

a far smaller proportion of sulfate in the crystals than in the case of decahydrate, but is quite enough to account for the difficulty in eliminating sodium sulfate from chromate by crystallization as tetrahydrate.

When sodium sulfate was in large excess, in repeated trials, no crystallization could be induced by inoculating the saturated mixture with the crystal of the tetrahydrate above the transition temperature of sodium sulfate, and below this temperature only crystals of the decahydrate could be made to form. Thus under these conditions the tetrahydrate is so much more soluble than the phases containing more sodium sulfate as to be incapable even of meta-stable existence.

### Summary.

In brief, this paper shows that crystals of  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  dissolve sodium sulfate as  $\text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (a form otherwise unknown) to the extent of somewhat less than half the quantity corresponding to the same weight of sodium chromate in the supernatant solution.

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## THE SOLUBILITIES OF ACIDS IN AQUEOUS SOLUTIONS OF OTHER ACIDS.

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The factors controlling addition-compound formation in systems of the type  $\text{HX}:\text{HY}$  have been investigated in an earlier article.<sup>1</sup> It has been established that a weak acid in the presence of a strong acid behaves as a base, the stability of the resultant "salt" depending upon the difference in acidic strengths. Precisely the same factors are operative in determining the hydration of an acid in aqueous solution, the extent of compound formation between acid and water increasing uniformly with the strength of the acid.<sup>2</sup> When we come to consider the three-component system  $\text{HX}:\text{HY}:\text{H}_2\text{O}$ , the equilibria involved are naturally more complicated. By investigation of the solubility curve for one acid  $\text{HX}$  in solutions containing increasing concentrations of the second acid  $\text{HY}$ , however, we can obtain valuable evidence with regard to the existence and stability of compounds between the two acids in aqueous solution. The problem resembles in certain respects one already taken up in a previous paper<sup>3</sup>—the effect of other chlorides upon the solubility of silver chloride in water—but is obviously considerably more intricate in view of the wide variations possible in the solubilities and in the ionization constants of the two acids selected.

<sup>1</sup> Kendall, *THIS JOURNAL*, **36**, 1722 (1914).

<sup>2</sup> Kendall, Booge and Andrews, *ibid.*, **39**, 2303 (1917).

<sup>3</sup> Kendall, Davidson and Adler, *ibid.*, **43**, 1496 (1921).

It must be admitted that final conclusions upon systems of this nature cannot be arrived at until considerable advances in our general theory of solutions have been made (at present, the nature of the equilibria in the simple system  $HX:H_2O$  is still debatable), but by the comparison and correlation of typical cases we may hope to gain some insight into the factors concerned which will prove of assistance in the subsequent development of this general theory.

The case where  $HX$  is a typical weak acid and  $HY$  a typical strong acid may be briefly analyzed as an illustration. If no compound formation occurs in aqueous solution, the addition of  $HY$  to a saturated solution of  $HX$  in water theoretically necessitates a sharp dip in the solubility curve of  $HX$  until the "constant undissociated value" is reached,<sup>4</sup> since the ionization of the weak acid will be reduced practically to zero in the presence of the strong acid. Further addition of  $HY$  will have little effect.<sup>5</sup> If compound formation does occur, however, an opposing factor upon the solubility curve is immediately introduced. Addition of  $HY$  now involves the removal of  $HX$  molecules as such from the solution to form molecules of the complex, consequently more solid  $HX$  must dissolve to re-establish equilibrium. The more stable the compound, the more marked will be this effect. In an extreme case it may even wipe out the sharp initial "ionic" decrease in solubility, increasing values being recorded from the very start. If the dissociation of the compound into its components in the solution is extensive,<sup>6</sup> on the other hand, the increase in the solubility may not appear until very high concentrations of  $HY$  are reached. In such a system the solubility curve will exhibit a characteristic minimum.

Other types of solubility curve will result when two acids of similar character are chosen, or when the order of acidic strengths is reversed. Assuming that the generalizations derived from the study of two-component systems are still valid, we may predict the following behavior for the various possible combinations.

(A) $HX$ weak; $HY$ strong	Extensive compound formation	Curve with a minimum
(B) $HX$ weak; $HY$ weak	Little compound formation	Curve variable; generally rising
(C) $HX$ strong; $HY$ strong	Extensive hydration; little compound formation	Curve steadily falling
(D) $HX$ strong; $HY$ weak	Extensive compound formation	Curve generally rising

<sup>4</sup>Nernst, *Z. physik. Chem.*, **4**, 372 (1889); Kendall, *Proc. Roy. Soc.*, **85A**, 200 (1911). See however Stieglitz, *This Journal*, **30**, 946 (1908).

<sup>5</sup>The actual course of the curve will depend primarily upon the method employed for expressing concentrations, a point which is discussed in the text later. In general, removal of water as solvent by hydration of the strong acid  $HY$  will result in a gradual further decrease in the solubility of  $HX$ .

<sup>6</sup>In view of the large excess of water present, this may in practically all systems be presumed to be the case.

In systems of the Type B the predominant factor in determining the final course of the solubility curve will be changes in internal pressure, the effect of which has been discussed in detail by Hildebrand and his collaborators in a recent series of articles.<sup>7</sup> If the difference in the internal pressures of HX and HY in the liquid state is smaller than the difference in the internal pressures of HX and H<sub>2</sub>O we may expect the solubility to increase, if it is larger we may predict a decrease. Since most weak acids are organic and closely similar in character, a rising solubility value will be more frequently encountered.<sup>8</sup>

In systems of Type C, where both acids are highly polar, the chief factors will be repression of ionization and removal of solvent water by hydration of the added acid; hence in general a steadily decreasing solubility of the original acid will result. Changes in the degree of hydration as the water concentration diminishes may, however, involve changes in the nature of the stable phase and consequently induce sharp breaks in the curve.

In systems of Type D, finally, the formation of addition compounds will (as in Type A) bring about a continuous increase in solubility after the initial "ionic" effect in the opposite direction is overcome. This initial effect, however, will here be much smaller (often indeed scarcely noticeable), since the weak acid HX will not be appreciably ionized in the presence of excess of the strong acid HY. A generally rising curve may therefore be expected.

The nature of the accordance of the available experimental data with these several predictions will be taken up in a later section, after the results obtained for the systems investigated in this research have been described.<sup>9</sup>

### Experimental.

The solubility curves here examined are : (1) hydrogen sulfide in hydrochloric acid solution; (2) boric acid in hydrochloric acid and nitric acid solutions; (3) benzoic acid in hydrochloric acid and nitric acid solutions; (4) salicylic acid in hydrochloric acid and nitric acid solutions. A series of weak acids with extremely divergent properties was intentionally

<sup>7</sup> See in particular, Hildebrand, *THIS JOURNAL*, **38**, 1452 (1916).

<sup>8</sup> Compare Kendall, *Proc. Roy. Soc.*, **85A**, 218 (1911).

<sup>9</sup> The experimental part of this paper was completed in 1917. Owing to the absence of one of the authors on naval duty and to the pressure of other work, however, its publication has been delayed. In the interim an important investigation by Knox and Richards (*J. Chem. Soc.*, **115**, 508 (1919)) has appeared, in which solubility curves for no fewer than 48 different systems of the various types discussed above are examined. The conclusions of Knox and Richards are in substantial agreement with those here expressed, and their results have been drawn upon freely in illustrating the argument in the later sections of this article.

selected, in the expectation that the comparison of the results obtained would show (a) whether weak acids of widely different acidic strengths<sup>10</sup> give curves of the same type with the same strong acids, (b) whether inorganic and organic acids behave similarly, and (c) whether a gas gives the same type of curve as a solid. In order to obtain additional information with regard to the equilibria existent in mixed acid solutions, conductivity determinations were also carried out on certain of the above systems.

After considerable hesitation as to the best method of expressing concentrations, it was decided to employ volume units (gram molecules solute per liter solution) throughout. The comparison of the results here obtained with those of previous investigators is thereby greatly facilitated.<sup>11</sup> It is recognized that the representation of all compositions in terms of mol fractions is theoretically preferable,<sup>12</sup> but until we know more about the nature of the molecular types present in the solutions here examined the evaluation of their respective mol fractions is not feasible. A possible alternative procedure is to use weight concentrations, *i. e.*, to compare solubilities in a fixed weight of water. This has the disadvantage of neglecting the added acid entirely, and since this frequently exerts a greater solubility effect than water itself, values obtained on this basis for high concentrations of added acid would often be absurdly large. The use of the volume units here adopted, it must be noted, is more apt to lead to errors in the opposite direction, owing to the fact that the molecular volumes of the added acids are, in general, considerably higher than that of water.<sup>13</sup> This is a factor which must be borne in mind throughout in making comparisons, although its exact magnitude for any particular case cannot at present be calculated. It will be partially counterbalanced in all cases by the progressive disassociation of water as the concentration of added acid is increased.

<sup>10</sup> The respective ionization constants in water are:  $\text{H}_2\text{S}$ ,  $k_{18}^\circ = 5.7 \times 10^{-8}$ ;  $\text{H}_3\text{BO}_3$ ,  $k_{25}^\circ = 6.6 \times 10^{-10}$ ;  $\text{C}_6\text{H}_5\text{COOH}$ ,  $k_{25}^\circ = 6.6 \times 10^{-5}$ ;  $\text{C}_6\text{H}_4\text{OH.COOH}$ ,  $k_{25}^\circ = 1.06 \times 10^{-5}$  (Landolt-Börnstein, "Tabellén," 1912, p. 1132, *et seq.*). Boric acid was specifically chosen because of the availability of previous conductivity data for comparison with the results here obtained (see the discussion in a later section); benzoic and salicylic acids, similarly, because of previous solubility determinations.

<sup>11</sup> Density data will be added in a subsequent article, in which the evidence afforded by solution volume changes upon hydration and compound formation will be discussed (compare Bousfield, *J. Chem. Soc.*, 107, 1405 (1915)).

<sup>12</sup> See Kendall, Davidson and Adler, *THIS JOURNAL*, 43, 1481 (1921).

<sup>13</sup> If both water and HY were quite indifferent substances with respect to HX the mol fraction of HX in the saturated solution would remain constant as HY replaced  $\text{H}_2\text{O}$ . Hence, if the average molecular volume of the solvent increases as HY is added, the volume concentration of HX will diminish. Hydration of HY, which will increase the average molecular volume of the solvent still further, involves a more rapid diminution in the volume concentration of HX.

### The System $\text{H}_2\text{S} : \text{HCl} : \text{H}_2\text{O}$ .

A steady current of hydrogen sulfide was obtained by running ammonium sulfide solution into conc. hydrochloric acid.<sup>14</sup> The gas first passed through wash-bottles containing dil. sulfuric acid (to remove ammonia)<sup>15</sup> and concentrated sodium sulfide solution (to remove hydrochloric acid and possible traces of carbon dioxide).<sup>16</sup> It was then bubbled over a long column of aqueous hydrogen chloride solution, of the same concentration and at the same temperature as that in which its solubility was being determined,<sup>17</sup> and thence it was finally passed, by means of a capillary tube, through a standardized solution of hydrochloric acid in an absorption buret, immersed in a Freas thermostat at  $25 \pm 0.01^\circ$ . The lower portion of this buret consisted of a 50-cc. bulb above and below which the tube was calibrated. When equilibrium was established,<sup>18</sup> the buret was disconnected, a known volume of the solution was run out into a measured excess of standardized iodine solution, and the remaining free iodine titrated back by means of sodium thiosulfate.

The results given below express, first of all, the usual absorption coefficient (*i. e.*, the number of volumes of hydrogen sulfide, reduced to  $0^\circ$  and 760 mm., taken up by one volume of the solution under a pressure of hydrogen sulfide<sup>19</sup> of 760 mm.) and secondly the concentration of the saturated solution under the same conditions in gram molecules of hydrogen sulfide per liter. The values shown represent the mean of several determinations at each concentration of hydrochloric acid,<sup>20</sup> checking within 0.2 to 0.3%.

TABLE I.—SOLUBILITY OF  $\text{H}_2\text{S}$  IN AQUEOUS SOLUTIONS OF  $\text{HCl}$ .  $25^\circ$ .

Normality of $\text{HCl}$ solution.	Absorption coefficient.	G. mols of $\text{H}_2\text{S}$ per liter.
0.0	2.266*	0.1023
0.1348	2.253	0.1018
0.2828	2.247	0.1015
0.6308	2.250	0.1016
1.180	2.260	0.1020
1.848	2.272	0.1026
2.498	2.281	0.1030
3.040	2.291	0.1034
3.308	2.301	0.1039
4.410	2.384	0.1076
4.874	2.413	0.1090

\*Accurate determinations of the solubility of  $\text{H}_2\text{S}$  in water at various temperatures have been made by Winkler, *Z. physik. Chem.*, **55**, 350 (1906). Winkler's interpolated value for  $25^\circ$  is 2.257.

<sup>14</sup> It was first attempted to prepare  $\text{H}_2\text{S}$  by treating granulated  $\text{ZnS}$  with  $\text{HCl}$  in a Kipp generator. The  $\text{ZnS}$  available, however, varied too much in quality to give consistent results.

<sup>15</sup> Subsequent tests showed this to be unnecessary.

<sup>16</sup> Four wash-bottles were used; at the end of the experiments all except the first gave negative tests for chloride and carbonate.

<sup>17</sup> This was done in order to bring the gas to equilibrium with the final solution in advance, so avoiding concentration changes in this solution during determinations.

<sup>18</sup> With the apparatus employed it was found that absorption was complete in 2 or 3 hours.

<sup>19</sup> Pressure corrections were necessary for the vapor tension of the solution, the barometric pressure at the time of the experiment, and the average head of liquid over the portion of the solution titrated. The weight of 1 liter of  $\text{H}_2\text{S}$  under standard conditions was taken as 1.5392 g. (Baume and Perrot, *J. chim. phys.*, **6**, 610 (1909).)

<sup>20</sup> The change in volume of the solution (and hence the change in  $\text{HCl}$  concentration) during absorption of the  $\text{H}_2\text{S}$  was found to be negligible.

The solubility curve evidently shows a minimum at about 0.4 *N* hydrochloric acid, and for concentrations of hydrochloric acid above 1.5 *N* the solubility of hydrogen sulfide is (contrary to the prevalent opinion) greater than in pure water. A still more rapid increase in solubility was found by Pollitzer<sup>21</sup> for hydrogen sulfide in aqueous solutions of hydrogen iodide; unfortunately the lack of data for concentrations of hydrogen iodide below 1 *N* obscures the position of the probable minimum.

Solubility determinations for hydrogen sulfide in other common strong acids (nitric and sulfuric) cannot be made, owing to their rapid oxidizing action. Even the presence of dissolved oxygen in the hydrochloric acid solutions here employed resulted in the slow precipitation of minute amounts of free sulfur from the solutions. This was minimized by boiling the solutions vigorously before standardization and exposing them to the air as little as possible before use.

The results of conductivity measurements<sup>22</sup> upon this system were entirely negative. Over a series of concentrations of hydrochloric acid ranging from 0.0074 *N* to 4.410 *N*, saturation of the solution with hydrogen sulfide produced no measureable change in the bridge reading.

### The System $\text{H}_3\text{BO}_3 : \text{HCl} : \text{H}_2\text{O}$ .

Standardized hydrochloric acid solutions were rotated with excess of powdered boric acid (purified by recrystallization from water) in the thermostat until saturation was reached. Samples of the clear solutions were pipetted out into tared porcelain crucibles and dried to constant weight at 60°. <sup>23</sup> The boric acid content of the final solutions was thus directly obtained; the small changes in hydrochloric acid concentration involved in the increase of volume during solution of boric acid were corrected for by interpolated density determinations. Attempts to make a differential titration of the two acids in the final solution, as recommended by Herz,<sup>24</sup> were not satisfactory.

The results of conductivity determinations upon the saturated solutions, and upon hydrochloric acid solutions of the same concentrations, are included in the table below. Specific conductivities are expressed in reciprocal ohms throughout.

As will be seen from the figures in the second column,<sup>25</sup> a solubility minimum is again obtained, but only at a very high concentration (about 8.0 *N* hydrochloric acid). The conductivity changes due to the presence of dissolved boric acid are quite con-

<sup>21</sup> Pollitzer, *Z. anorg. Chem.*, **64**, 121 (1909).

<sup>22</sup> A 3-meter Leeds and Northrup bridge was employed. Alternating current at 1000 cycles per second was obtained from a constant-speed high-frequency generator. The telephone receiver was tuned to the same frequency. The conductivity cell was of the Cantor type (Cantor, *Z. Elektrochem.*, **9**, 922 (1903)).

<sup>23</sup> Preliminary trials with boric acid solutions of known concentration established the fact that this temperature was low enough to preclude appreciable loss of  $\text{H}_3\text{BO}_3$  by volatilization during evaporation.

<sup>24</sup> Herz, *Z. anorg. Chem.*, **33**, 353 (1903).

<sup>25</sup> These values are not in accordance with those obtained by Herz (*loc. cit.*, p. 355) for the same system, although the form of the curve is precisely similar. The fact that Herz made no correction for changes in concentration of the solvent acid during solution of  $\text{H}_3\text{BO}_3$  is presumably the cause of this disagreement. Herz obtained the concentration of  $\text{H}_3\text{BO}_3$  in each solution from the difference between original and final titrations, and with very high concentrations of HCl a small total error involves a considerable error in  $\text{H}_3\text{BO}_3$ .

TABLE II.— $\text{H}_3\text{BO}_3$  IN AQUEOUS  $\text{HCl}$ . SOLUBILITY AND CONDUCTIVITY DATA.  $25^\circ$ .

Normality of $\text{HCl}$ soln.	$\text{H}_3\text{BO}_3$ dissolved (g. mols per liter).	Spec. cond. of $\text{HCl}$ soln.	Spec. cond. of final solution.	Decrease due to $\text{H}_3\text{BO}_3$ .
0.0	0.8950 <sup>a</sup>	.....	.....	.....
0.0660	0.8810	0.02599	0.02368	0.0023
0.1302	0.8580	0.04953	0.04494	0.0046
0.2733	0.8380	0.09740	0.08833	0.0091
0.6112	0.7761	0.1943	0.1774	0.0169
1.147	0.7042	0.3104	0.2854	0.0250
1.802	0.6270	0.4068	0.3768	0.0300
2.617	0.5431	0.4880	0.4603	0.0277
3.126	0.4976	0.5271	0.5013	0.0268
4.336	0.4189	0.5788	0.5539	0.0249
5.160	0.3715	0.5804	0.5606	0.0198
7.073	0.3446	.....	.....	.....
9.389	0.3501	.....	.....	.....
11.56	0.3687	.....	.....	.....

<sup>a</sup>The values obtained by previous investigators are extremely discordant (see Seidell, "*Solubilities of Inorganic and Organic Compounds*," 1919, p. 153). The result here obtained, however, agrees fairly well with the more recent data (e. g., 0.901 *N* (Herz) and 0.887 *N* (Ageno and Valla)).

siderable, as evidenced by the results in the last column. The decreases recorded cannot be entirely ascribed to viscosity changes in the solution, although direct experiment showed that the viscosities of boric acid solutions near the saturation point<sup>26</sup> are considerably higher than that of pure water, since the corresponding benzoic acid systems (see below) where the viscosity effect is negligible, exhibit exactly the same behavior. Their significance will be taken up in a later section.

### The System $\text{H}_3\text{BO}_3 : \text{HNO}_3 : \text{H}_2\text{O}$ .

The experimental procedure was exactly as in the previous system; solubility and conductivity results obtained are given in Table III below.

TABLE III.— $\text{H}_3\text{BO}_3$  IN AQUEOUS  $\text{HNO}_3$ . SOLUBILITY AND CONDUCTIVITY DATA.  $25^\circ$ .

Normality of $\text{HNO}_3$ soln.	$\text{H}_3\text{BO}_3$ dissolved (g. mols per liter).	Spec. cond. of $\text{HNO}_3$ soln.	Spec. cond. of final soln.	Decrease due to $\text{H}_3\text{BO}_3$ .
0.0	0.8950	.....	.....	.....
0.0779	0.8820	0.02951	0.02673	0.0028
0.1951	0.8610	0.07100	0.06409	0.0069
0.5337	0.8028	0.1726	0.1558	0.0168
0.9890	0.7361	0.2783	0.2528	0.0255
1.580	0.6685	0.3766	0.3469	0.0297
2.372	0.5943	0.4774	0.4429	0.0345
3.118	0.5444	0.5319	0.5021	0.0298
3.806	0.4977	0.5634	0.5350	0.0284
4.698	0.4471	0.5811	0.5572	0.0239
8.41	0.2963	.....	.....	.....
10.95	0.2305	.....	.....	.....
15.81	0.1973	.....	.....	.....

<sup>26</sup>Experiments with a Bingham viscometer at  $25^\circ$  (carried out by Dr. J. J. Beaver) gave the following results:  $\text{H}_3\text{BO}_3$  0.6448 molar,  $d_4^{25}$  1.0096, relative viscosity 1.0603;  $\text{H}_3\text{BO}_3$  0.8 molar,  $d_4^{25}$  1.0160, relative viscosity 1.0833.

When the solubility results of the second column are plotted on a diagram, it becomes evident that the minimum on the curve is approximately at the last concentration examined—about 16.0 *N*. The decrease in specific conductivity of the solutions due to dissolved boric acid is similar to that shown in the preceding table.

### The System $C_6H_5.COOH : HCl : H_2O$ .

Solubility determinations were carried out as described in the case of boric acid above, the only difference (necessitated by the greater volatility of the benzoic acid) being that the solutions were allowed to evaporate to constant weight in a desiccator at room temperature. The residues gave no test for chloride.

The solubility and conductivity results obtained are tabulated as before. The correction in the hydrochloric acid concentration for volume change during solution is here inappreciable, owing to the low solubility of benzoic acid.

TABLE IV.—BENZOIC ACID IN AQUEOUS HCl. SOLUBILITY AND CONDUCTIVITY DATA. 25°.

Normality of HCl soln.	Normality of dissolved $C_6H_5.COOH$ .	Spec. cond. of HCl soln.	Spec. cond. of final soln.	Decrease due to $C_6H_5.COOH$ .
0.0	0.0276 <sup>a</sup>	.....	.....	.....
0.2828	0.0254	0.1003	0.0821	0.0182
0.6308	0.0235	0.1992	0.1659	0.0333
1.180	0.0211	0.3162	0.2740	0.0422
1.848	0.0185	0.4119	0.3683	0.0436
3.308	0.0153	0.5234	0.4922	0.0312
4.410	0.0140	0.5808	0.5580	0.0228
5.238	0.0130	.....	.....	.....
7.172	0.0113	.....	.....	.....
9.522	0.0109	.....	.....	.....

<sup>a</sup>Philip and Garner (*J. Chem. Soc.*, 95, 1466 (1909)) obtained the value 0.0277.

Once more a solubility minimum at a high concentration of solvent acid (approximately 8.5 *N*) is indicated. The decrease in conductivity due to the presence of the solute acid is, as in the case of the boric acid systems, quite considerable.

### The System $C_6H_5.COOH : HNO_3 : H_2O$ .

Measurements for this system were not extended beyond 5.0 *N* nitric acid, since it was desired to avoid nitration effects.<sup>27</sup>

TABLE V.—BENZOIC ACID IN AQUEOUS  $HNO_3$ . SOLUBILITY AND CONDUCTIVITY DATA. 25°.

Normality of $HNO_3$ soln.	Normality of dissolved $C_6H_5.COOH$ .	Spec. cond. of $HNO_3$ soln.	Spec. cond. of final soln.	Decrease due to $C_6H_5.COOH$ .
0.0	0.0276	.....	.....	.....
0.0208	0.0272	0.00838	0.00787	0.0005
0.0807	0.0269	.....	.....	.....
0.1351	0.0268	.....	.....	.....
0.2021	0.0268	0.07338	0.06908	0.0043

<sup>27</sup>Careful tests for nitrogen on the benzoic residues gave negative results in all cases except for the last concentration examined, where nitration was just becoming appreciable.



TABLE V.—(Continued).

Normality of HNO <sub>3</sub> solu.	Normality of dissolved C <sub>6</sub> H <sub>5</sub> .COOH.	Spec. cond. of HNO <sub>3</sub> soln.	Spec. cond. of final soln.	Decrease due to C <sub>6</sub> H <sub>5</sub> .COOH.
0.5514	0.0270	0.1772	0.1652	0.0120
1.019	0.0271	.....	.....	.....
1.623	0.0272	0.3827	0.3656	0.0171
2.430	0.0275	0.4832	0.4658	0.0174
3.883	0.0277	0.5657	0.5573	0.0084
4.784	0.0284	.....	.....	.....

The minimum in the solubility curve is here at a much lower concentration of the solvent acid—about 0.2 *N*. The conductivity results, however, again closely resemble those of the corresponding hydrochloric acid system.

### The System C<sub>6</sub>H<sub>4</sub>OH.COOH : HCl : H<sub>2</sub>O.

This system has already been investigated by Kendall<sup>28</sup> and by Knox and Richards,<sup>29</sup> the results here presented are in fair agreement with their values. The experimental procedure was essentially that followed in the case of benzoic acid systems.

TABLE VI.—SALICYLIC ACID IN AQUEOUS HCl. SOLUBILITY AND CONDUCTIVITY DATA.

Normality of HCl soln.	Normality of dissolved salicylic acid.	Spec. cond. of HCl soln.	Spec. cond. of final solution.	Decrease due to salicylic acid.
0.0	0.0162 <sup>b</sup>	.....	.....	.....
0.500	0.0112	.....	.....	.....
1.180	0.0101	0.3162	0.3168	0.0006 <sup>a</sup>
1.848	0.00912	0.4119	0.4134	0.0015 <sup>a</sup>
2.498	0.00834	0.4749	0.4805	0.0056 <sup>a</sup>
3.308	0.00777	0.5234	0.5423	0.0189 <sup>a</sup>
4.410	0.00732	0.5808	0.6122	0.0314 <sup>a</sup>
7.172	0.00695	.....	.....	.....
9.522	0.00721	.....	.....	.....
11.73	0.00768	.....	.....	.....

<sup>a</sup> Increase in specific conductivity

<sup>b</sup> The previous values for the solubility in pure water are 0.01634 (Kendall) and 0.01613 (Knox and Richards).

A very flat minimum in the solubility curve is obtained at about 6.0 *N* hydrochloric acid; the conductivity results, however, differ from those of the previous tables in that an increase, instead of a decrease, is induced by the solute acid. This increase is negligible at low concentrations, but becomes very marked above 2.0 *N* hydrochloric acid.

### The System C<sub>6</sub>H<sub>4</sub>OH.COOH : HNO<sub>3</sub> : H<sub>2</sub>O.

The solubility curve for this system could not be carried very far, owing to rapid nitration of the salicylic acid at concentrations of nitric acid above 0.5 *N*.

<sup>28</sup> Kendall, *Proc. Roy. Soc.*, [A] **85**, 204 (1911).

<sup>29</sup> Knox and Richards, *loc. cit.*

TABLE VII.—SOLUBILITY OF SALICYLIC ACID IN AQUEOUS SOLUTIONS OF HNO<sub>3</sub>.

Normality of HNO <sub>3</sub> soln.	Normality of dissolved salicylic acid.	Normality of HNO <sub>3</sub> soln.	Normality of dissolved salicylic acid.
0.0	0.0162	0.2408	0.0141
0.0109	0.0149	0.5514	0.0150
0.0420	0.0140	1.019	0.0184
0.0807	0.0139	.....	.....

The minimum on the curve is here at a very low concentration of solvent acid—less than 0.1 *N* nitric acid. Above 0.5 *N* the results are only approximate, since the residues obtained were appreciably nitrated. For this reason no conductivity determinations were attempted on this system.

### Discussion of Solubility Results.

The solubility curves for a number of systems of the general type HX:HY:H<sub>2</sub>O are represented in Figs. 1, 2 and 3 below. In the first two diagrams the solvent acid is hydrochloric. The curves for the 4 solute

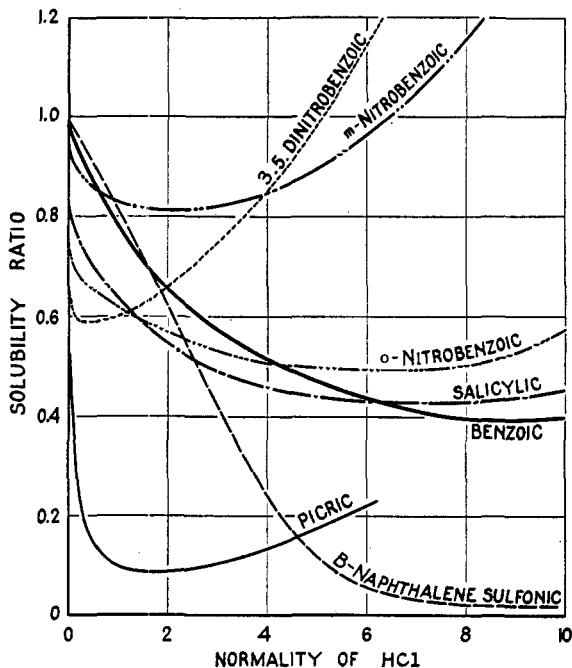


Fig. 1.

acids here investigated are shown, and a selection of the data from previous articles<sup>30</sup> has been added to assist in the discussion. In the third diagram

<sup>30</sup>Most of the data are due to Knox and Richards (*loc. cit.*). Results by Masson (*J. Chem. Soc.*, 101, 103 (1912)); Stepanov (*Ann.*, 373, 221 (1910)); Geffcken (*Z. physik. Chem.*, 49, 254 (1904)), and Herz (*Z. anorg. Chem.*, 34, 205 (1903)) are also included.

the solvent acid is acetic, a weak acid. To render all results directly comparable, the solubilities are expressed throughout as ratios of the solubility at any given concentration to the solubility in pure water.

At first glance it seems hopeless to attempt to draw any significant general conclusions from the course of the curves; they appear to run almost at random. Closer inspection, however, enables us to note the following facts.

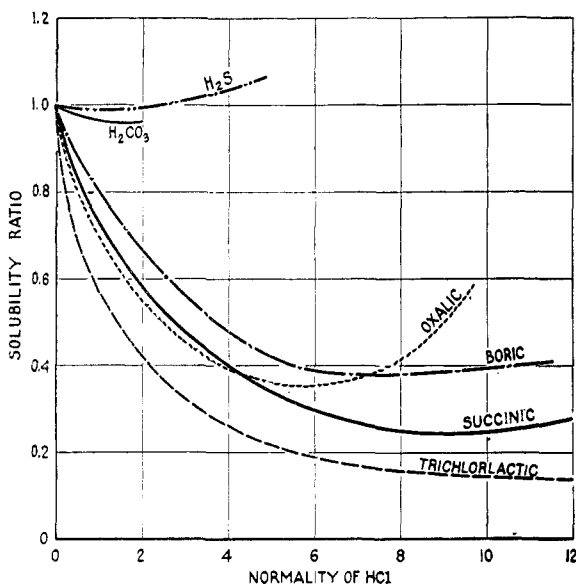


Fig. 2.

(1) When the solvent acid is strong, the sudden initial "ionic dip" in solubility is very marked in all cases except (a) when the solute acid is very weak, or (b) when the solute acid is very soluble in pure water. In Fig. 1 benzoic acid falls under (a),  $\beta$ -naphthalene sulfonic acid under (b). The remaining acids all show a very sharp solubility decrease when hydrochloric acid is first added. That this decrease is due to the suppression of their ionized fractions is evident from the variation in its magnitude as the strength of the solute acid is changed. Thus for picric acid the decline is exceedingly abrupt; it becomes less and less violent as we proceed through the weaker nitrobenzoic acids, until for benzoic acid it is almost absent. With this acid (see also succinic acid in Fig. 2) the solubility falls off regularly as the concentration of hydrochloric acid increases, there is only a trace of a sharp introductory drop. This is only natural, and since there is only a very small ionic portion to repress in such weak acids, inversely, the regularity of the decline in the case of the more soluble stronger acids (*e. g.*,  $\beta$ -naphthalene sulfonic in Fig. 1, oxalic and trichloro-

lactic in Fig. 2) is to be ascribed to the fact that their ionic concentrations in pure water are too high to be annihilated suddenly by small additions of hydrochloric acid: the suppression of their ionized fractions is consequently a gradual process.

(2) When the solvent acid is weak, the ionic dip is (as might be expected) much less frequently recognizable. In Fig. 3 oxalic acid shows a brief initial solubility decrease; more distinct evidence would, no doubt, be given by less soluble strong acids (*e.g.*, picric) in acetic acid solutions, but confirmatory experimental data are lacking.

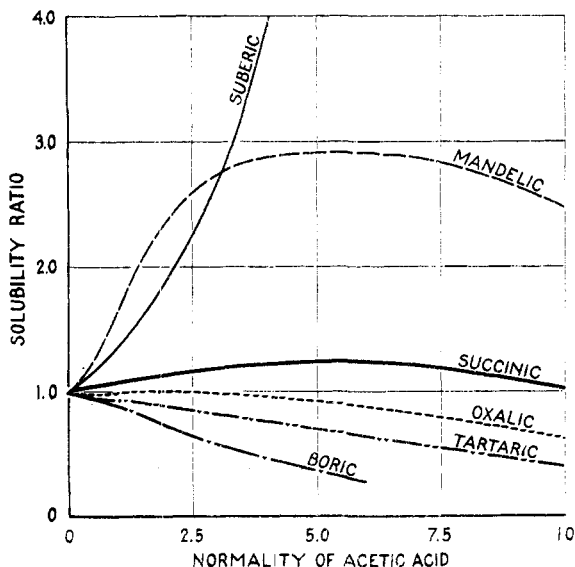


Fig. 3.

(3) When the solvent acid is strong, the decline in solubility persists in all cases well beyond the "constant undissociated value" postulated by Nernst. Thus the solubility ratios for weak acids such as boric acid and benzoic acid fall below 0.4 at high concentrations of hydrochloric acid, although their saturated solutions in pure water are only very slightly ionized. Similarly the solubilities of transition acids (*e.g.*, salicylic, *o*-nitrobenzoic) undergo an abnormal decrease, as indicated in a previous article,<sup>31</sup> while that for  $\beta$ -naphthalene sulfonic acid approaches very closely to zero. This characteristic in the curves must be ascribed to extensive hydration of the solvent acid (hydrochloric acid), as indicated in the introductory sections.<sup>32</sup>

<sup>31</sup> Kendall, *Proc. Roy. Soc.*, [A] 85, 217 (1911).

<sup>32</sup> The solubility of a weak base (ammonia) in water is similarly depressed to an abnormal extent on addition of a strong base (potassium or sodium hydroxide), as has been shown by Abegg and Riesenfeld (*Z. physik. Chem.*, 40, 84 (1902)). In the

(4) When the solvent acid is strong, the excessive decline is in all cases but one followed, at high concentrations, by an increase in solubility. The single exception is  $\beta$ -naphthalene sulfonic acid in hydrochloric acid; this must be regarded as a typical example of a system containing 2 strong acids.<sup>33</sup> The change in direction in all other systems<sup>34</sup> can be explained only on the basis of compound formation between the two acids present. Its late appearance indicates that such compounds are in general, highly dissociated in aqueous solution, but this again is only to be expected, since water is a competing base, stronger and present in much higher concentration. Hydration will therefore outbalance compound formation between the acids until the water concentration is considerably reduced. No connection can be established at present between the position or the sharpness of the minimum and the relative strengths of the two acids. We should anticipate that the weaker the solute acid the greater its tendency to combine with hydrochloric acid, but even such weak acids as hydrogen sulfide<sup>35</sup> and boric acid give a very flat minimum, while stronger acids such as 3,5-dinitrobenzoic and oxalic show a sharp turn in the curve. The very variable solubilities of the different solute acids in pure water certainly introduce complicating factors here for which it is difficult to correct,<sup>36</sup> and more work is evidently necessary to elucidate the irregularities exhibited.

(5) When the solvent acid is weak, the course of the curves is extremely variable (see Fig. 3). Changes in internal pressure and in the average molecular volume of the solvent here seem to be the predominant factors in affecting solubilities, so long as the solute acid is also weak. When the solute acid is strong, we should expect compound formation to be indicated by a rising portion on the solubility curve. Data for this type are, however, not very plentiful. Boric acid, which gives a falling curve in acetic acid solutions, does show steadily increasing solubility values with

same way, the solubility of a non-electrolyte in water is lowered by the presence of a hydrated second solute. Thus Gefcken (*ibid.*, 49, 268 (1904)) found the solubility of hydrogen to fall off rapidly in the presence of strong acids ( $H_2SO_4$ ,  $HNO_3$ ,  $HCl$ ). Transition acids (chloro-acetic) induce a smaller decrease; weak acids (acetic) have still less effect. Compare also Philip, *Trans. Faraday Soc.*, 3, 140 (1907).

<sup>33</sup> Other systems of a similar character, with the same type of curve, are  $HCl$  in  $H_2SO_4$  solutions (Coppadoro, *Gazz. chim. ital.*, II 39, 625 (1909)), and  $HIO_3$  in  $HNO_3$  solutions (Groschuff, *Z. anorg. Chem.*, 47, 344 (1905)).

<sup>34</sup> The curves given by the gaseous solutes are of substantially the same type as those given by solid acids. No marked difference in behavior, moreover, can be noted between inorganic and organic acids.

<sup>35</sup> Baume and Georgitses (*J. chim. phys.*, 12, 242 (1914)) did not isolate any compounds from the system  $HCl:H_2S$ , but found that a continuous series of solid solutions was formed.

<sup>36</sup> Compare Knox and Richards, *op. cit.*, p. 530.

stronger organic acids such as oxalic,<sup>37</sup> lactic<sup>38</sup> and tartaric,<sup>39</sup> but this may be due in the case of the last two acids to a special effect, as will appear in the following section.

### Discussion of Conductivity Results.

Compound formation between a weak acid and a strong acid in aqueous solution may be predicted to bring about a decrease in specific conductivity at the lower concentrations here examined,<sup>40</sup> since the mobilities of the ions of the resultant *salt*<sup>41</sup> will not equal those of the strong acid which have disappeared in its formation. At the higher concentrations, on the other hand, where the salt is produced mainly at the expense of non-ionized acid, the decrease will tend to diminish.

This anticipated behavior is actually realized in Tables II to V of this paper, *i. e.*, for solutions of boric and benzoic acids in hydrochloric and nitric acids. The specific conductivity changes in all 4 series, due to the presence of the dissolved weak acid, are substantially as described above. At low concentrations the decrease is roughly proportional to the product of the concentrations of the two acids. It reaches a maximum at approximately 2.0 *N* concentration of strong acid and subsequently exhibits declining values.

Not all of those systems, however, which indicate the existence of compound formation by the solubility curves give similar conductivity results. Thus the conductivity of hydrochloric acid solutions is unaffected, within the limits of experimental error, by the presence of hydrogen sulfide. In the same way, it was found that saturation of hydrochloric or nitric acid solutions with other gases of a weakly acidic nature—such as carbon dioxide or acetylene—involved no measurable change in their specific conductivities, although very careful determinations were made and all possible precautions taken to establish small variations.<sup>42</sup> No theoretical reason for this uniformity of negative results with gaseous solutes can at present be suggested.

<sup>37</sup> Herz, *Z. anorg. Chem.*, **66**, 93 (1910). Oxalic acid is also more soluble in boric acid solutions than in pure water.

<sup>38</sup> Mueller and Abegg, *Z. physik. Chem.*, **57**, 514 (1906).

<sup>39</sup> Herz, *Z. anorg. Chem.*, **70**, 71 (1911).

<sup>40</sup> At extremely low concentrations of strong acid, it must be noted, addition of the weak acid involves a small *increase* in specific conductivity, since its ionization will not be significantly repressed. This effect was confirmed for all systems at concentrations of HCl or HNO<sub>3</sub> below 0.005 *N*, but since the present discussion is restricted to much higher concentrations, further consideration of this point is not necessary here.

<sup>41</sup> That addition compounds of this type exhibit electrolytic dissociation in solution has been proved by Rördam, *THIS JOURNAL*, **37**, 557 (1915).

<sup>42</sup> At extremely low concentrations of the strong acid, as explained in the preceding note, a very small increase in specific conductivity is obtained. (Compare Whetham, *Z. physik. Chem.*, **55**, 200 (1906); Drucker, *Z. Elektrochem.*, **13**, 81 (1907)).

In solutions of salicylic acid in hydrochloric acid, an inverse effect— increase in specific conductivity—is actually apparent. If this increase were most noticeable at low concentrations of hydrochloric acid, it might be explained as due to the persistence of ionized salicylic acid in the solutions. At low concentrations, however, the effect is practically absent; it is only at higher concentrations of hydrochloric acid, where the concentration of salicylic acid has decreased far beyond its "constant undissociated value," that the increase in specific conductivity becomes appreciable. It becomes necessary, therefore, to seek an alternative explanation for the anomalous behavior of this system.

Magnanini<sup>43</sup> found that addition of small amounts of polyhydric alcohols increased the specific conductivity of boric acid solutions, owing to the formation of more readily ionized complexes. He also discovered that while addition of boric acid to aqueous solutions of organic acids caused no change in specific conductivity if these acids contained no hydroxyl group, yet a noticeable increase was obtained with aliphatic acids possessing an hydroxyl group in the  $\alpha$ -position and with aromatic acids possessing an hydroxyl group in the *ortho* position. More extensive investigations in this field have recently been made by Böeseken and his co-workers.<sup>44</sup> In view of their results, which indicate that the complexes formed by boric acid and suitable weak organic acids are comparable in strength with the strongest inorganic acids, it would seem logical to ascribe the increase here observed in the system salicylic acid (*o*-hydroxy-benzoic acid)—hydrochloric acid at high concentrations to the formation of an especially highly-ionized complex of a similar character. The examination of additional systems of this type by the conductivity method is obviously necessary, however, before final conclusions can be drawn.

Combination of solubility and conductivity data furnishes us, it may be noted, with a very strong method of attacking the question of the laws governing compound formation in systems of the type weak acid (solute): strong acid (solvent), here particularly studied. From the solubility results we can establish the effect of the strong acid on the weak acid, from the conductivity results the effect of the weak acid on the strong acid. The correlation of the data from sufficient systems should enable us, therefore, to obtain some insight into what is at present a very confused portion of the field of aqueous solutions. In all such investigations, however, the effect of the third component—water—upon all of the equilibria involved must, in addition, be much more intensively examined.

<sup>43</sup> Magnanini, *Gazz. chim. ital.*, **20**, 448 (1890); **21**, 215 (1891); **22**, 541 (1892); **23**, 197 (1893).

<sup>44</sup> Böeseken, *et al.*, *Rec. trav. chim.*, **35**, 211, 309 (1916) and subsequent papers.

### Summary.

The solubility curves for hydrogen sulfide, boric acid, benzoic acid and salicylic acid in aqueous solutions of hydrogen chloride, and for the last three of the above mentioned weak acids in aqueous solutions of nitric acid, have been determined. The changes in the specific conductivities of the solvent acids, due to the presence of the weak acids in solution, have also been investigated.

The results obtained, together with those of previous investigators, have been critically discussed in connection with the rule, established in an earlier article, that compound formation between acids in pairs increases in extent with increasing diversity of acidic strengths. The predicted and observed solubility curves for systems of various types have been compared, and satisfactory agreement, in general, has been obtained. The conductivity results also fall into line in most cases. Further experimental work, however, is required to elucidate certain abnormalities in particular systems. To establish the rules here outlined upon a final basis, a better understanding of the part played by the third component—water—is also necessary.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

## A MODIFIED METHOD FOR THE DETERMINATION OF IRON AND VANADIUM AFTER REDUCTION BY HYDROGEN SULFIDE.<sup>1</sup>

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### I. Introduction.

Some time ago the authors had occasion to determine whether uranyl compounds suffered reduction when their ammoniacal solutions were saturated with hydrogen sulfide and then slightly acidified with sulfuric acid and boiled. Experiments were accordingly carried out which demonstrated that while there was no reduction of uranium, some compound was formed in sufficient amount to consume appreciable quantities of a potassium permanganate solution. It was suspected that this reduction was occasioned by polythionic acids which had been formed during the course of the reactions and it was realized that if such was the case, the observation would be of importance in operations dealing with sulfide reductions in general and those of iron and vanadium in particular.

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.