

2. A comprehensive study has been made of the effects on this relationship of the following factors: (1) rate of centrifuging; (2) duration of centrifuging; (3) temperature of precipitation; (4) rate of precipitation; (5) concentration of solutions; (6) time of standing of precipitates before centrifuging; and (7) nature of the precipitant.

3. The centrifuge method has been applied to the following determinations: (1) sulfur in steel; (2) calcium as oxalate; (3) aluminum as hydrous oxide; (4) nickel as dimethylglyoxime salt; (5) nitrate as nitron salt.

4. The bore of the capillary should vary from 1.1 mm. with dense crystalline precipitates to 10 mm. with those of a gelatinous character.

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THE SOLUBILITY OF OXALIC ACID IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID¹

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The solubility of oxalic acid in aqueous solutions of hydrochloric acid has been studied by Masson² at 30° and by Herz and Neukirch³ at 25°. In both of these researches a minimum solubility was found at a concentration of hydrochloric acid of about 6 *N*, this minimum solubility being about one-third that in pure water. At increasing concentrations above 6 *N* the solubility of oxalic acid increases rapidly. Additional data are here presented at three other temperatures: 0, 50 and 80°. At each of these temperatures similar results are encountered, the solubility curve rising more rapidly from the minimum point than its approach to the minimum point. The position of this minimum shifts with the temperature, being at 10% hydrochloric acid at 80°, at 18% hydrochloric acid at 50° and at 20% hydrochloric acid at 0 and at 30°.

To various solutions of hydrochloric acid in water, oxalic acid was added in excess, and the mixture was heated above the temperature of the determination. Then the bottles were placed in a thermostat regulated within 0.05° of the desired temperature. For the equilibria at 0°, a bucket of cracked ice was used as the thermostat. In all cases equilibrium was reached from above, and was reached within a few hours. Samples of the saturated solutions were drawn off, weighed and analyzed for oxalic

¹ Part of the material presented here was used by Ethel M. Chapin in a thesis presented to the University of North Carolina in June, 1930, in partial fulfillment of the requirements for the degree of Master of Science.

² Masson, *J. Chem. Soc.*, 101, 103 (1912).

³ Herz and Neukirch, *Z. anorg. allgem. Chem.*, 131, 303 (1923).

acid by hot titration with permanganate, and for total acid by titration with sodium hydroxide. The pipets into which the solutions were drawn were previously heated above the temperature of the experiment, so as to avoid crystallization from the solution before transfer to weighing bottles. The specific gravities of the solutions saturated at 0° were determined in pycnometers. These were filled with the solutions and brought to 25° in a thermostat. From the specific gravities so found, the normalities of the solutions (at 25°) can also be calculated. The percentage composition of hydrochloric acid is found from the difference between total acid and the oxalic acid. This percentage is, of course, subject to a large experimental error, where the percentage is small. For the series at 0° the percentage of hydrochloric acid (up to 5% HCl) was determined directly by precipitation with silver nitrate in the presence of sufficient nitric acid to prevent the precipitation of silver oxalate.

The results of the experiments are given in the tables, which include a column for "solubility ratio." This ratio is obtained by dividing the

TABLE I

SOLUBILITY OF OXALIC ACID IN AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE AT 0°				SOLUBILITY OF OXALIC ACID IN AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE AT 0°			
Sp. gr. 25°/25°	HCl, %	H ₂ C ₂ O ₄ , %	Solubility ratio	Sp. gr. 25°/25°	HCl, %	H ₂ C ₂ O ₄ , %	Solubility ratio
1.0178	0	3.43	1.000	1.0497	8.17	1.41	0.411
	.11	3.28	0.956	1.0518	8.51	1.34	.391
	.23	3.13	.913	1.0690	12.01	1.13	.330
	.31	3.05	.889	1.0855	15.31	1.03	.300
	.44	2.96	.863	1.1083	19.67	0.97	.283
	.55	2.86	.834	1.1227	22.15	.98	.286
1.0190	1.25	2.45	.714	1.1428	25.72	1.05	.306
1.0214	1.95	2.20	.641	1.1609	28.83	1.28	.373
1.0278	3.67	1.87	.545	1.1796	31.57	1.73	.504
1.0356	5.15	1.65	.481	1.1977	34.49	2.39	.697

TABLE II

SOLUBILITY OF OXALIC ACID IN AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE AT 50°		
HCl, %	H ₂ C ₂ O ₄ , %	Solubility ratio
0	24.00	1.000
1.63	21.45	.894
5.17	17.17	.715
9.13	14.06	.586
12.17	12.38	.516
14.66	11.47	.478
17.10	11.02	.459
20.16	11.08	.462
22.61	11.76	.490
24.91	13.20	.550
26.38	15.07	.629
27.20	17.52	.730

TABLE III

SOLUBILITY OF OXALIC ACID IN AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE AT 80°		
HCl, %	H ₂ C ₂ O ₄ , %	Solubility ratio
0	47.63	1.000
1.60	44.84	0.941
4.77	40.77	.856
6.33	39.37	.827
7.86	38.44	.807
9.27	37.70	.792
9.87	37.80	.794
11.18	37.91	.796
12.51	39.34	.827
13.66	41.22	.865
14.67	43.74	.918

percentage of oxalic acid by that in water. These solubility ratios are plotted in the figure, which also includes the results of Masson at 30°. It was not possible to include the results of Herz and Neukirch at 25° since they gave results in normalities only.

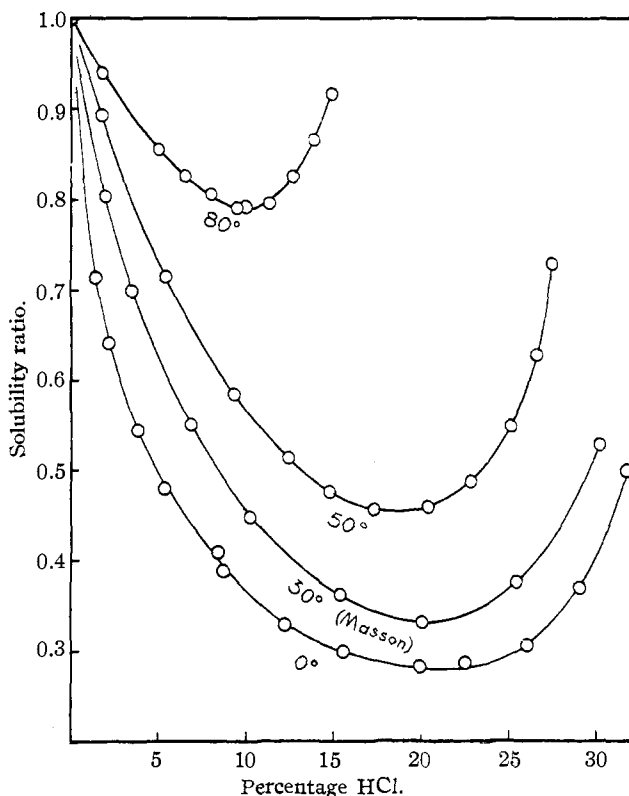


Fig. 1.

In no case was there evidence of any solid phase other than the dihydrate of oxalic acid. Confirmation of this result is had from an examination of vapor pressure data. At 0°, Baxter and Lansing⁴ and Baxter and Cooper⁵ have found that the dehydration of the dihydrate of oxalic acid occurs at 0.38 mm. and 0.34 mm., respectively, or a mean of 0.36 mm. At this same temperature the partial vapor pressure of water from aqueous hydrochloric acid solutions is given⁶ as 0.85 mm. at 34% HCl. This value would, of course, be slightly lower with 2.5% of oxalic acid also present, but is still higher than the pressure at which the dihydrate loses water. Again at 25°, Baxter and his associates find the dehydration pressure for

⁴ Baxter and Lansing, *THIS JOURNAL*, **42**, 419 (1920).

⁵ Baxter and Cooper, *ibid.*, **46**, 929 (1924).

⁶ "International Critical Tables," Vol. III, p. 301.

oxalic acid to be 2.67 mm. We have found that the dihydrate of oxalic acid loses water over a 67.5% solution of sulfuric acid, but does not lose water over a 62% solution, both at room temperature, about 25°. These solutions have vapor pressures of 1.6 mm. and 3.0 mm.⁷ The aqueous partial pressure from 34% hydrochloric acid solution is given as 5.35 mm. and, while this would be a little lower in the presence of the dissolved oxalic acid, would still be above the pressure at which the dihydrate dehydrates. Similar calculations at 50 and 80° show that anhydrous oxalic acid should not be expected as a solid phase in contact with hydrochloric acid solutions of the concentrations of the present experiments.

It is obvious that many factors enter to effect the solubility of the oxalic acid in these solutions. The initial depression of solubility in dilute hydrochloric acid solutions may be explained qualitatively by the "common ion" effect. On this basis Herz and Neukirch have calculated the solubility of oxalic acid, assuming both acids to be completely ionized. At concentrations of hydrochloric acid above normal the accord between observed and calculated solubilities is far from satisfactory, while below normal the accord is within 2%. Similar calculations with data at other temperatures yield results just as unsatisfactory. The increasing solubility at the higher concentrations of hydrochloric acid is more difficult of explanation. Masson attributes this to a competition between the two acids for water molecules, a competition resulting in the dehydration of part of the hydrated oxalic acid. This brings about an increase in the total oxalic acid in solution. Kendall, in similar cases of solubility curves passing through a minimum, attributes the effect in part to compound formation with the consequent increase of the total solute in solution, and in part to other causes as yet too difficult to disentangle.

Résumé

Data and curves are given for the solubility of oxalic acid in aqueous solutions at temperatures from 0 to 80°. The solid phase at all temperatures and at all concentrations was $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

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⁷ Interpolated from results in "International Critical Tables," Vol. III, p. 303.