previously reported by Groschuff, but his statement that it undergoes transition before melting is obviously unjustified. The two remaining compounds have not been isolated before. Analysis of solid phase (c) gave an acid content of  $67.9 \pm 1.0$  mol. %, evidently corresponding to the compound H.COOK, 2H.COOH. Because of the low temperature ( $-17.5^\circ$ ) at which it undergoes transition, the composition of solid phase (b) could not be definitely determined. From the slope of the curve, however, the probable formula H.COOK, 3H.COOH is deduced.

**Ammonium Formate: Formic Acid.**—The ammonium salt was prepared by passing ammonia into 90% formic acid. Towards the end of the absorption, the temperature was raised sufficiently to ensure the deposition of the neutral (instead of the acid) salt. The product obtained was recrystallized from absolute alcohol and then desiccated over 99% sulfuric acid *in vacuo*. The melting point of the final material was  $117.3 \pm 0.2^\circ$ , that reported by Groschuff being  $116^\circ$ .

<sup>12</sup> Groschuff, *loc. cit.*

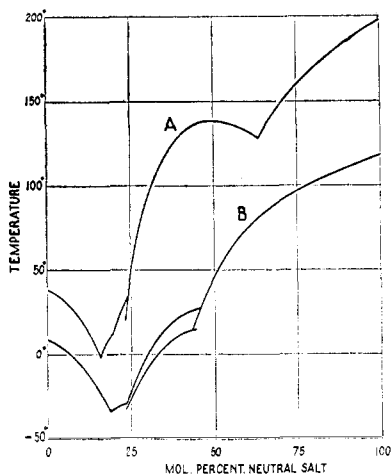


Fig. 1.—(A) Potassium formate:formic acid (subtract  $30^{\circ}$  from the temperature readings); (B) ammonium formate:formic acid.

(a) Solid phase  $\text{H.COOH}$ .

% $\text{H.COO.NH}_4$	0.0	1.53	3.70	6.28	8.19	10.14	12.43	14.86	17.11	18.95
$T$ .....	8.47	7.0	4.5	0.6	-2.8	-6.9	-12.6	-19.8	-26.9	-33.8

(b) Solid phase  $\text{H.COO.NH}_4, 3\text{H.COOH}$ .

% $\text{H.COO.NH}_4$	20.43	21.73	23.33
$T$ .....	-31.3	-30.0	-29.3

(c) Solid phase  $\text{H.COO.NH}_4, \text{H.COOH}$ .

% $\text{H.COO.NH}_4$ .....	23.33	24.83	25.41	26.64	27.90	30.11	33.25
$T$ (unstable modification)	-32.5	-26.0	-23.5	-18.7	-14.0	...	1.3
$T$ (stable modification)	....	....	....	-13.7	-8.7	0.7	10.4
% $\text{H.COO.NH}_4$	36.29	39.30	41.90	42.94	44.38	....	....
$T$ (unstable modification)	7.4	11.3	13.8	14.3	15.0	....	....
$T$ (stable modification)	17.3	22.2	24.9	25.8	....	....	....

(d) Solid phase  $\text{H.COO.NH}_4$ .

% $\text{H.COO.NH}_4$	44.38	46.06	47.87	51.88	59.98	68.23	74.32	76.20
$T$ .....	20.4	29.3	37.5	53.1	74.3	89.5	96.5	98.5
% $\text{H.COO.NH}_4$	83.46	88.41	91.64	100.0	....	....	....	....
$T$ .....	103.7	108.5	111.7	117.3	....	....	....	....

Two distinct acidsalts are indicated, as will be seen from the diagram (Fig. 1). Both undergo transition before their melting points are reached, but in the case of solid phase (b) the curve so nearly reaches its maximum point before the salt becomes unstable that it is possible to assign to the compound the formula  $\text{H.COO.NH}_4, 3\text{H.COOH}$  and the approximate melting point of  $-29^{\circ}$ . The remaining compound exists in two different crystalline modifications, the stable form appearing from solution as needles, the unstable as prisms. Analyses of both forms gave the same acid content ( $49.4 \pm 0.6$  mol. % acid), indicating the equimolecular salt<sup>13</sup>  $\text{H.COO.NH}_4, \text{H.COOH}$ .

<sup>13</sup> This compound has been previously isolated by Groschuff (*loc. cit.*). An earlier investigation by Reik (*Monats.*, 23, 1033 (1902)) failed to indicate its existence.

**Sodium Formate:Formic Acid.**—The sodium salt was prepared from a reputed c. p. sample by two recrystallizations from water and desiccation at 140° to constant weight. The melting point obtained was 255 ± 1°; the value given by Groschuff is 253°.

(a) Solid phase H.CO<sub>2</sub>H.

% H.CO <sub>2</sub> Na	0.0	1.04	2.92	4.61	6.35	8.72	10.50	12.58
T.....	8.4	7.5	5.3	3.0	0.4	-3.8	-7.6	-12.8

(b) Solid phase H.CO<sub>2</sub>Na, 2H.CO<sub>2</sub>H.

% H.CO <sub>2</sub> Na..	14.52	16.45	18.18	20.69	21.13	21.86	23.23	24.43	24.91
T.....	-17.4	0.3	10.7	22.9	24.4	26.3	30.5	33.1	34.5

(c) Solid phase H.CO<sub>2</sub>Na, H.CO<sub>2</sub>H.

% H.CO <sub>2</sub> Na	25.18	25.90	27.00	27.10	28.39	29.80	31.15	31.65	32.14
T.....	31.0	37.3	45.2	45.6	52.2	59.0	65.1	67.5	69.6

(d) Solid phase H.CO<sub>2</sub>Na.

% H.CO <sub>2</sub> Na	29.80	31.65	33.40	35.71	39.10	42.79	43.47
T.....	45.1	63.6	81.2	99.3	118.6	135.2	137.7

Two acid salts are shown by the curves (see Fig. 2), both becoming unstable before their melting points are reached. Analyses of solid phase (b) gave an acid content of 66.1 ± 0.5 mol. %, corresponding to the compound H.CO<sub>2</sub>Na, 2H.CO<sub>2</sub>H. Analyses of solid phase (c) gave an acid content of 50.1 ± 0.2 mol %, corresponding to the compound H.CO<sub>2</sub>Na, H.CO<sub>2</sub>H.

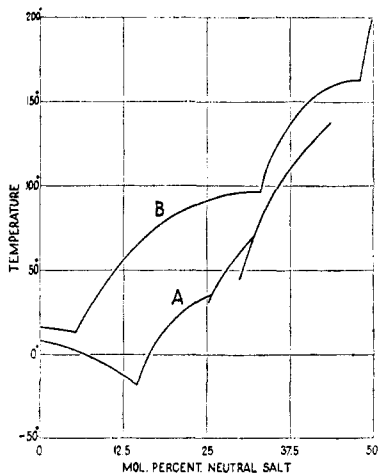


Fig. 2.—(A) Sodium formate:formic acid; (B) sodium acetate:acetic acid.

The curve could not be extended to the pure neutral salt, owing to the decomposition of the acid at temperatures above 160°. This places an automatic upper limit upon all other systems in which formic acid is one component.

It may be noted that the previous results of Groschuff upon this system are entirely in error.

**Lithium Formate:Formic Acid.**—Lithium formate was prepared from a pure sample of the carbonate and 90% formic acid. The hydrated salt which crystallized out from the solution was dehydrated at 100°, and final purification secured by recrystallization from alcohol and desiccation over sulfuric acid *in vacuo*.

## (a) Solid phase H.COOH.

% H.COOLi	0.0	1.58	3.47	5.33	7.09	8.93	10.75	12.23	13.99
T.....	8.4	7.0	5.2	3.2	1.1	-1.3	-3.5	-5.6	-8.2
% H.COOLi	18.19	19.56	21.25	22.24	23.49	24.33	....	....	....
T.....	-14.6	-17.1	-19.8	-21.7	-23.5	-25.0	..	....	....

## (b) Solid phase H.COOLi.

% H.COOLi	23.49	23.93	25.31	25.91	26.38	27.71	29.87	31.98
T.....	18.0	34.0	80.0	90.5	97.9	113.1	131.2	145.1
% H.COOLi	33.04	35.01	36.13	...	...	....	....	....
T.....	150.4	159.1	163.5	...	...	....	....	....

Contrary to expectations, no acid salts are indicated. The curve could not be carried to completion, but analyses of solid phase (b) showed it to be the neutral salt.

**Barium Formate:Formic Acid.**—The barium salt was obtained by the action of 90% acid on the carbonate, as described above. It was recrystallized from water 3 times and dried to constant weight at 140°.

## (a) Solid phase H.COOH.

% (H.COO) <sub>2</sub> Ba	0.0	0.91	1.74	2.30	3.73	4.67	5.12	6.95
T.....	8.4	7.2	6.1	5.1	2.6	0.5	-0.3	-4.9

(b) Solid phase (H.COO)<sub>2</sub>Ba, H.COOH.

% (H.COO) <sub>2</sub> Ba	8.52	8.86	9.23	9.83	10.03	10.75
T.....	9.5	15.5	19.0	24.9	26.5	31.8

Owing to extreme retardation in the attainment of equilibrium<sup>14</sup> the system could not be investigated at concentrations greater than 10.7 mol % salt.<sup>15</sup> Analyses of solid phase (b) gave an acid content of 50.6 ± 0.7 mol %, corresponding to the compound (H.COO)<sub>2</sub>Ba, H.COOH. This salt has not been previously reported.

**Calcium Formate:Formic Acid.**—The method of preparation for calcium formate was the same as given for the barium salt.

## (a) Solid phase H.COOH.

% (H.COO) <sub>2</sub> Ca	0.0	0.16	0.48	0.71	0.93	1.27	1.53
T.....	8.4	8.1	7.7	7.4	7.2	6.9	6.6

(b) Solid phase (H.COO)<sub>2</sub>Ca.

% (H.COO) <sub>2</sub> Ca	0.39	0.57	0.83	1.10	1.26	1.35	1.54	1.61
T.....	128.6	100.0	79.0	61.0	49.7	45.5	35.0	30.0

Analyses showed solid phase (b) to be the neutral salt. As will be seen from the curve (Fig. 3), this exhibits retrograde solubility in formic acid, the solubility at 130° being less than a quarter of that at 30°. It is interesting to find that a phenomenon which is so characteristic of calcium salts in aqueous solutions is here again evident.

**Magnesium Formate:Formic Acid.**—The salt was prepared by dissolving c. p. magnesia in 90% acid, and dehydrating the product obtained (a dihydrate) to constant weight at 110°. Analysis showed that hydrolysis and consequent loss of acid during dehydration was negligible.

No curve could be obtained for this system owing to the insolubility of the salt in the pure acid. At 25° the saturated solution contains only 0.20 mol % of salt. At-

<sup>14</sup> Compare the system BaSO<sub>4</sub>:H<sub>2</sub>SO<sub>4</sub>; Kendall and Davidson, *loc. cit.*

<sup>15</sup> The last points determined represent metastable equilibria, since the solutions deposit, on long standing, crystals of a different form, probably the neutral salt. The solubility curve for this phase must be extremely steep, since a mixture containing 11 mol % of salt did not give a clear solution even at 140°.

tempts to obtain values at higher temperatures failed, equilibrium conditions in the sealed bulbs not being attainable.

**Zinc Formate : Formic Acid.**—The neutral salt was prepared from the carbonate. Its solubility in formic acid is practically zero, a mixture containing less than 0.16 mol % of salt not giving a clear solution even at 140°.

**Nickel Formate : Formic Acid.**—The hydrated salt was prepared from the carbonate and 90% acid, recrystallized from water, and dehydrated at 140°. The neutral salt obtained was soluble in formic acid to an extent of less than 0.10 mol % at 140°.

**Lead Formate : Formic Acid.**—The lead salt was prepared by precipitation from lead nitrate and sodium formate in aqueous solution. The precipitate was thoroughly washed, recrystallized twice from water and dried at 140°.

(a) Solid phase  $(\text{H.COO})_2\text{Pb}$ .

% $(\text{H.COO})_2\text{Pb}$	0.21	0.30	0.42	0.51
T.....	20.0	73.1	109.4	124.5

The solubility, while still extremely slight, is just measurable in this system. While the solid phase in equilibrium with the solutions could not be analyzed, the steepness of the curve leaves little doubt that it is the neutral salt.

**Copper Formate : Formic Acid.**—The hydrated salt was prepared from a pure sample of basic carbonate and 90% acid. After recrystallization from water it was dehydrated to constant weight at 80°, the bright blue neutral salt being obtained.<sup>16</sup> The solubility of this in pure formic acid is less than 0.10 mol % at 140°.

**Silver Formate : Formic Acid.**—Strenuous efforts were made to investigate this system, but the instability of the silver salt rendered all determinations useless. In the presence of water the salt decomposes extremely rapidly. It may be isolated by precipitation in absolute methyl alcohol, but the product so obtained decomposes during desiccation over sulfuric acid even though protected from the light.

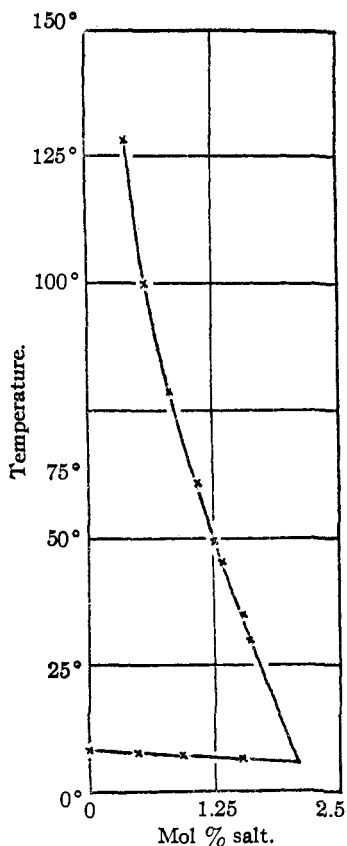


Fig. 3.—Calcium formate : formic acid.

(B) Acetic Acid Systems.

**Sodium Acetate : Acetic Acid.**—The salt was prepared from a c. p. hydrate, which was recrystallized from water and dehydrated to constant weight at 140°. Analysis showed complete removal of water.

(a) Solid phase  $\text{CH}_3\text{COOH}$ .

% $\text{CH}_3\text{COONa}$	0.0	0.83	3.59	5.40
T.....	16.5	16.1	14.3	13.1

<sup>16</sup> Voss, *Ann.*, 266, 33 (1891).



(b) Solid phase $\text{CH}_3\text{COONa}$ , $2\text{CH}_3\text{COOH}$ .										
% $\text{CH}_3\text{COONa}$	7.11	8.92	12.17	15.27	16.58	21.55	26.86	30.72	33.03	33.16
T.....	25.3	36.7	54.3	66.9	71.9	85.7	93.2	96.1	96.25	96.3
(c) Solid phase $\text{CH}_3\text{COONa}$ , $\text{CH}_3\text{COOH}$ .										
% $\text{CH}_3\text{COONa}$	34.03	36.87	39.06	42.54	44.25	46.28				
T.....	112.0	132.3	145.2	157.0	160.6	162.3				
(d) Solid phase $\text{CH}_3\text{COONa}$ .										
% $\text{CH}_3\text{COONa}$			48.76			49.49				
T.....			174.4			195.5				

Two acid salts are indicated by the curves (see Fig. 2); both undergo transition just before reaching their maxima. By slight extrapolations on the diagram, however, the compositions of the compounds are obtained as  $\text{CH}_3\text{COONa}$ ,  $2\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COOH}$ , with melting points of  $96.3^\circ$  and  $164^\circ$  respectively. Both of these salts have been previously reported,<sup>17</sup> but the melting points given ( $80^\circ$  and  $140^\circ$ ) are considerably too low.

**Calcium Acetate:Acetic Acid.**—Anhydrous calcium acetate was found to be only slightly soluble in acetic acid. At  $30^\circ$  the saturated solution contains less than 0.35 mol % salt; no attempt was made to follow the curve to higher temperatures.

**Zinc Acetate:Acetic Acid.**—A c. p. sample of the salt was dehydrated at  $100^\circ$ . The anhydrous salt is practically insoluble in the pure acid, a mixture containing 0.10 mol % of salt giving a clear solution only at  $130^\circ$ .

**Ferric Acetate:Acetic Acid.**—A solution of ferric acetate in 90% acetic acid was treated with acetic anhydride and the mixture refluxed. The crystals deposited on cooling were dried with ether. Analysis showed the product obtained to be anhydrous and very slightly basic. The solubility in acetic acid was practically zero, a mixture containing only 0.07 mol % of salt not giving a clear solution even at  $140^\circ$ .

**Silver Acetate:Acetic Acid.**—The silver salt was prepared by precipitation from silver nitrate and sodium acetate. The precipitate was washed thoroughly, recrystallized from water and dried to constant weight over sulfuric acid *in vacuo*.

(a) Solid phase $\text{CH}_3\text{COOAg}$ .		
% $\text{CH}_3\text{COOAg}$	0.094	0.204
T.....	76.	115.

As will be seen, the solubility in acetic acid is very small. The measurements could not be carried to higher temperatures, owing to decomposition of the salt.

### Consideration of Results.

**Compounds isolated and their stability.**—The only formates that have been found to give isolable acid salts with formic acid are those of potassium, ammonium, sodium and barium. Of the 8 compounds obtained (one of which is existent in two crystalline modifications), only one is of sufficient stability to reach its melting point before undergoing transition. This is the equimolecular acid potassium salt, melting at  $108.6^\circ$ .

Obviously compound formation is here, as in the corresponding case of sulfates, most pronounced with the more electropositive metals, falling off rapidly as the electrode potential of the metal approaches that of hydrogen.

<sup>17</sup> Lescoeur, *Ann. chim. phys.*, [6] 28, 241 (1893). Vasiliev (*J. Russ. Phys. Chem. Soc.*, 41, 753 (1909)) has also studied the cryohydric point of this system.

The acid formates of potassium are more stable than those of sodium,<sup>18</sup> barium formate gives a single acid salt, while calcium and magnesium formates show no isolable compounds. Owing to the instability of silver formate, the increase in compound formation for metals below hydrogen in the electromotive series, so well illustrated in the case of the sulfates, is not here observable.

With acetates in acetic acid, although the full series has not been examined, the same behavior is evident. Sodium acetate gives 2 acid salts, both of which decompose just before reaching their melting points. Compounds of potassium,<sup>19</sup> ammonium<sup>20</sup> and lithium<sup>21</sup> acetates with acetic acid have been reported by previous investigators. The acetates of the less electropositive metals are practically insoluble in acetic acid.

It is of importance to note that the rate at which compound formation decreases in stability, as we go down the series from potassium to hydrogen, increases as the acid radical becomes weaker. Thus isolable acid sulfates are obtained even with zinc and ferrous iron, but the last isolable acid formate is reached as high up as barium. In general, therefore, the stability of the acid salts of any particular metal increases with the strength of the acid radical. Thus silver sulfate gives two acid salts with sulfuric acid, while silver acetate in acetic acid is scarcely soluble. Sufficient scattered observations may be collected from the literature to test this generalization for two other acid radicals. Acid *fluorides* have been reported for lithium,<sup>22</sup> potassium,<sup>23</sup> sodium,<sup>24</sup> ammonium<sup>25</sup> and silver.<sup>26</sup> With the last-named metal, 2 compounds (AgF, 3HF and AgF, HF) have been isolated; evidently compound formation in this series approaches in stability that given by the sulfates. With the much weaker *hydroxyl* radical, on the other hand, no tendency towards the formation of complexes is exhibited except with the highly electropositive metals. The only hydroxides which give isolable hydrates are those of the alkali metals,<sup>27</sup> ammonium,<sup>28</sup> barium<sup>29</sup> and strontium.<sup>30</sup>

<sup>18</sup> Lithium, the most electropositive metal of all, is out of line in giving a negative result; this, however, is a point which will be taken up later.

<sup>19</sup> Lescoeur, *Ann. chim. phys.*, [6] **28**, 245 (1893); Melsens, *Compt. rend.*, **19**, 611 (1844).

<sup>20</sup> Reik, *Monats.* **23**, 1033 (1902).

<sup>21</sup> Lescoeur, *Bull. soc. chim.*, **24**, 517 (1875).

<sup>22</sup> Abegg, *Handbuch der anorg. Chem.*, [1] **2**, 120 (1908).

<sup>23</sup> Moissan, *Compt. rend.*, **106**, 547 (1888).

<sup>24</sup> Abegg, *op. cit.*, p. 220.

<sup>25</sup> Marignac, *Ann. min.*, [5] **15**, 221 (1859).

<sup>26</sup> Gore, *Proc. Roy. Soc.*, **18**, 157 (1870); Guntz, *Bull. soc. chim.*, [3] **13**, 114 (1895).

<sup>27</sup> Pickering, *J. Chem. Soc.*, **63**, 890 (1893).

<sup>28</sup> Rupert, *THIS JOURNAL*, **31**, 866 (1909); **32**, 148 (1910).

<sup>29</sup> Abegg, *op. cit.*, [2] **2**, 259 (1905).

<sup>30</sup> Müller-Erbach, *Ber.*, **20**, 1628 (1887); **22**, 3180 (1889).

**Solubility Relationships.**—The parallelism between compound formation and solubility discovered in the case of the sulfates is again obvious in this work. The alkali formates are exceedingly soluble in formic acid, the salts of less electropositive metals are decreasingly soluble, practically zero solubility is shown by the formates of metals below magnesium in the electromotive series. The following table<sup>31</sup> exhibits the quantitative results at a single fixed temperature (25°).

Metal.	Electrode potential.	Mol % solubility 25°.	Solid phase.
Li	−3.02	23.7	H.COOLi
K	−2.92	25.5	H.COOK, H.COOH
Ba	−2.8 (?)	9.8	(H.COO) <sub>2</sub> Ba, H.COOH
Na	−2.72	21.3	H.COONa, 2H.COOH
Ca	−2.5 (?)	1.7	(H.COO) <sub>2</sub> Ca
Mg	−1.55	0.2	(H.COO) <sub>2</sub> Mg
Zn	−0.76	<0.1	(H.COO) <sub>2</sub> Zn
Ni	−0.22	<0.1	(H.COO) <sub>2</sub> Ni
Pb	−0.13	0.2	(H.COO) <sub>2</sub> Pb
Cu	+0.35	<0.1	(H.COO) <sub>2</sub> Cu

In the acetic acid series, solubilities follow the same course, as far as can be judged from the limited results available. Sodium acetate is very soluble in acetic acid, calcium acetate only slightly soluble, the acetates of less electropositive metals practically insoluble.

### Summary.

An examination of the freezing-point curves of metal formates in formic acid has resulted in the isolation of the following compounds.

Salt.	Acid compounds isolated.
Potassium formate	(a) H.COOK, 3H.COOH } (not previously reported) (b) H.COOK, 2H.COOH } (c) H.COOK, H.COOH; m. p. 108.6°
Ammonium formate	(a) H.COONH <sub>4</sub> , 3H.COOH (not previously reported) (b) H.COONH <sub>4</sub> , H.COOH; existent in 2 crystalline modifications
Sodium formate	(a) H.COONa, 2H.COOH (not previously reported) (b) H.COONa, H.COOH
Barium formate	(H.COO) <sub>2</sub> Ba, H.COOH (not previously reported)

The neutral formates of lithium, calcium, magnesium, zinc, nickel, lead and copper gave no isolable acid salts.

A few corresponding curves for metal acetates in acetic acid have been determined. With sodium acetate 2 acid salts (CH<sub>3</sub>.COONa, 2CH<sub>3</sub>.COOH

<sup>31</sup> Compare Kendall and Davidson, *loc. cit.*, p. 989. The only marked irregularity in the present table consists in the superior solubility of sodium formate over that of barium. This will be discussed in connection with the "valence factor" in compound formation in a later paper.

and  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COOH}$ ) were isolated; calcium, zinc, ferric and silver acetates gave negative results.

The results of this work resemble those obtained with sulfate systems in following the general rule previously deduced, that compound formation increases in extent with increasing diversity in the character of the components, the significant variable in systems of this general type  $\text{HX}:\text{RX}$  being the position of R relative to H in the electromotive series. An examination of the data for sulfates, formates, acetates, fluorides and hydroxides shows that the rate of decrease in compound formation as we proceed from more positive radicals (such as potassium) or less positive radicals (such as silver) towards hydrogen increases, the weaker the acid radical.

Solubility and compound formation are again found to proceed in parallel throughout the series. Salts which show extensive compound formation (such as salts of the alkali metals) are also extremely soluble. As we pass down the electromotive series towards hydrogen, solubility rapidly diminishes and finally becomes inappreciable.

The correlation of solubility with compound formation and of compound formation with ionization in solutions of metal formates in formic acid will be further dealt with in subsequent communications, and additional rules connecting these properties in systems of the general type  $\text{HX}:\text{RX}$  will there be formulated.

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## THE PREDICTION OF SOLUBILITY IN POLAR SOLUTIONS.

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If all solutions were ideal, the answer to most of our solubility problems could be very simply stated.<sup>1</sup> At any given temperature the solubility of a solid substance A in a series of different solvents B, C, D, etc. would be, when expressed in terms of mol fractions, a fixed quantity, independent of the particular solvent and immediately calculable from the heat of fusion of A, the temperature of fusion of A and the specific heats of A in the solid and liquid states. All liquids would be completely miscible under all conditions. The solubility of a gas in a liquid, expressed again in terms of mol fractions, would depend only upon the ratio of its partial pressure over the solution to its vapor pressure in the liquid state at the same temperature.<sup>2</sup>

<sup>1</sup> Roozeboom, "Heterogene Gleichgewichte," [1] 2, 273, et seq. (1904); Washburn, "Principles of Physical Chemistry," Chap. 14 (1915).

<sup>2</sup> Strictly speaking, this would be true only for a perfect gas. More accurately, solubility is proportional to fugacity instead of to vapor pressure.