

XXXVIII.—*The Basic Properties of Oxygen in Organic Acids and Phenols; and the Quadrivalency of Oxygen.*

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OXYGEN is usually regarded as a bivalent element in most compounds, but its position in Group VI of the Periodic Table affords good ground for the assumption that it may in certain cases have a higher valency from analogy to sulphur, selenium, and tellurium, all of which may function, not only as bivalent, but also as quadrivalent and sexavalent elements.

The quadrivalency of oxygen has been assumed from time to time to explain the constitution of certain compounds, a summary of the earlier assumptions of this nature being given by Walden (*Ber.*, 1901, **34**, 4185). The work of Collie and Tickle on

dimethylpyrone (T., 1899, **75**, 710), and of Baeyer and Villiger (*Ber.*, 1901, **34**, 2679; 1902, **35**, 1201), first drew general attention to the subject. The former were of the opinion that only in specially favourable cases could additive compounds containing quadrivalent oxygen be formed, but the latter showed that organic compounds of practically all classes containing oxygen, such as ethers, alcohols, aldehydes, ketones, etc., could combine with acids to give crystalline salts. Since that time, many similar assumptions of the quadrivalency of oxygen have been made, for example, by Bülow and Sicherer for salts of anhydrobenzopyranols and benzopyranols (*Ber.*, 1901, **34**, 3916), by Kehrmann and Mattisson for salts of phenanthraquinone (*Ber.*, 1902, **35**, 343), by Willstätter and Pummerer for compounds of pyrone with acids (*Ber.*, 1904, **37**, 3740), by Farmer for acid salts of monobasic acids (T., 1903, **83**, 1440), by Cohen and Gatecliff for compounds of ethers with nitric acid (P., 1904, **20**, 194; but see also McIntosh, *J. Amer. Chem. Soc.*, 1905, **27**, 1013), by Blaise for compounds of magnesium iodide and zinc iodide with ethers (*Compt. rend.*, 1904, **139**, 1211; 1905, **140**, 661), and by Meyer for salt-like compounds of quinones with acids (*Ber.*, 1908, **41**, 2568).

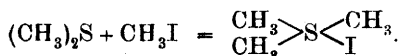
Much work on this subject has been done by McIntosh and his collaborators, who have prepared additive compounds of ethers, alcohols, aldehydes, ketones, etc., with halogens and anhydrous halogen hydrides (T., 1904, **85**, 919, 1098; 1905, **87**, 784; *J. Amer. Chem. Soc.*, 1905, **27**, 26, 1013; 1906, **28**, 588; 1908, **30**, 1097; 1910, **32**, 542, 1330; 1911, **33**, 70; 1912, **34**, 1273).

Fewer instances have been recorded of the formation of additive compounds of organic acids and phenols with other acids. Baeyer and Villiger obtained no crystalline compounds of acids with acids (*Ber.*, 1901, **34**, 2692). Hoogewerff and van Dorp, however, prepared additive products of sulphuric acid with various organic acids, and of phenols with phosphoric acid (*Rec. trav. chim.*, 1899, **18**, 211; 1902, **21**, 349). Maass and McIntosh obtained a compound of benzoic acid with hydrogen bromide, and of resorcinol with hydrogen bromide and hydrogen chloride (*J. Amer. Chem. Soc.*, 1911, **33**, 70). Pfeiffer also has prepared a number of compounds of organic acids with acids (*Ber.*, 1914, **47**, 1593), and in a recent series of papers Kendall has described the isolation, by the freezing-point method, of additive compounds of organic acids in pairs, of organic acids and phenols with sulphuric acid, and of phenols with organic acids (*J. Amer. Chem. Soc.*, 1914, **36**, 1722, 2498; 1916, **38**, 1309).

It will be seen that the organic compounds which form these

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additive products are of the most diverse types. In practically all the cases cited, the organic compound is combined with an acid, forming an unstable additive compound, so that evidently the compound formation is due to basic properties in oxygen of higher valency than two. These additive compounds are generally regarded as "oxonium" compounds, containing quadrivalent oxygen, derived from the hypothetical base $\text{H}_3\text{O}\cdot\text{OH}$, analogous to the sulphonium compounds formed by the passage of sulphur from bivalency to quadrivalency. A typical example is Friedel's dimethyl ether hydrochloride (*Bull. Soc. chim.*, 1875, [ii], **24**, 160): $(\text{CH}_3)_2\text{O} + \text{HCl} = \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} \text{O} \begin{matrix} \text{H} \\ \text{Cl} \end{matrix}$, the analogy of which to a sulphonium compound is evident:



The sulphonium salts are derivatives of the strongly basic sulphonium hydroxide, $\text{R}_3\text{S}\cdot\text{OH}$, so that in the salt-like character of the oxonium compounds, and the basic properties of quadrivalent oxygen, there is a parallel in the case of well-known sulphur compounds.

To explain the formation of these additive compounds, special kinds of valencies of oxygen have from time to time been assumed—crypto-valencies, complex valencies, residual affinities. In view of the fact, however, that oxygen may exhibit a higher valency than two in the ordinarily accepted sense, there seems to be no reason to assign special kinds of valencies to oxygen, any more than to sulphur or the other elements of the same group.

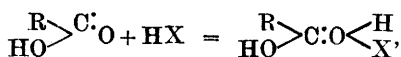
The additive products of organic oxygen compounds with acids have mainly been isolated in the solid state, and very little work has been done on the investigation of these compounds in solution. The compounds are all more or less unstable, and for the most part are decomposed by water into their original constituents. Farmer, for instance, could find no evidence for the existence of acid salts in solution (T., 1903, **83**, 1440), but there is evidence to show that oxonium compounds do exist to a certain extent, at least, in solution. Thus Maass and McIntosh (*J. Amer. Chem. Soc.*, 1913, **35**, 535), by a study of the conductivity measurements of the two component systems—hydrochloric acid and ethyl ether, hydrochloric acid and methyl ether, hydrochloric acid and ethyl alcohol, hydrochloric acid and methyl alcohol—showed the probability of the existence of the compounds in solution. Rørdam (*J. Amer. Chem. Soc.*, 1915, **37**, 557), by comparing the conductivity of a solution

of dimethylpyrone hydrochloride with that of a solution of hydrochloric acid with the same concentration of chlorine ions, electrometrically measured, proved that dimethylpyrone hydrochloride is a real salt showing electrolytic dissociation as well as hydrolytic dissociation into its components. Schuncke (*Zeitsch. physikal. Chem.*, 1894, **14**, 331) found that the solubility of ether is greater in hydrochloric acid solutions than in water, and increases with the concentration of the hydrochloric acid, and Jüttner (*Zeitsch. physikal. Chem.*, 1901, **38**, 56) gave as the reason the formation of ether hydrochloride in solution. Similarly, Sackur (*Ber.*, 1902, **35**, 1242) found that the solubility of cineole increases in hydrochloric, nitric, and acetic acid solutions.

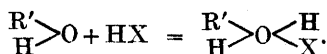
It is possible, therefore, that the existence of other oxonium compounds in solution may be shown by solubility determinations. If additive compounds of organic acids with acids exist in solution, we should expect to find some influence of this salt-formation on the solubility of the organic acid in solutions of the other acids. If no such disturbing influence comes into play, the solubility of the organic acid should continuously diminish with increasing concentration of the solvent acid, in accordance with the law that the solubility of an electrolyte is diminished by the addition of another electrolyte with a common ion.

A few instances have actually been recorded where organic acids do not obey this law. Thus, Herz (*Zeitsch. anorg. Chem.*, 1910, **66**, 93) found that for solutions of oxalic acid in boric acid the solubility increases continuously with the concentration of the boric acid. Stépanov (*Annalen*, 1910, **373**, 221) found that for picric acid in hydrochloric acid solutions the solubility diminishes to a certain point, after which it begins to increase. Masson (*T.*, 1912, **101**, 103) found a similar result for solutions of oxalic acid in hydrochloric and nitric acid solutions.

It seems very probable that these cases may be instances of a general phenomenon, and that the unexpected results obtained for the solubility curves are caused by the existence in solution of an oxonium compound, formed by direct addition of the ions of the solvent acid to an oxygen atom of the organic acid, according to the equation



or, for phenols,



This assumption would be sufficient to account for the observed results. At first with a strong solvent acid, such as hydrochloric or nitric, the effect of the common hydrogen ion prevails, and the solubility diminishes. With increasing concentration of the solvent acid, however, the influence of the formation of the more readily soluble salt becomes stronger, and the solubility reaches a minimum, and finally begins to increase. If the solvent acid is weak, for example, boric acid, the initial decrease may be too small to be measurable; hence the only perceptible effect would be the continuous increase observed by Herz.

If the true explanation of the results observed by Herz, Stépanov, and Masson is the formation of an oxonium compound in solution, we should expect other organic acids to behave in a similar manner, and the present investigation serves to prove that this is actually the case.

EXPERIMENTAL.

I. *Acids.*

The solubilities of a number of organic acids of practically all classes have been determined in solutions of other acids. The number of organic acids which could be used was greatly limited by the lack of suitable methods of analysis. Many of the commonest acids could not be employed, since no sufficiently accurate method is known for their estimation, or since, even at the ordinary temperature, they volatilise from solution on evaporation. Much time was spent in testing various analytical methods given in the literature for a large number of acids, and in determining whether the acids volatilised from solution on evaporation. Amino-acids were avoided, as the presence of the basic amino-group might lead to the formation of salts of the ammonium type. In most cases, the solvent acid is hydrochloric, but experiments have also been performed in nitric, sulphuric, acetic, formic, and lactic acids.

The following series have been investigated :

Monobasic Acids.—Phenylacetic, diphenylacetic, benzilic, *o*-nitrobenzoic, *m*-nitrobenzoic, 3:5-dinitrobenzoic, cinnamic, diphenylene-glycollic, trichlorolactic, mandelic, diphenic, and salicylic acids in hydrochloric acid solutions; trichlorolactic acid in sulphuric acid; mandelic acid in sulphuric, acetic, and formic acids.

Dibasic Acids.—Malonic acid in hydrochloric and sulphuric acids; oxalic acid in sulphuric, acetic, formic, and lactic acids;

phthalic acid in hydrochloric and nitric acids; suberic acid in hydrochloric, nitric, sulphuric, and acetic acids; succinic acid in hydrochloric, nitric, sulphuric, acetic, and formic acids; and tartaric acid in hydrochloric, sulphuric, and acetic acids.

Tribasic Acid.—Citric acid in hydrochloric and sulphuric acids.

Method.—The solubilities were determined at 25°, excess of the solid being shaken for several days in a thermostat with solutions of the solvent acid of varying concentration. After saturation, the clear solution was analysed both for dissolved and solvent acid by one of the following methods:

(1) Solvent acid determined gravimetrically; dissolved acid by direct weighing after evaporation in a vacuum over soda-lime.

This method was used for most of the sparingly soluble acids in hydrochloric acid solutions.

(2) Total acidity determined by titration with standard sodium hydroxide; dissolved acid by weighing after evaporation either (a) in a vacuum, or (b) on the steam-bath; solvent acid by difference.

This method was used for nitric, acetic, and formic, and in a few cases for hydrochloric, acid solutions.

(3) Total acidity by titration; solvent acid gravimetrically; dissolved acid by difference.

Sulphuric acid solutions were analysed by this method, also cases of acids very readily soluble in hydrochloric acid.

(4) Permanganate methods for oxalic acid solutions: total acidity by alkali; oxalic acid by potassium permanganate, either (a) directly, in sulphuric acid solutions, or (b) after precipitation as calcium oxalate in other cases; solvent acid by difference.

Where an evaporation method was used, a preliminary test was made to ascertain whether the organic acid was left unchanged after evaporation from a solution in the solvent acid.

The results of the various experiments are given in the following tables. The method of analysis is indicated in each case by a number corresponding with the above arrangement, and reference is made to the diagram in which the corresponding solubility curve is to be found. In all cases, the concentrations of the acids are expressed in equivalent normalities.

(1) *Phenylacetic Acid in Hydrochloric Acid. Method 1. Fig. 1.*

HCl.....	0	1.417	2.890	4.313	5.770	7.175	8.590	9.988	11.36
C ₈ H ₈ O ₂	0.1310	0.0884	0.0833	0.0763	0.0739	0.0756	0.0815	0.0916	0.1099

(2) *Diphenylacetic Acid in Hydrochloric Acid. Method 2(b).*

HCl.....	0	1.620	2.913	4.512	5.973	7.349	8.889	10.27	11.74
C ₁₄ H ₁₂ O ₂	0.00060	0.00047	0.00040	0.00036	0.00038	0.00041	0.00042	0.00046	0.00053

(3) *Benzilic Acid in Hydrochloric Acid. Method 2(b).*

HCl.....	0	1.537	2.977	4.440	5.934	7.356	8.803	10.25	11.69
C ₁₄ H ₁₂ O ₃	0.00769	0.00332	0.00233	0.00182	0.00172	0.00150	0.00167	0.00195	0.00217

(4) *o-Nitrobenzoic Acid in Hydrochloric Acid.* Method 1.*

HCl.....	0	1.314	2.607	3.909	5.013	6.509	7.795	9.080	10.30
C ₇ H ₅ O ₄ N	0.0470	0.0280	0.0256	0.0239	0.0235	0.0233	0.0237	0.0250	0.0267

(5) *m-Nitrobenzoic Acid in Hydrochloric Acid. Method 1.*

HCl.....	0	1.416	3.310	4.308	5.953	7.044	8.380	9.793	11.54
C ₇ H ₅ O ₄ N	0.0214	0.0175	0.0178	0.0183	0.0205	0.0225	0.0256	0.0293	0.0368

* It may be mentioned that Kendall (*Proc. Roy. Soc.*, 1911, [A], 85, 200) gives results for the solubilities of *o*-nitrobenzoic acid, and salicylic acid, in hydrochloric acid solutions; but with the low concentrations of hydrochloric acid used in his experiments, only the decrease in solubility is observed.

(6) 3:5-Dinitrobenzoic Acid in Hydrochloric Acid. Method 2(b)

HCl.....	0	1.565	2.908	4.594	5.657	7.336	8.855	10.27	11.73
C ₇ H ₄ O ₆ N ₂	0.00635	0.00398	0.00470	0.00583	0.00690	0.00841	0.00965	0.01095	0.01240

(7) Cinnamic Acid in Hydrochloric Acid. Method 1.

HCl.....	0	2.100	4.174	6.250	8.007	10.29	10.47
C ₉ H ₈ O ₂	0.00385	0.00283	0.00272	0.00318	0.00400	0.00556	0.00572

(8) Diphenylglycollic Acid in Hydrochloric Acid. Method 2(b).

HCl.....	0	1.952	3.907	5.843	7.745
C ₁₄ H ₁₀ O ₃	0.01082	0.00492	0.00355	0.00343	0.00352

(9) Trichlorolactic Acid in Hydrochloric Acid. Method 3.

HCl.....	0	1.234	2.837	4.388	5.982	7.675	8.959	10.65	11.86	12.17
C ₃ H ₃ O ₃ Cl ₃	4.024	2.545	1.425	0.984	0.760	0.659	0.624	0.57	0.57	0.60

(10) Trichlorolactic Acid in Sulphuric Acid. Method 3.

H ₂ SO ₄	0	2.525	6.166	9.588	12.75	16.28	19.38	22.28	25.34
C ₃ H ₃ O ₃ Cl ₃	4.024	1.896	0.671	0.353	0.26	0.15	0.18	0.21	0.26

(11) Salicylic Acid in Hydrochloric Acid.* Method 1.

HCl.....	0	1.459	3.057	4.374	6.164	7.311	8.730	10.20	11.54	12.20
C ₇ H ₆ O ₃	0.01613	0.00982	0.00822	0.00715	0.00654	0.00656	0.00666	0.00710	0.00794	0.00856

* See footnote on preceding page.

(12) *Diphenic Acid in Hydrochloric Acid, Method 2(b).*

HCl	0	2.103	3.985	5.928	7.748
C ₁₄ H ₁₀ O ₄	0.00520	0.00182	0.00144	0.00112	0.00118

(13) *Mandelic Acid in Hydrochloric Acid, Method 1, Fig. 2.*

HCl	0	1.202	2.481	3.753	5.017	6.271	7.523	8.748	9.937	10.35
C ₈ H ₈ O ₃	1.191	0.691	0.488	0.387	0.332	0.307	0.302	0.316	0.353	0.375

(14) *Mandelic Acid in Sulphuric Acid, Method 3, Fig. 2.*

H ₂ SO ₄	0	2.695	5.390	8.294	11.05	13.62	16.50	18.89	21.17
C ₈ H ₈ O ₃	1.191	0.484	0.278	0.186	0.18	0.18	0.16	0.23	0.27

(15) *Mandelic Acid in Acetic Acid, Method 2(a), Fig. 2.*

C ₂ H ₄ O ₂	0	0.870	1.338	1.860	2.618	3.644	4.249	4.738	6.485	8.60	9.85	12.30
C ₈ H ₈ O ₃	1.191	1.808	2.312	2.664	3.186	3.444	3.472	3.487	3.509	3.234	2.996	2.178

(16) *Mandelic Acid in Formic Acid, Method 2(a), Fig. 2.*

CH ₂ O ₂	0	2.268	4.340	6.320	8.09	10.38	12.20	13.41	13.78
C ₈ H ₈ O ₃	1.191	1.768	2.180	2.383	2.430	2.434	2.525	2.750	3.327

(17) *Malonic Acid in Hydrochloric Acid, Method 3, Fig. 3.*

HCl	0	4.443	6.210	8.658	10.47	11.09	11.22
C ₃ H ₄ O ₄	15.01	7.70	5.99	4.71	4.32	4.26	4.30

(18) *Malonic Acid in Sulphuric Acid, Method 3, Fig. 3.*

H_2SO_4	0	2.727	7.050	11.76	16.05	19.92	21.84
$\text{C}_3\text{H}_4\text{O}_4$	15.01	11.44	6.79	4.07	3.01	3.20	4.55

(19) *Oxalic Acid in Sulphuric Acid, Method 4(a), Fig. 4.*

H_2SO_4	0	2.187	4.524	6.835	9.225	11.45	13.63	15.57	17.15
$\text{C}_2\text{H}_2\text{O}_4$	2.409	1.519	1.057	0.791	0.675	0.691	0.830	1.157	1.804

(20) *Oxalic Acid in Lactic Acid, Method 4(b), Fig. 4.*

$\text{C}_3\text{H}_6\text{O}_3$	0	1.337	2.718	4.051	5.357	6.477	7.647	8.709	9.52
$\text{C}_2\text{H}_2\text{O}_4$	2.409	2.228	2.054	1.856	1.633	1.412	1.171	0.938	0.832

(21) *Oxalic Acid in Formic Acid, Method 4(b), Fig. 4.*

CH_2O_2	0	0.097	0.437	0.967	1.287	1.825	2.678	3.360	4.13	4.90	5.68	6.45	7.22	8.00	8.77	9.55	10.32	11.10	11.87	12.65	13.42	14.20	14.97	15.75	16.52	17.30	18.07	18.85	19.62	20.40	21.17	21.95	22.72	23.50	24.27	25.05	25.82	26.60	27.37	28.15	28.92	29.70	30.47	31.25	32.02	32.80	33.57	34.35	35.12	35.90	36.67	37.45	38.22	39.00	39.77	40.55	41.32	42.10	42.87	43.65	44.42	45.20	45.97	46.75	47.52	48.30	49.07	49.85	50.62	51.40	52.17	52.95	53.72	54.50	55.27	56.05	56.82	57.60	58.37	59.15	59.92	60.70	61.47	62.25	63.02	63.80	64.57	65.35	66.12	66.90	67.67	68.45	69.22	70.00	70.77	71.55	72.32	73.10	73.87	74.65	75.42	76.20	76.97	77.75	78.52	79.30	80.07	80.85	81.62	82.40	83.17	83.95	84.72	85.50	86.27	87.05	87.82	88.60	89.37	90.15	90.92	91.70	92.47	93.25	94.02	94.80	95.57	96.35	97.12	97.90	98.67	99.45	100.22	101.00	101.77	102.55	103.32	104.10	104.87	105.65	106.42	107.20	107.97	108.75	109.52	110.30	111.07	111.85	112.62	113.40	114.17	114.95	115.72	116.50	117.27	118.05	118.82	119.60	120.37	121.15	121.92	122.70	123.47	124.25	125.02	125.80	126.57	127.35	128.12	128.90	129.67	130.45	131.22	132.00	132.77	133.55	134.32	135.10	135.87	136.65	137.42	138.20	138.97	139.75	140.52	141.30	142.07	142.85	143.62	144.40	145.17	145.95	146.72	147.50	148.27	149.05	149.82	150.60	151.37	152.15	152.92	153.70	154.47	155.25	156.02	156.80	157.57	158.35	159.12	159.90	160.67	161.45	162.22	163.00	163.77	164.55	165.32	166.10	166.87	167.65	168.42	169.20	170.00	170.77	171.55	172.32	173.10	173.87	174.65	175.42	176.20	176.97	177.75	178.52	179.30	180.07	180.85	181.62	182.40	183.17	183.95	184.72	185.50	186.27	187.05	187.82	188.60	189.37	190.15	190.92	191.70	192.47	193.25	194.02	194.80	195.57	196.35	197.12	197.90	198.67	199.45	200.22	201.00	201.77	202.55	203.32	204.10	204.87	205.65	206.42	207.20	207.97	208.75	209.52	210.30	211.07	211.85	212.62	213.40	214.17	214.95	215.72	216.50	217.27	218.05	218.82	219.60	220.37	221.15	221.92	222.70	223.47	224.25	225.02	225.80	226.57	227.35	228.12	228.90	229.67	230.45	231.22	232.00	232.77	233.55	234.32	235.10	235.87	236.65	237.42	238.20	238.97	239.75	240.52	241.30	242.07	242.85	243.62	244.40	245.17	245.95	246.72	247.50	248.27	249.05	249.82	250.60	251.37	252.15	252.92	253.70	254.47	255.25	256.02	256.80	257.57	258.35	259.12	259.90	260.67	261.45	262.22	263.00	263.77	264.55	265.32	266.10	266.87	267.65	268.42	269.20	270.00	270.77	271.55	272.32	273.10	273.87	274.65	275.42	276.20	276.97	277.75	278.52	279.30	280.07	280.85	281.62	282.40	283.17	283.95	284.72	285.50	286.27	287.05	287.82	288.60	289.37	290.15	290.92	291.70	292.47	293.25	294.02	294.80	295.57	296.35	297.12	297.90	298.67	299.45	300.22	301.00	301.77	302.55	303.32	304.10	304.87	305.65	306.42	307.20	307.97	308.75	309.52	310.30	311.07	311.85	312.62	313.40	314.17	314.95	315.72	316.50	317.27	318.05	318.82	319.60	320.37	321.15	321.92	322.70	323.47	324.25	325.02	325.80	326.57	327.35	328.12	328.90	329.67	330.45	331.22	332.00	332.77	333.55	334.32	335.10	335.87	336.65	337.42	338.20	338.97	339.75	340.52	341.30	342.07	342.85	343.62	344.40	345.17	345.95	346.72	347.50	348.27	349.05	349.82	350.60	351.37	352.15	352.92	353.70	354.47	355.25	356.02	356.80	357.57	358.35	359.12	359.90	360.67	361.45	362.22	363.00	363.77	364.55	365.32	366.10	366.87	367.65	368.42	369.20	370.00	370.77	371.55	372.32	373.10	373.87	374.65	375.42	376.20	376.97	377.75	378.52	379.30	380.07	380.85	381.62	382.40	383.17	383.95	384.72	385.50	386.27	387.05	387.82	388.60	389.37	390.15	390.92	391.70	392.47	393.25	394.02	394.80	395.57	396.35	397.12	397.90	398.67	399.45	400.22	401.00	401.77	402.55	403.32	404.10	404.87	405.65	406.42	407.20	407.97	408.75	409.52	410.30	411.07	411.85	412.62	413.40	414.17	414.95	415.72	416.50	417.27	418.05	418.82	419.60	420.37	421.15	421.92	422.70	423.47	424.25	425.02	425.80	426.57	427.35	428.12	428.90	429.67	430.45	431.22	432.00	432.77	433.55	434.32	435.10	435.87	436.65	437.42	438.20	438.97	439.75	440.52	441.30	442.07	442.85	443.62	444.40	445.17	445.95	446.72	447.50	448.27	449.05	449.82	450.60	451.37	452.15	452.92	453.70	454.47	455.25	456.02	456.80	457.57	458.35	459.12	459.90	460.67	461.45	462.22	463.00	463.77	464.55	465.32	466.10	466.87	467.65	468.42	469.20	470.00	470.77	471.55	472.32	473.10	473.87	474.65	475.42	476.20	476.97	477.75	478.52	479.30	480.07	480.85	481.62	482.40	483.17	483.95	484.72	485.50	486.27	487.05	487.82	488.60	489.37	490.15	490.92	491.70	492.47	493.25	494.02	494.80	495.57	496.35	497.12	497.90	498.67	499.45	500.22	501.00	501.77	502.55	503.32	504.10	504.87	505.65	506.42	507.20	507.97	508.75	509.52	510.30	511.07	511.85	512.62	513.40	514.17	514.95	515.72	516.50	517.27	518.05	518.82	519.60	520.37	521.15	521.92	522.70	523.47	524.25	525.02	525.80	526.57	527.35	528.12	528.90	529.67	530.45	531.22	532.00	532.77	533.55	534.32	535.10	535.87	536.65	537.42	538.20	538.97	539.75	540.52	541.30	542.07	542.85	543.62	544.40	545.17	545.95	546.72	547.50	548.27	549.05	549.82	550.60	551.37	552.15	552.92	553.70	554.47	555.25	556.02	556.80	557.57	558.35	559.12	559.90	560.67	561.45	562.22	563.00	563.77	564.55	565.32	566.10	566.87	567.65	568.42	569.20	570.00	570.77	571.55	572.32	573.10	573.87	574.65	575.42	576.20	576.97	577.75	578.52	579.30	580.07	580.85	581.62	582.40	583.17	583.95	584.72	585.50	586.27	587.05	587.82	588.60	589.37	590.15	590.92	591.70	592.47	593.25	594.02	594.80	595.57	596.35	597.12	597.90	598.67	599.45	600.22	601.00	601.77	602.55	603.32	604.10	604.87	605.65	606.42	607.20	607.97	608.75	609.52	610.30	611.07	611.85	612.62	613.40	614.17	614.95	615.72	616.50	617.27	618.05	618.82	619.60	620.37	621.15	621.92	622.70	623.47	624.25	625.02	625.80	626.57	627.35	628.12	628.90	629.67	630.45	631.22	632.00	632.77	633.55	634.32	635.10	635.87	636.65	637.42	638.20	638.97	639.75	640.52	641.30	642.07	642.85	643.62	644.40	645.17	645.95	646.72	647.50	648.27	649.05	649.82	650.60	651.37	652.15	652.92	653.70	654.47	655.25	656.02	656.80	657.57	658.35	659.12	659.90	660.67	661.45	662.22	663.00	663.77	664.55	665.32	666.10	666.87	667.65	668.42	669.20	670.00	670.77	671.55	672.32	673.10	673.87	674.65	675.42	676.20	676.97	677.75	678.52	679.30	680.07	680.85	681.62	682.40	683.17	683.95	684.72	685.50	686.27	687.05	687.82	688.60	689.37	690.15	690.92	691.70	692.47	693.25	694.02	694.80	695.57	696.35	697.12	697.90	698.67	699.45	700.22	701.00	701.77	702.55	703.32	704.10	704.87	705.65	706.42	707.20	707.97	708.75	709.52	710.30	711.07	711.85	712.62	713.40	714.17	714.95	715.72	716.50	717.27	718.05	718.82	719.60	720.37	721.15	721.92	722.70	723.47	724.25
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(24) *Phthalic Acid in Nitric Acid, Method 2(a).*

HNO_3	0	2.077	4.077	6.718	9.027	10.40	12.60	14.42	15.99
$\text{C}_6\text{H}_6\text{O}_4$	0.0852	0.0582	0.0470	0.0375	0.0331	0.0325	0.0350	0.0420	0.0577

(25) *Suberic Acid in Hydrochloric Acid, Method 1, Fig. 1.*

HCl	0	1.423	2.858	4.281	5.691	7.130	8.378	9.865	11.20
$\text{C}_8\text{H}_{14}\text{O}_4$	0.0680	0.0498	0.0428	0.0412	0.0432	0.0504	0.0633	0.0905	0.1370

(26) *Suberic Acid in Nitric Acid, Method 2(a).*

HNO_3	0	0.307	0.555	0.906	1.543	2.021	4.035	5.749	8.091	10.05	11.77	13.30
$\text{C}_8\text{H}_{14}\text{O}_4$	0.0680	0.0594	0.0590	0.0634	0.0695	0.0839	0.0999	0.1133	0.1575	0.2231	0.3896	0.6049

(27) *Suberic Acid in Sulphuric Acid, Method 3.*

H_2SO_4	0	1.858	5.233	7.524	11.33	18.65
$\text{C}_8\text{H}_{14}\text{O}_4$	0.068	0.039	0.037	0.042	0.06	0.20

(28) *Suberic Acid in Acetic Acid, Method 2(a).*

$\text{C}_2\text{H}_4\text{O}_2$	0	0.435	0.887	2.112	4.262	6.350	8.402
$\text{C}_8\text{H}_{14}\text{O}_4$	0.0680	0.0776	0.0902	0.1340	0.2891	0.4317	0.5846

(29) *Succinic Acid in Hydrochloric Acid, Method 1, Fig. 5.*

HCl	0	2.751	5.964	7.335	8.950	9.732	10.40	11.98
$\text{C}_4\text{H}_6\text{O}_4$	1.352	0.681	0.402	0.353	0.333	0.328	0.337	0.378

(30) <i>Succinic Acid in Nitric Acid. Method 2(a). Fig. 5.</i>												
	0	1.299	3.034	5.236	6.616	9.710	11.11	13.51	15.43			
HNO ₃	1.352	1.134	0.941	0.724	0.652	0.528	0.518	0.561	0.731			
C ₄ H ₆ O ₄												
(31) <i>Succinic Acid in Sulphuric Acid. Method 3. Fig. 5.</i>												
	0	1.981	3.816	4.926	8.122	10.22	13.81	17.05	23.18			
H ₂ SO ₄	1.352	0.908	0.683	0.563	0.388	0.34	0.30	0.30	0.39	0.28	0.39	0.69
C ₄ H ₆ O ₄												
(32) <i>Succinic Acid in Acetic Acid. Method 2(a). Fig. 5.</i>												
	0	0.078	0.448	0.916	2.828	4.536	6.655	8.661	10.34	12.40	14.64	16.85
C ₂ H ₄ O ₂	1.352	1.384	1.415	1.452	1.592	1.643	1.639	1.519	1.357	1.097	0.797	0.514
C ₄ H ₆ O ₄												
(33) <i>Succinic Acid in Formic Acid. Method 2(a). Fig. 5.</i>												
	0	0.090	0.446	0.930	3.730	5.547	7.500	11.29	15.29	17.67	19.16	20.53
CH ₂ O ₂	1.352	1.369	1.408	1.501	1.531	1.449	1.228	0.944	0.796	0.715	0.667	0.604
C ₄ H ₆ O ₄												
(34) <i>Tartaric Acid in Hydrochloric Acid. Method 3. Fig. 6.</i>												
	0	1.257	2.568	4.466	6.303	8.144	9.890	10.51	11.17			
HCl	10.26	8.528	7.092	5.434	4.35	3.77	3.43	3.42	3.42			
C ₄ H ₆ O ₆												

(35) *Tartaric Acid in Sulphuric Acid, Method 3, Fig. 6.*

H_2SO_4	0	1.798	4.043	6.807	9.895	12.54	15.46	18.10	19.85	22.17
$\text{C}_4\text{H}_6\text{O}_6$	10.26	8.51	6.64	4.73	3.18	2.43	1.95	1.77	1.86	2.74

(36) *Tartaric Acid in Acetic Acid, Method 2(a), Fig. 6.*

$\text{C}_2\text{H}_4\text{O}_2$	0	0.25	0.60	1.23	2.63	4.24	6.12	8.30	10.89	14.14	16.92
$\text{C}_4\text{H}_6\text{O}_6$	10.26	10.09	9.875	9.515	8.717	7.718	6.548	5.151	3.505	1.594	0.344

(37) *Citric Acid in Hydrochloric Acid, Method 3.*

HCl	0	0.949	2.189	3.795	5.718	7.736	9.635	10.36	11.09	3.29
$\text{C}_6\text{H}_8\text{O}_7$	12.54	11.03	9.30	7.36	5.38	4.09	3.46	3.35		

(38) *Citric Acid in Sulphuric Acid, Method 3.*

H_2SO_4	0	1.689	4.206	7.145	10.83	11.46	14.24	18.18	20.59	22.37
$\text{C}_6\text{H}_8\text{O}_7$	12.54	10.57	7.97	5.61	3.28	3.07	2.23	1.76	2.00	2.88

(39) *p-Nitrophenol in Hydrochloric Acid, Method 5(a), Fig. 7.*

HCl	0	1.650	3.277	4.993	6.552	8.196	9.817	11.29		
$\text{C}_6\text{H}_5\text{O}_2\text{N}$	0.1097	0.0962	0.0913	0.0934	0.0990	0.1093	0.1230	0.1421		

(40) *m*-Nitrophenol in Hydrochloric Acid. Method 5(a). Fig. 7.

HCl	0	1.925	3.822	5.720	7.550	9.213	10.96	11.20
C ₆ H ₅ O ₂ N	0.0974*	0.0849	0.0834	0.0885	0.1009	0.1130	0.1284	0.1307

(41) Picric Acid in Nitric Acid. Method 6(b).

HNO ₃	0	1.022	2.059	4.161	6.289	8.334	10.47	12.47	14.29
C ₆ H ₃ O ₃ N ₃	0.0578	0.0108	0.0124	0.0237	0.0405	0.0612	0.1006	0.1763	0.3533

(42) β -Naphthol in Hydrochloric Acid. Method 5(a).

HCl	0	1.466	2.952	4.343	5.785	7.122	8.674	11.47
C ₁₀ H ₈ O	0.00524	0.00410	0.00360	0.00333	0.00319	0.00316	0.00307	0.00341

(43) Resorcinol in Hydrochloric Acid. Method 5(a).

HCl	0	0.656	1.671	3.410	4.402	6.076	7.567	9.157	11.31
C ₆ H ₆ O ₂	6.515	5.705	4.570	3.020	2.307	1.616	1.287	1.125	1.118

* It may be remarked that the value found for the solubility of *m*-nitrophenol in water differs considerably from that given by Vaubel (*J. pr. Chem.*, 1895, [ii], 52, 73), but as no definite particulars are given of the method employed, or of the source of his result, it cannot be regarded as very trustworthy. The compound used in the present case, which was prepared from *m*-nitroaniline, was recrystallised from water, and melted at 96—97°.

(44) *Quinol in Hydrochloric Acid. Method 5(a).*

HCl	0	1-892	3-793	5-729	7-597	9-237	10-97
C ₆ H ₆ O ₂	0-666	0-402	0-282	0-215	0-188	0-178	0-166

(45) *Catechol* in Hydrochloric Acid. Method 5(a).*

HCl	0	1-68	3-53	5-39	7-30	9-11	10-83
C ₆ H ₆ O ₂	4-19	2-13	1-18	0-81	0-62	0-55	0-55

(46) *Styphnic Acid in Hydrochloric Acid. Method 5(b).*

HCl	0	1-410	2-814	4-221	5-634	6-997	8-418	11-10	11-16
C ₆ H ₃ O ₈ N ₃	0-02179	0-00062	0-00060	0-00072	0-00093	0-00163	0-00197	0-00379	0-00387

(47) *Styphnic Acid in Nitric Acid. Method 6(a).*

HNO ₃	0	1-785	4-171	6-234	8-368	10-31	11-97	13-97	15-57
C ₆ H ₃ O ₈ N ₃	0-02179	0-001403	0-002180	0-003274	0-005108	0-007944	0-01298	0-02742	0-05611

(48) *Pyrogallol in Hydrochloric Acid. Method 5(a).*

HCl	0	1-53	3-18	5-12	6-86	8-68	10-43
C ₆ H ₆ O ₃	4-02	2-81	1-86	1-25	1-01	0-91	0-92

* The preliminary test showed that catechol is very slightly volatile at the ordinary temperature in a vacuum, but the regularity of the curve obtained seems to show that in spite of this the results are fairly accurate.

II. *Phenols.*

The solubility of a number of phenols has been determined in the same way, the series investigated being:

Monohydric Phenols.—*p*-Nitrophenol, *m*-nitrophenol, and β -naphthol in hydrochloric acid; trinitrophenol (picric acid) in nitric acid.

Dihydric Phenols.—Resorcinol, quinol, catechol, and trinitroresorcinol (styphnic acid) in hydrochloric acid; trinitroresorcinol in nitric acid.

Trihydric Phenol.—Pyrogallol in hydrochloric acid.

Methods of Analysis.—5. For all phenols in hydrochloric acid, the acid was determined gravimetrically, and the phenol by weighing after evaporation (*a*) in a vacuum, or (*b*) on the steam-bath.

6. For picric acid and styphnic acid in nitric acid, the concentrations of the nitric acid solutions were determined at 25° before adding the solid, owing to the difficulty of titrating solutions containing these phenols. As the phenols are only sparingly soluble, however, any change in volume that might occur when they dissolve could have no appreciable effect on the results. The phenol was determined by weighing, after evaporation (*a*) in a vacuum, or (*b*) on the steam-bath.

Some of the phenols gave deeply coloured solutions, but the residues obtained on evaporation were practically colourless, and a preliminary experiment showed that they were left unchanged when evaporated to dryness with hydrochloric acid or nitric acid.

The results are given in tables 39 to 48, the solubilities of the phenols being given in gram-molecules per litre, whilst the concentrations of the solvent acid are expressed, as before, in equivalent normalities.

Consideration of Results.

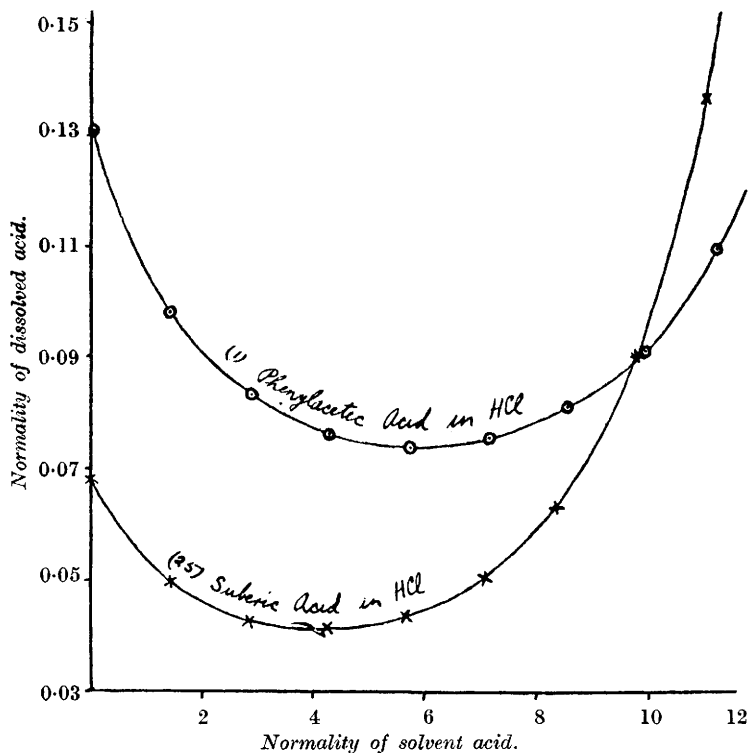
A glance at the solubility curves will suffice to show that the results observed by Herz, Stépanov, and Masson were no isolated phenomena, but that, as regards the solubility of organic acids and phenols in solutions of other acids, deviation from Nernst's law is the rule and not the exception. It will be seen that the curves obtained are of two main types, according as the solvent acid is a mineral or an organic acid, but in each case the assumption of oxonium salt-formation is sufficient to account for the observed results.

Owing to exigencies of space, only a few typical solubility curves can be reproduced. The other solubility curves, which can be

constructed from the tables, will be referred to by the number of the table containing the necessary data. Thus (1) refers to the solubility of phenylacetic acid in hydrochloric acid, and so on.

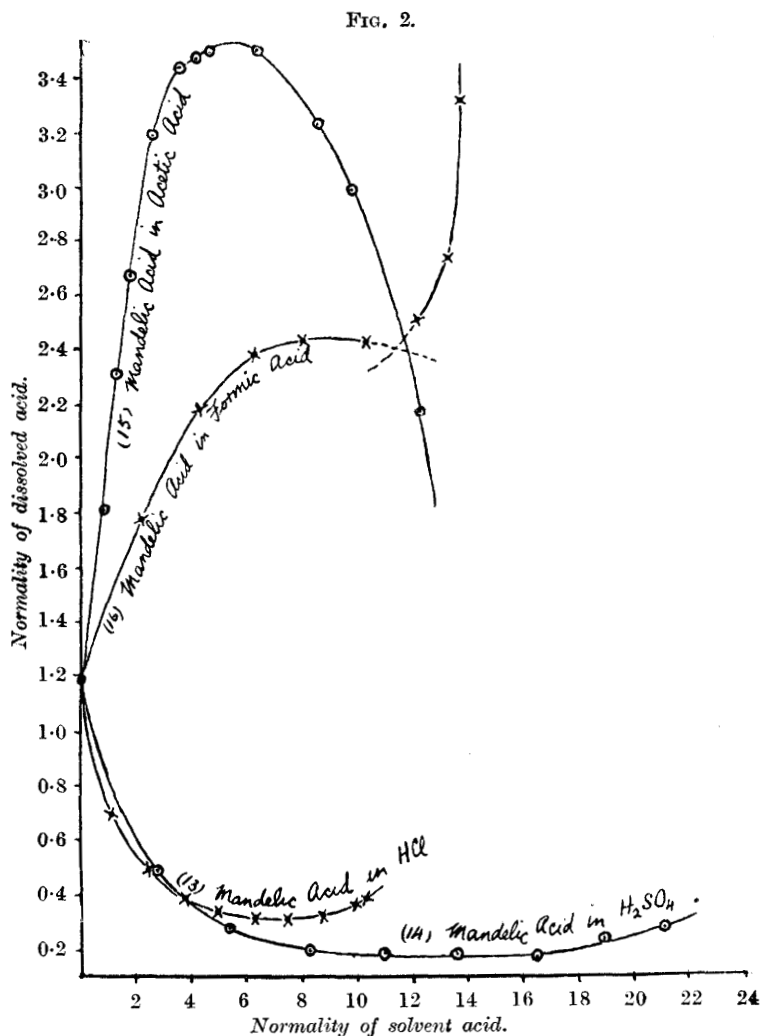
The curves obtained for solutions in the mineral acids all resemble more or less those obtained by Stépanov and Masson, that is, the solubility diminishes rapidly at first, reaches a minimum, and afterwards increases steadily with increasing concentration of the solvent acid. The results, however, vary somewhat according

FIG. 1.



to the solubility of the organic acid or phenol, and the concentrations attainable with the mineral acid. Thus with sparingly soluble acids and phenols, such as phenylacetic (1, 25, Fig. 1) and nitrobenzoic acids (4, 5), and the nitrophenols (39, 40, Fig. 7), the curve in every case shows a distinct turning point. Other examples are 2, 3, 6, 7, 8, 11, 12, 23, 24, 25, 26, 27, 39, 40, 41, 42, 46, 47. With very readily soluble substances, such as malonic, citric, and tartaric acids, quinol, and catechol (17, Fig. 3), (34,

Fig. 6), (37, 43, 44, 45, 48), the concentration of hydrochloric acid reached is not sufficient to show clearly the upward tendency of the curve, although the general shape makes it evident that the



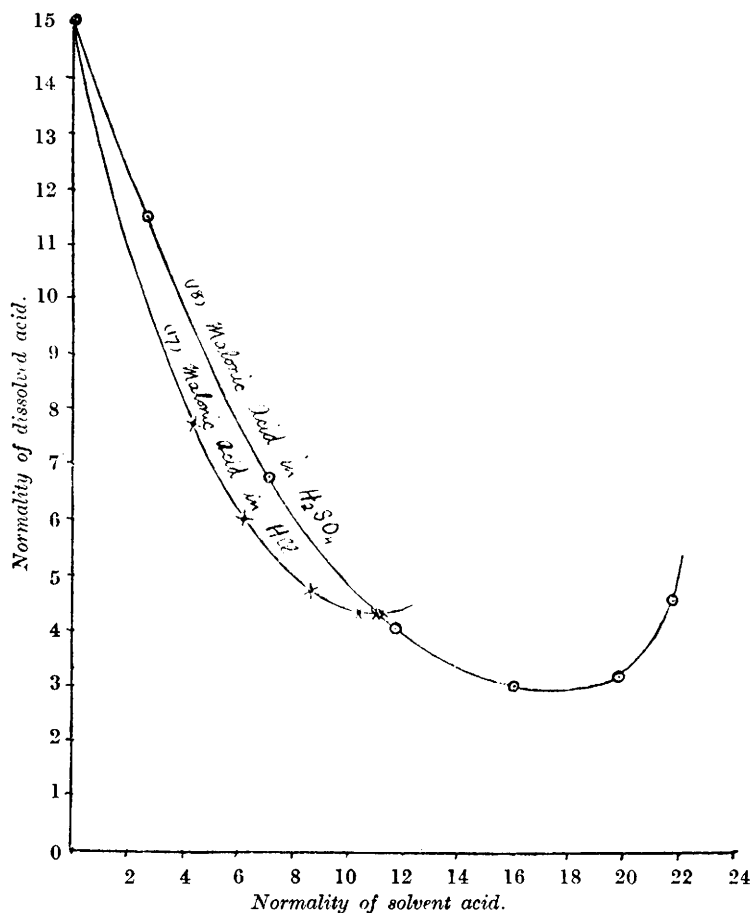
curve has reached its minimum at the concentration attained, and is just about to turn upwards—a conclusion which is further justified by the fact that in sulphuric acid solutions, where the concentrations attainable are considerably greater, even the very

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readily soluble acids give a definite turning point (18, Fig. 3), (35, Fig. 6), (38).

When the solvent acid is organic, modification of the shape of the curve results from two causes, namely, (a) the weakness of organic acids in general, and (b) the wide difference between the

FIG. 3.



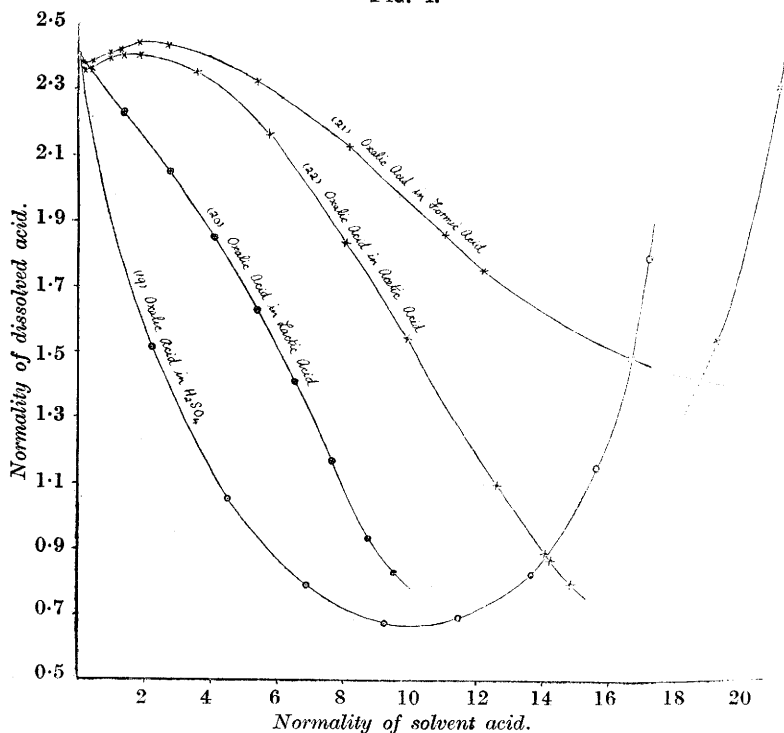
solubilities of the dissolved acid in water and in the organic acid solvent.

(a) When both solvent and dissolved acids are weak, the effect of the common hydrogen ion is, as a rule, too small to be measured. Of the acids the solubilities of which were determined in an organic acid solution, oxalic acid is the only one of sufficient acidic strength

to show any perceptible initial decrease in solubility (21, 22, Fig. 4). The others show increase in solubility from the beginning, except tartaric in acetic (36, Fig. 6), and oxalic in lactic acid (20, Fig. 4), where no evidence of salt-formation was obtained.

(b) If the dissolved acid is more readily soluble in the solvent organic acid than in water, the resulting curve shows a continuous increase—an increase which may be partly due to salt-formation or entirely due to increasing solubility in the solvent acid, so that

FIG. 4.

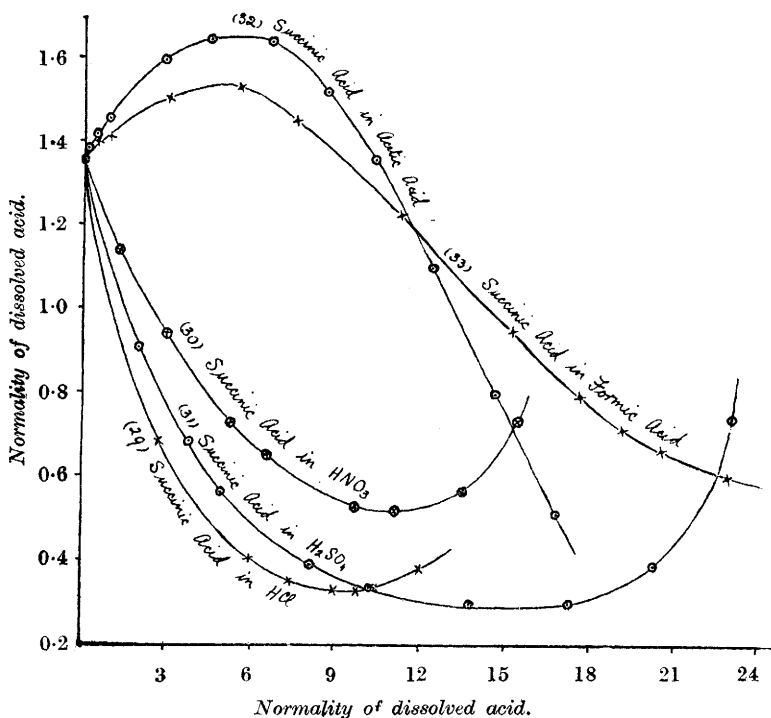


no conclusion as to salt-formation can be drawn. An instance of this may be seen in the curve for suberic acid in acetic acid (28). Other cases give clear evidence of salt-formation, the curve showing an initial increase in solubility, owing to the formation of the more readily soluble salt, with a subsequent decrease, caused by decreasing solubility in the solvent acid. The curves which show this effect clearly are: (1) succinic acid in acetic and formic acids (32, 33, Fig. 5), (2) oxalic acid in acetic and formic acids (here the ionic effect is first perceptible, before the increase due to salt-

formation) (21, 22, Fig. 4), and (3) mandelic acid in acetic and formic acids (15, 16, Fig. 2).

(It will be observed that in three of these cases, namely, oxalic acid in acetic and formic acid solutions, and mandelic acid in formic acid, there is apparently a break in the curve. The cause of this has not been investigated, but Masson, who obtained a similar break for oxalic acid in nitric acid, attributed the result to dehydration of the oxalic acid.)

FIG. 5.

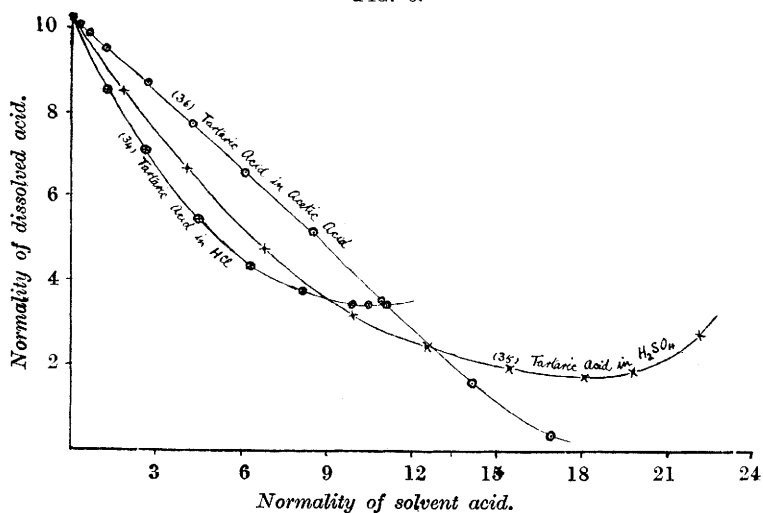


From the curves, it may be inferred that salt-formation does not take place with equal readiness in all the mineral acids. Where curves have been determined for the same organic acid or phenol both in hydrochloric and nitric acid solutions, it will be seen that in each case the nitric acid curve lies above that for hydrochloric acid, evidently indicating that additive compounds are formed more readily with nitric acid; see, for example, the curves for succinic (29, 30, Fig. 5), phthalic (23, 24), suberic (25, 26), and

styphnic acids (46, 47) in hydrochloric and nitric acid respectively.

Again, a comparison of the curves for the same acid in hydrochloric and sulphuric acid solutions shows uniformity of behaviour in all the cases investigated. There is at first a more rapid decrease in solubility in hydrochloric than in sulphuric acid (probably due to the greater acidic strength of hydrochloric acid, and the correspondingly greater ionic effect), but the turning point is more quickly reached and the hydrochloric acid curve soon cuts the other, from which we may infer that salt-formation takes place with greater ease in hydrochloric acid. A comparison of the curves for succinic (29, 31, Fig. 5), citric (37, 38), tartaric (34, 35, Fig. 6),

FIG. 6.

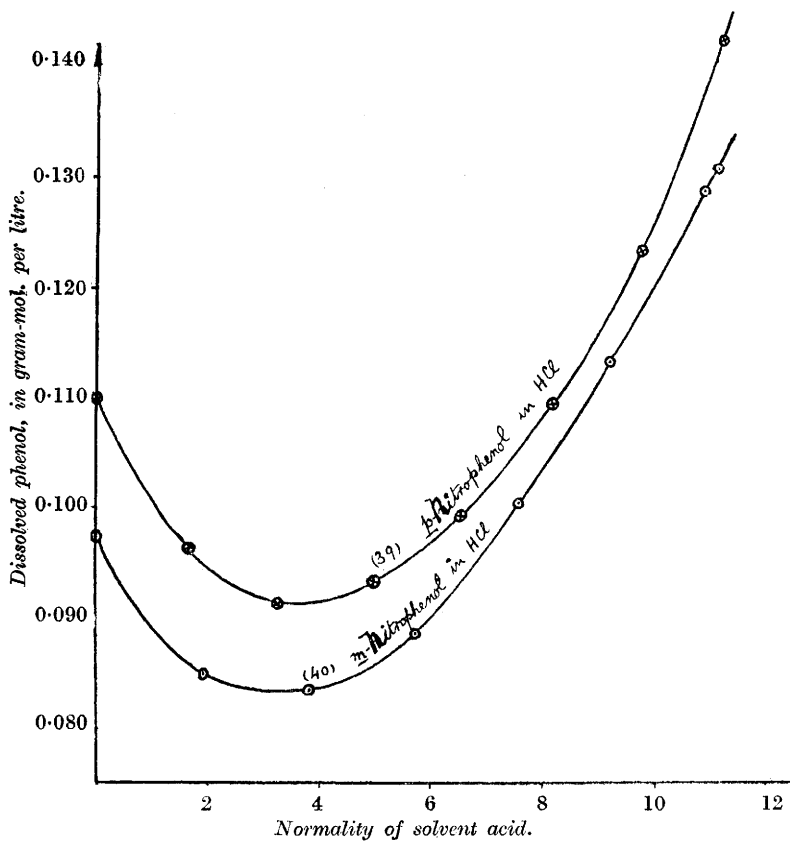


malonic (17, 18, Fig. 3), mandelic (13, 14, Fig. 2), and trichloro-lactic acids (9, 10) in hydrochloric and sulphuric acids, respectively, will make this clear. (In the case of suberic acid [25, 27], the result appears to be similar, but owing to the small solubility of suberic acid, and the necessity for estimating the suberic acid in sulphuric acid solutions by difference, this curve is not sufficiently accurate to enable the distinction between the two curves to be clearly seen.) It would therefore appear that, of the mineral acids, sulphuric acid shows the least tendency to salt-formation, whilst nitric acid shows the greatest.

No quantitative connexion can be established between the turning point of the curve and the strength of the organic acid in

question. Kendall found that, in general, for additive compounds, both of organic acids in pairs and of organic acids with sulphuric acid, the tendency towards the formation of additive compounds is dependent on the difference in acidic strengths. Very weak organic acids most readily form additive compounds, and an

FIG. 7.



increase in the acidic strength is accompanied by a diminution or loss of this property. The rule is, however, merely qualitative. This result is, in general, confirmed by the present investigation, although the question is complicated by the fact that the turning point in the solubility curve depends largely on the solubility of the organic acid.

General Summary of Results.

From determinations of the solubility of organic acids and phenols in solutions of other acids, it has been shown that in such solutions compounds are formed between the organic acid or phenol and the solvent acid. The most probable explanation is that the organic acids and phenols contain a basic oxygen atom, and that this forms salts of the oxonium type with the solvent acid, the oxygen becoming quadrivalent. This view is strongly supported by the work of Kendall, whose earlier papers were published during the progress of the present research.*

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