Conclusions.

The refractive indices and the densities of a number of organic liquids belonging to different classes were determined for a large number of temperatures between 15° and 75°, and the curves plotted showed the refractive index to be a linear function of the temperature within the experimental error in every case.

The refractive powers were calculated for temperatures from 10–80°; the expression $(n^2 - 1)/d$ gave decreasing values as the temperature increased, $(n^2 - 1)/(n^2 + 2)d$ gave increasing values for normal (not tautomeric) substances, $(n - 1)/d$ in some cases gave increasing, in others decreasing values.

It is shown that the molecular refractions calculated by using Brühl's values for atomic refractions gave results agreeing with the experimental values as well at high as at low temperatures.

The state of the equilibrium between the two forms of tautomeric substances can only be arrived at qualitatively by means of refractive powers.

COLUMBIA UNIVERSITY, NEW YORK CITY.

[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE SOLUBILITY OF SALTS IN CONCENTRATED ACIDS.[1]

BY ARTHUR E. HILL AND JOHN P. SIMMONS.

Received May 19, 1909.

Introduction.

That the solubility of chemical compounds in aqueous solutions is affected by the presence of other dissolved substances has long been known. Quantitative investigations of these solubility relations have been more numerous than almost any other physical-chemical studies, and since the introduction of the theory of electrolytic dissociation into chemical thought the field has been of increased interest to chemists, who have found in this theory an explanation, whether or not complete, of facts previously inexplicable. Of these almost countless investigations, those of Nernst,[2] A. A. Noyes,[3] and Arrhenius[4] may be noted as the most widely known and probably the most influential in shaping the opinions of chemists on this important matter.

The researches mentioned above, together with the many others not

---

[1] Presented before the New York Section of the American Chemical Society, on May 14, 1909.

[2] *Z. physik. Chem.*, **4**, 372 (1889).

[3] *Ibid.*, **6**, 241 and 385 (1890); **9**, 603 (1892); **12**, 162 (1893); **16**, 125 (1895); **27**, 267 and 279 (1898); **28**, 518 (1899).

[4] *Ibid.*, **31**, 197 (1899).

here cited, have made chemists familiar with the rôle of the "common ion" in reducing the solubility of compounds, and with the action of strong acids in increasing the solubility of salts of weak acids. In researches of this character, however, the experiments have usually been confined to dilute solutions, since it has long been realized that the theories which may be satisfactory applied in these cases often fail to give quantitative explanations of the conditions existing in concentrated solutions. As a result of this entirely natural restriction of the field, experimental results on solubility in concentrated solutions are few and unsystematic, and without experimental data theory of course cannot be developed.

The present investigation has been started with a two-fold object: first, to supply some data, systematically obtained, on solubility relations in concentrated solutions, and second, to apply existing theory to the results thus found.

In the absence of any fundamental theories of concentrated solutions, it seems to be the most natural, as well as the most scientific method to apply the laws of dilute solutions rigorously to results obtained in the more concentrated solutions; the direction in which and the extent to which the actual results differ from those calculated on the theoretical basis should give at least some information as to the nature of the changes which must be made in the accepted theory of solutions in order that the conditions in concentrated solutions may also be satisfactorily explained, and should help us somewhat toward the establishment of the much-desired general theory, which shall not make the entirely arbitrary distinction between dilute and concentrated solutions.

Experimental Part.

Experiments were carried out on the increase of solubility of a number of salts upon addition of nitric acid of varying concentration to their aqueous solutions. Beginning with fairly dilute acid, the experiments were in each case continued with increased concentrations of acid until oxidation of the salt, precipitation of nitrates, or other changes prevented the use of a more concentrated solvent. The strength of acid was determined by titration with potassium hydroxide solution, standardized by gravimetrically analyzed hydrochloric acid; methyl orange was used as indicator.

When concentrated acids are used and considerable quantities of salt are dissolved, the resulting expansion is so great that the molecular concentration of acid per liter of solution becomes very much less than in the pure solvent, as for example in Experiment 7 in Table I, in which the concentration of nitric acid has been decreased in this manner from 6.44 normal to 4.703 normal. In order to correct for these changes, it was necessary to know the percentage strength of the nitric acid, as well as its normality. The necessary specific gravity determinations were made at the temperatures of standardization, which varied from 17° to 23°; from these figures the percentage strength was calculated. It was found that the empirical equation

$$P = 0.257 + 5.993n - 0.1215n^2,$$

in which P and n represent respectively per cent. of acid by weight and the molecular concentration per liter of aqueous solution, holds for dilutions between 0.5 normal and 8.5 normal, with errors of ±0.2 per cent.

The compounds chosen as solutes were the silver salts of five acids of varying strength; *viz.*, silver acetate, chloracetate, oxalate, iodate, and sulphate. The series of acids runs from the very weak acetic to the moderately strong sulphuric acid. As a salt of a very strong acid, thallous chloride was chosen, since the great insolubility of the silver halides renders them unsuitable for the purposes of this investigation. The salts selected are all of moderate insolubility, yet sufficiently soluble to give solutions which can be accurately analyzed by ordinary methods.

The temperature of the experiments was 25°, maintained by gas heating of an Ostwald thermostat. The solubility equilibria were approached with undersaturated and with supersaturated solutions; the latter were prepared by stirring the salt and solvent at a temperature of 35° (except where otherwise stated), the supersaturation being confirmed by analysis. The solutions were agitated by a mechanical stirrer.

(*a*) *Solubility of Silver Acetate in Nitric Acid.*—The salt used in the experiments was prepared by double decomposition of sodium acetate and silver nitrate in hot dilute solution. The silver acetate was recrystallized from hot water and was shielded from the action of light during the process. The dried salt, which was nearly colorless in appearance, gave upon analysis by Volhard's method, 64.42 per cent. Ag; calculated, 64.64. In each experiment sufficiently large quantities of the purified compound were added to two small flasks of nitric acid solutions of known strength; the one was put in the thermostat at 25° while the other was warmed to about 35° for two hours, being briskly stirred by a glass paddle driven by an electric motor. The flasks were closed with well-fitted cork stoppers, and the stirring apparatus so constructed that the only opening for escape of volatile matter was through a tight glass bearing lubricated with vaseline. After two hours' stirring of the warm solution, a 10 cc. sample was withdrawn and analyzed to insure supersaturation. The flask was then put in the thermostat, with the first, and both stirred over night. Samples were pipetted out after this interval and the specific gravity of the solutions determined by direct weighing. The samples were then analyzed for their silver content by titration with standardized ammonium thiocyanate solution, according to Volhard's method. In Table I, in which the results are tabulated, the first column gives the normality of the acid used as solvent; the second column gives the per cent. of acid by weight in the solvent; the third column gives the specific gravity of the solution, the figures being means of the determinations of the supersaturated and undersaturated solutions; the fourth column gives the weight of salt dissolved in grams per liter, U referring to the undersaturated and S to the supersaturated solution; the fifth column gives the mean of these two values, calculated to gram-equivalents per liter. The sixth column has been calculated to show the concentration of nitric acid present per liter of solution.

TABLE I.

$AgC_2H_3O_2$ in HNO_3 at 25°.

	Normality of HNO_3.	Percentage strength of HNO_3.	Spec. grav. of solution.	Grams salt per liter.	Equivalents salt per liter.	Equivalents HNO_3 per liter.
1	0.000	0.000	1.005	11.07U 11.19S	0.0667	....
2	0.500	3.096	1.072	85.57U 85.05S	0.511	0.4845
3	1.000	6.128	1.140	161.3U 162.5S	0.970	0.9506
4	2.000	11.757	1.267	305.8U 309.0S	1.841	1.789
5	4.020	22.386	1.470	549.0U 549.6S	3.290	3.269
6	5.030	27.328	1.561	656.3U 655.7S	3.929	3.923
7	6.44	33.813	1.670	791.7U 792.7S	4.745	4.703

The value for the solubility in water agrees well with Goldschmidt's[1] figure (0.0669) for the normality of a saturated solution at 25°.

When nitric acid of about seven times normal strength was used in an experiment not here tabulated, silver nitrate appeared as a solid phase and the solution was found to be much less concentrated in respect to silver than the value found in Experiment 6. In order to establish definitely the position of the point of maximum solubility thus indicated, the solutions already saturated with silver acetate were treated with solid $AgNO_3$ and again stirred until saturated with respect to both salts; the solutions were then analyzed by Volhard's method for their total silver content. The results are given in Table II.

TABLE II.

Solubility of $AgC_2H_3O_2$ and $AgNO_3$ in HNO_3 at 25° C.

	Normality of HNO_3.	Equivalents Ag per liter.
1	0.000	10.07
2	2.000	8.42
3	4.020	6.71
4	5.030	5.90

Plotting the values given in column two on a system of coordinates with the normality of acid in the solvent, a straight line was obtained, which intersects the curve for the solubility of silver acetate, derived from experiments one to six of Table I and plotted on the same system, at a value of about 6.44 for the concentration of acid. Experiment 7 of Table I was then carried out with acid of 6.44 normal concentration as solvent; to the saturated solution, containing 4.745 gram equivalents of silver, silver nitrate crystals were added, and after six hours of stirring a sample was withdrawn and analyzed. The concentration of silver in the solution had altered but slightly (4.84), indicating that the maximum solubility of silver acetate is within 2 per cent. of the value given in Experiment 7 (792 grams per liter) of Table I.

[1] *Z. physik. Chem.*, **25**, 93 (1898).

In Plate 1 the solubility of silver acetate has been plotted in terms of the normality of acid in the saturated solution. The increase in solubility is directly proportional to the concentration of acid throughout the entire range of experiments, in which the solubility of the salt has been increased to seventy-one times its value in aqueous solution. The equation

$$y = 0.041 + 0.998x,$$

in which x is the concentration of nitric acid and y the concentration of silver acetate, gives values for the solubility which agree with the experimental values excellently except in the case of Experiment 1, the maximum variation being 0.66 per cent. and the average variation being 0.32 per cent.

(*b*) *Solubility of Silver Chloracetate in Nitric Acid.*—Silver chloracetate was prepared by double decomposition of the sodium salt of the acid and silver nitrate, the operation being carried out by allowing a dilute solution of silver nitrate to fall in drops into a mechanically stirred cold solution of sodium chloracetate. The salt thus formed was thoroughly washed, and dried at a temperature of 55°. Contrary to the experience of Otto and Ruckert,[1] it was not found possible to economically recrystallize the salt from hot water, because of its pronounced tendency to form silver chloride when heated. Samples formed by double decomposition of hot solutions of the above-named salts were also found to contain considerable quantities of silver chloride. When formed in cold solutions, however, the salt dissolves in water, leaving only a very slight residue. Analysis gave 53.43 per cent. Ag; calculated, 53.59.

The solubility determinations were carried out as in the case of silver acetate, the silver in the saturated solutions being determined volumetrically by Volhard's method. The results are given in the following table:

TABLE III.

$AgC_2H_2ClO_2$ in HNO_3 at 25° C.

	Normality of HNO_3.	Percentage strength of HNO_3.	Spec. grav. of solution.	Grams salt per liter.	Equivalents salt per liter.	Equivalents HNO_3 per liter.
1........	0.00	0.00	1.0095	15.17U 15.19S	0.0737	0.00
2........	0.25	1.564	1.0426	51.13U 49.53S	0.2546	0.2405
3........	0.50	3.096	1.0791	91.81U 91.86S	0.4560	0.4738
4........	1.00	6.128	1.1473	166.8U 167.8S	0.8309	0.9525
5........	2.00	11.757	1.2716	309.8U 311.8S	1.543	1.751
6........	4.00	22.277	1.4749	547.6U 550.6S	2.726	3.271
7........	5.00	27.185	1.5673	660.4U 658.0S	3.273	3.916

The increase in solubility is proportional to the concentration of acid in the solution, as appears in Plate 1. The equation

$$y = 0.0522 + 0.822x$$

expresses the values found with an average variation of ±0.7 per cent. excluding Experiment 1.

---

[1] *Ber.*, **14**, 577 (1881).

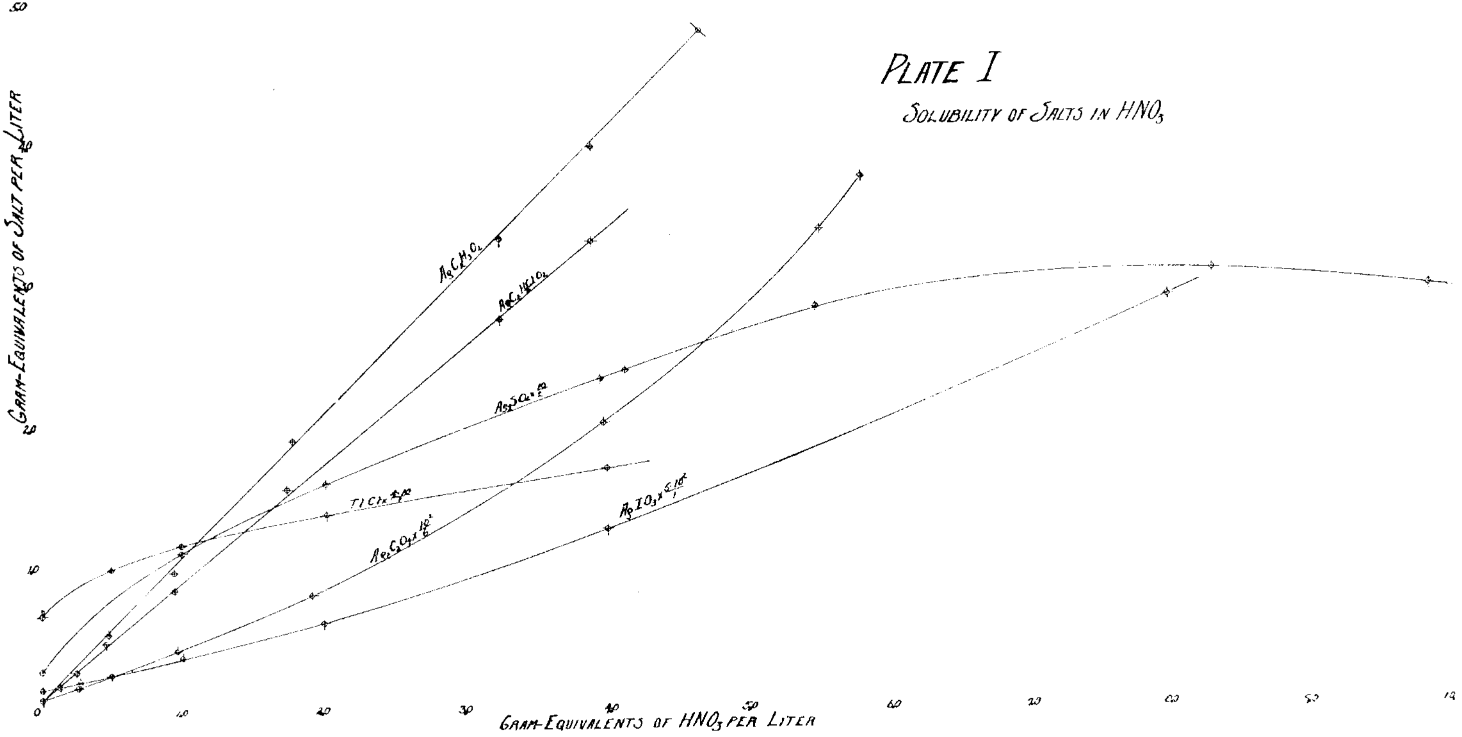

PLATE I

SOLUBILITY OF SALTS IN HNO_3

(*c*) *Solubility of Silver Oxalate in Nitric Acid.*—Silver oxalate was prepared from silver nitrate and potassium oxalate in hot dilute solutions. After being well washed, the salt was recrystallized from dilute nitric acid. The compound was thoroughly dried, since it retains water tenaciously, and was then analyzed gravimetrically, giving 70.91 per cent. Ag; calculated, 71.04.

The concentration of silver oxalate in the saturated solutions as given in Table IV was determined by gravimetric analysis, the silver being weighed as chloride. In Experiments 6 and 7 the values are given as determined from the undersaturated solutions only, since the effort to supersaturate by heating the salt with nitric acid of five times normal strength or stronger always resulted in a slight decomposition of the oxalate.

TABLE IV.

$Ag_2C_2O_4$ in HNO_3 at 25°.

	Normality of HNO_3.	Percentage strength of HNO_3.	Spec. grav. of solution.	Grams salt per liter.	Equivalents salt per liter $\times 10^2$.	Equivalents HNO_3 per liter.
1.......	0.2517	1.574	1.0080	1.342U 1.348S	0.8853	0.2513
2........	0.5025	3.117	1.0186	2.184U 2.194S	1.411	0.5025
3........	0.9806	6.017	1.0339	3.707U 3.734S	2.449	0.9608
4........	1.040	11.476	1.0647	7.164U 7.177S	4.720	1.925
5........	4.017	22.37	1.1415	17.98U 18.25S	11.92	3.986
6........	5.564	29.84	1.1996	29.96U	19.98	5.534
7........	5.83	31.085	1.2162	33.88U	22.30	5.829

(*d*) *Solubility of Silver Iodate in Nitric Acid.*—In the first experiments conducted with this salt, a sample was prepared by action of potassium iodate upon silver nitrate in dilute solution; the product was washed thoroughly, dissolved in ammonium hydroxide, reprecipitated by addition of nitric acid, and washed again. The preparation, though very pure, gave rise to some unexpected results which were found to be due to its amorphous condition, from which state it is slowly changed into the crystalline modification when stirred with nitric acid. The amorphous modification has a solubility considerably greater than the crystalline variety, so that a sample stirred at the temperature of experiment gives a solution supersaturated with respect to the crystals, the concentration of which solution falls in the course of a number of hours as the change into the crystalline variety becomes complete. It is therefore impossible to approach the solubility equilibrium from the undersaturated side if the amorphous form of silver iodate is used. How general this phenomenon may be cannot of course be asserted; the experience with this salt however puts emphasis upon the necessity for proof that the physical form of a salt shall not have changed during experimentation when a solubility equilibrium is supposed to have been reached from two directions.

The salt used in the experiments tabulated below was purified by recrystallization from dilute nitric acid solution, and gave 83.04 per cent. AgI; calculated, 83.06.

The equilibrium is reached somewhat slowly, so that one to two days' stirring was found necessary in the majority of cases. The solutions were analyzed by reduction of the dissolved silver iodate to silver iodide by means of sulphur dioxide; the iodide was filtered off on a Gooch crucible and dried to constant weight at 120°. The silver iodide formed by reduction is in an extremely fine state of division, but can be coagulated by being heated for several hours and then allowed to stand in the cold for several hours longer. The method gives excellent results, but is extremely slow in execution. The results of the experiments are given in Table V.

TABLE V.

$AgIO_3$ in HNO_3 at 25° C.

	Normality of HNO_3.	Percentage strength of HNO_3.	Grams salt per liter.	Equivalents salt per liter × 10^3.
1	0.000	1.000	0.0500U 0.0506S	0.178
2	0.125	0.788	0.0852U 0.0876S	0.304
3	0.250	1.564	0.1084U 0.1065S	0.379
4	0.500	3.096	0.1394U 0.1433S	0.499
5	1.00	6.128	0.2065U 0.2069S	0.731
6	2.00	11.757	0.3310U 0.3328S	1.174
7	4.00	22.277	0.6913U 0.7057S	2.469
8	8.00	40.425	1.590U 1.585S	5.608

The solubility in water is found to be slightly lower than the value $0.189(10)^{-3}$ equivalents found by Noyes,[1] who worked with the amorphous form of the salt.

Specific gravity determinations of the saturated solutions were not made since the amount of salt dissolved is never large. The experiments were concluded with the determination of the solubility in eight times normal acid; it was found that in acid of higher concentration the iodate suffered decomposition. When treated with the ordinary concentrated nitric acid, the salt dissolves with the formation of a deep red solution, from which a yellow crystalline substance can be obtained by partial evaporation. Although of the appearance of silver iodide, the compound dissolves completely in dilute ammonium hydroxide. The substance was not studied further.

(*e*) *Solubility of Silver Sulphate in Nitric Acid.*—The silver sulphate was obtained by adding sulphuric acid to a hot, dilute solution of silver nitrate. The salt settled out in well-crystallized particles, which were thoroughly washed, dried at 100°, and gave 68.92 and 68.85 per cent. Ag; calculated, 69.20.

The solubility determinations are given in Table VI. The silver was determined volumetrically.

---

[1] THIS JOURNAL, **24**, 1143 (1902).

TABLE VI.

Ag_2SO_4 in HNO_3 at 25°.

	Normality of HNO_3.	Percentage strength of HNO_3.	Spec. grav. of solution.	Grams salt per liter.	Equivalents salt per liter × 10².	Equivalents HNO_3 per liter.
1........	0.000	0.00	1.0054	8.327U 8.372S	5.354	0.00
2........	1.0046	6.154	1.061	34.077U 34.095S	21.86	1.002
3........	2.0452	12.005	1.1069	49.032U 48.987S	31.43	2.014
4........	4.017	22.37	1.1871	71.224U 71.108S	45.63	3.959
5........	4.209	23.33	1.1956	73.202U 73.222S	46.95	4.144
6........	5.564	29.84	1.2456	84.556U 84.662S	53.90	5.495
7........	8.487	42.37	1.3326	94.698U 94.644S	60.70	8.318
8........	10.034	48.77	1.3676	91.002U 90.610S	58.22	9.873

The value for the solubility of the salt in water is appreciably higher than the value $5.14(10)^{-2}$ equivalents found by Drucker,[1] who did not, however, approach the equilibrium from supersaturated solutions.

It will be noted that Experiment 8 indicates that the salt is less soluble in nitric acid of 9.873 normal strength than in the weaker acid used in Experiment 7. The solubility curve drawn in Plate I indicates that the maximum solubility of the salt is reached when acid of about eight times normal strength is used. When a sample of the salt was treated with 12.2 normal acid, crystals of silver nitrate were formed.

(*f*) *Solubility of Thallous Chloride in Nitric Acid.*—The compound was prepared from metallic thallium, which was dissolved in sulphuric acid, and precipitated by a slight excess of hydrochloric acid. The amorphous salt was well washed and recrystallized from water. Its purity was established both by gravimetric analysis and by volumetric analysis, following Volhard's method. Found, gravimetrically, 14.70, 14.71 per cent Cl; volumetrically, 14.72, 14.69; calculated, 14.80.

Since the accuracy of the volumetric method for determining chlorine in thallous chloride has been questioned by Meyer,[2] it seems well to note that the method gives entirely reliable results, provided, of course, that the silver chloride is filtered off,[3] before the solution is titrated with a sulphocyanate. The earlier results obtained by A. A. Noyes,[4] as well as the above analyses and those on which the following table depends, afford sufficient assurance that the volumetric method for analysis of thallous chloride is as accurate as the same method has been found in the analysis of other chlorides.

---

[1] *Z. anorg. Chem.*, **28,** 362 (1901).

[2] *Ibid.*, **24,** 367 (1900).

[3] Rosanoff and Hill, THIS JOURNAL, **29,** 269 (1907).

[4] *Z. physik. Chem.*, **6,** 248 (1890).

TABLE VII.

TlCl in HNO_3 at 25°.

	Normality of HNO_3.	Percentage strength of HNO_3.	Spec. grav. of solution.	Grams salt per liter.	Equivalents salt per liter $\times 10^2$.	Equivalents HNO_3 per liter.
1	0.000	0.000	0.996	3.950U 3.953S	1.650	0.000
2	0.4977	3.093	1.0184	5.930U 5.944S	2.475	0.4967
3	1.0046	6.155	1.0359	6.881U 6.884S	2.875	1.004
4	2.0452	12.005	1.0705	8.154U 8.132S	3.401	2.023
5	4.017	22.370	1.1362	9.973U 9.878S	4.145	3.996

The solubility of the salt in pure water was found to be slightly greater than the value (0.0161) given by Noyes.[1] The experiments were concluded with No. 5, since it was found that five times normal nitric acid oxidizes the thallium to the trivalent condition, causing precipitation of a yellow crystalline compound (probably $TlCl.TlCl_3$). That no such oxidation had taken place in Experiment 5 was known by the absence of the yellow crystals and by the fact that the concentration of the solutions remained unaltered on twenty-four hours' additional stirring after equilibrium had been attained. The time given for saturation in each previous experiment was about sixteen hours.

Although it proved impossible to continue the experiments far enough to determine whether or not a point of maximum solubility exists, it is yet at least indicated by the likeness of the solubility curve in Plate 1 to that of silver sulphate that such a point, if it could be experimentally realized, would be reached when the concentration of nitric acid used was between six and seven times normal.

The results of Tables II–VII are represented in graphic form on Plate 1; the values for the more insoluble salts have been multiplied by suitable factors. The curves for silver acetate and silver chloracetate are straight lines, the equations for which have been previously given. From the pitch of the six curves, it appears that the increase in solubility follows qualitatively the inverse order of the strength of acid represented in the salt, silver acetate giving a curve strongly inclined toward the vertical axis, while thallous chloride gives a curve nearly horizontal. The quantitative study of these results follows.

Theoretical Part.

The increased solubility of a salt in dilute acid solutions was fully discussed some time ago by A. A. Noyes,[2] who based his calculations on the dissociation theory and the law of mass action. The excellent agreement which Noyes found between his experimental results and his calculations would not be expected when concentrated solutions are considered, since two factors which are of negligible value in dilute solution become of great importance in the case under discussion. These factors are respectively the divergence of strong electrolytes from the law of mass action as expressed in Ostwald's dilution formula, and

---

[1] *Z. physik. Chem.*, **6**, 249 (1890).

[2] *Ibid.*, **27**, 267 (1898); THIS JOURNAL, **20**, 742 (1898).

the effect of one salt upon the dissociation of another, as distinct from chemical interaction—the "neutral salt effect" of Arrhenius. It is possible to take the former of these factors into account by use of a suitable form of the dilution law; the second factor has not as yet been given any quantitative form of expression, and must therefore be left out of consideration in quantitative work until chemical theory has made further advances.

Using the terminology of Noyes,[1] we may consider a moderately insoluble binary electrolyte AB to be acted on by a univalent acid CD. In the resulting chemical reaction,

$$\mathrm{AB} + \mathrm{CD} \rightleftarrows \mathrm{AD} + \mathrm{CB},$$

let the capital letters stand for the concentrations of the four ions which are present, and let a, b, c, and d stand for the concentrations of the four undissociated compounds. Expressing the total concentration of the dissolved salt AB by m, and the concentration of the solvent CD by n, we have the following equations:

$$(1) \qquad m = \mathrm{A} + a + c;$$

$$(2) \qquad m = \mathrm{B} + a + d;$$

$$(3) \qquad n = \mathrm{C} + b + d;$$

$$(4) \qquad n = \mathrm{D} + b + c.$$

The state of dissociation of the four compounds may be expressed by the following equations, of which 7, 8, and 9 are in the form of the dilution law preposed by Storch,[2] and elaborated by Bancroft.[3]

$$(5) \qquad \mathrm{AB} = k;$$

$$(6) \qquad a = k_a = m_0\,(1 - a_0);$$

$$(7) \qquad \frac{(\mathrm{CD})^{n_b}}{b} = k_b;$$

$$(8) \qquad \frac{(\mathrm{AD})^{n_c}}{c} = k_c;$$

$$(9) \qquad \frac{(\mathrm{CB})^{n_d}}{d} = k_d.$$

In these expressions n_b, n_c, and n_d are exponential constants determined independently for each substance, and k_b, k_c, and k_d, equilibrium constants which are also independently calculated.

Equation (5) depends on the constancy of the solubility product, which is a fundamental conception of the theory of solutions, and which recently received new corroboration from the calculations of Stieglitz.[4]

---

[1] *Loc. cit.*

[2] *Z. physik. Chem.*, **19**, 13 (1895).

[3] *Ibid.*, **31**, 188 (1899).

[4] THIS JOURNAL, **30**, 946 (1908).

In Equation (6) the concentration of undissociated AB (a) is assumed to be a constant (k_a), the value of which is calculated from the solubility of the compound in pure water (m_0) and its dissociation in concentrated solution (a_0). Equations 7, 8, and 9 have been shown to express with great exactness the dissociation of electrolytes in dilute solution, and are believed by Bancroft[1] to express the conditions in concentrated solutions more accurately than any other form of the dilution law. The equations thus proposed differ from those used by Noyes in his calculations by the substitution of the empirical dilution law in 7, 8 and 9 for the Ostwald dilution law, which is known to be far from a true expression for the dissociation of strong electrolytes.

Under the ordinary conditions of experimentation, all terms would be known except the concentration of the four ions, A, B, C and D, the concentration of the four molecular compounds, a, b, c and d, and the total solubility m. For these nine unknown terms the necessary nine equations are at hand, so that a solution for m is possible. Noyes, in considering the case where equations 7, 8 and 9 are in the simpler form which he uses, estimates that an equation containing only m as an unknown value could be constructed, but that such an equation would probably contain over 100 terms. For the sake of simplicity, he therefore proposes a method of approximation which gives excellent results when used to calculate solubilities in dilute solution, but which cannot be applied to solutions of the concentration here studied without introducing very great errors. A method for complete mathematical solution is therefore necessary for the purposes of this investigation, and such a method will be discussed in the following two divisions of this paper, which will consider the two more important cases covered by the experimental part of the work.

a. Solution of the Equations without Simplifying Assumptions.

Algebraical solution, which Noyes found possible, though difficult, in the case of the equations proposed by himself, is impossible in the case of the equations here proposed, since the exponents in equations 7, 8 and 9 are fractional numbers usually bearing no simple relation to each other. It has been found possible, however, to carry through a process of solution partly algebraical and partly graphical, which, though extremely laborious, may be made to yield entirely reliable results.

The method consists in assuming a value for A, whence follows a value for B by Equation (5). As a second assumption a value for C is arbitrarily taken and d then calculated from Equation (9). From Equation (3) b may be found. By Equation (7), we have

$$(10) \qquad \mathrm{D} = \frac{[\mathrm{K}_b(b)]^{\frac{1}{n_b}}}{c}$$

---

[1] *Z. physik. Chem.*, **31**, 196 (1899).

by which D becomes known. Finally c may be derived from Equation (8) and a from Equation (6). We may therefore derive by simple algebra values for all the unknown terms from the arbitrarily assumed values of A and C.

The correct values of A and C are determined by graphic methods. From Equations (1) and (2) we have

$$A + c = B + d; \tag{11}$$

and from (3) and (4),

$$C + d = D + c. \tag{12}$$

By combination of (11) and (12), we obtain

$$A + C = B + D. \tag{13}$$

Retaining the value of A first assumed, a new value for C is taken, and all the other unknown terms calculated as before. By repetition of this process and by proper choice of values of C, such values of the other terms may be obtained that $A + c$ and $B + d$, when plotted against C, give a point of intersection, which establishes the correct value of C corresponding to the assumed value A, and leaves the latter as the only assumed term. From these values, A + C and B + D of Equation (13) may be calculated. Another value of A is now assumed, and through the same calculation as given before, the corresponding value of C is obtained. By repeating this process, and by properly choosing values for A, we may finally obtain a point of intersection on plotting the values A + C and B + D (Equation (13)) against the assumed values of A. This point of intersection establishes the correct value of A, while the correct value of C may be found by plotting the various values of A and the corresponding values of C on a coordinate diagram. From these correct values of A and C thus found, the true value of the other terms may be obtained by the algebraical processes described in the first paragraph of this mathematical discussion; and by substitution of values in equations (1) or (2) the solubility of the salt may be found.

This method may be illustrated by a typical calculation, the results of which will be given in Table VIII. Let it be required to find the solubility of silver acetate in nitric acid of 3.923 times normal strength, corresponding to Experiment 6 of Table I. An arbitrary value of 1.75 is taken for A, which is intermediate between values found for that term when the concentration of nitric acid in the solution is respectively less and greater (lines (4) and (6), Table IX).[1] Using the value of 0.002261

---

[1] Where no information is at hand as to the probable value of A, it is necessary to assume some values of a magnitude suggested by the dissociation relations of the salt in question, and find by calculation whether the values of the other terms derived from it are such that the curves plotted on the values of $A + c$ and $B + d$ on the one hand and of A + C and B + D on the other have points of intersection. If the value chosen does not lead to intersecting curves, new values of A must be tried until the desired condition is found.

TABLE VIII.

Solubility of $AgC_2H_3O_2$ in 3.923 Normal HNO_3.

	A.	B.	C.	*d.*	*b.*	D.	*c.*	A + *c.*	B + *d.*	A + C.	B + D.
1	1.75	0.001292	0.05329	3.825037	0.044673	1.8347	2.1322	3.8822	3.8263	......	......
2	......	....	0.05330	3.825755	0.043945	1.7936	2.0949	3.8449	3.8270	......	......
3	......	....	0.05331	3.826473	0.043217	1.7527	2.0574	3.8074	3.8277	......	......
4	......	....	0.0533048	3.826100	0.043595	1.7739	2.0768	3.8268	3.8273	1.8033	1.7752
5	1.725	0.0013107	0.05254	3.825787	0.044673	1.8609	2.1319	3.8569	3.8270	......	......
6	......	....	0.05255	3.826515	0.043935	1.8186	2.0939	3.8139	3.8278	......	......
7	......	....	0.05256	3.827244	0.043196	1.7764	2.0560	3.7810	3.8285	......	......
8	......	....	0.0525475	3.826334	0.044118	1.8290	2.1033	3.8283	3.8276	1.7775	1.8303
9	1.70	0.00133	0.05177	3.825227	0.046003	1.9660	2.2000	3.9000	3.8266	......	......
10	......	....	0.05178	3.825966	0.045254	1.9223	2.1613	3.8613	3.8273	......	......
11	......	....	0.05179	3.826705	0.044505	1.8782	2.1225	3.8225	3.8280	......	......
12	......	....	0.0517887	3.826609	0.044603	1.8838	2.1279	3.8279	3.8279	1.7518	1.8851
13	1.7413	0.0012985	0.053040	3.826246	0.043714	1.7895	2.0830	3.8243	3.8275	1.7943	1.7908

$a = 0.019142$ (Table IX).

$m = A + a + c = 3.8434$

$m = B + a + d = 3.8466$

Mean value, 3.8450

for k for silver acetate from Table X, a value of 0.001292 for B is found by Equation 5. An assumption of a value for C must now be made. By trial it is found that an assumed value of 0.05329 will give a value 3.8822 for A + c and 3.8263 for B + d, the derived values for the other terms given in line 1 of Table VIII being found by the algebraical processes previously described. Keeping A and B constant, two slightly larger assumed values of C, 0.05330 and 0.05331 are taken, and the calculations whose results are given in lines 2 and 3 lead to values of 3.8449 and 3.8099 for A + c and of 3.8270 and 3.8277 for B + d. Inspection of the A + c and B + d values in lines 1 to 3 shows that their curves must have a point of intersection. These values are then plotted on a large scale on cross-section paper against the values of C. The values of B + d lie directly on a straight line, while A + c give a line nearly straight. The intersection lies at a point corresponding to a value of 0.0533048 for C, which is therefore used in line 4 for a new calculation. That the graphic work is accurate is shown by the agreement of the A + c and B + d values which are derived. The correct value of C corresponding to the value of 1.75 for A being established, values of A + C and B + D are added in line 4.

A fresh assumption of a value of 1.725 for A is made in line 5, and on that basis the calculation of lines 5, 6, and 7 are worked out, leading to a value of 0.0525475 for C (line 8), and resulting in a good agreement of A + c and B + d. The entire process is again repeated, taking A as 1.70, the results being given in lines 9–12. From the values of lines 4, 8, and 12, A + C and B + D are computed, as shown in columns 10 and 11. These values are now plotted against the corresponding values of A, which is shown by their intersection to be 1.7413. Finally, by plotting the values of C from lines 4, 8, and 12 against the corresponding values of A, it is found that C should equal 0.05304 when A equals 1.7413. These values are then used in the final calculations of line 13. The values of m, calculated from equations (1) and (2), agree very closely, giving a mean of 3.845 as the solubility of the salt in gram equivalents per liter.

It has been necessary to carry out the calculations for C, d and b to the sixth or seventh place of decimals, since small differences in their value affect the other terms greatly. The method, though very tedious, leads to a correct solution of the equations, and is free from all assumptions other than those contained in the equations.

b. **Solution of the Equations when AB is a Salt of a Strong Acid.**

The method may be greatly simplified when AB is a salt of a strong acid, whose solubility is therefore not greatly increased by the presence of the solvent CD. Under these conditions the quantities of c and d formed will be small, and the consequent diminution in the quantities of the ions C and D present will not be large. Equations (14) C =

$(n - d)a_b$ and (15) $D = (n - c)a_b$ may be written as approximations to the values of the latter terms, and are sufficiently accurate under the conditions assumed; a_b represents the percentage dissociation of the solvent CD at the concentration n. These approximations, first proposed by Noyes,[1] permit a much easier solution of the problem than that outlined previously. Let it be required to calculate the solubility of thallous chloride in nitric acid of a normality of 2.023, corresponding to Experiment 4 of Table VII. The results are given in Table IX. It is here necessary to make assumptions only in the case of A, to which six arbitrary values between 0.01485 and 0.00800 have been given in the first column. The six corresponding values of B follow from equation (5), the solubility product being taken from Table X. C and D are calculated by equations (14) and (15), in which a_b has the value 0.77, calculated from the constants for nitric acid (Table X); c and d for these two equations are taken in each case from the preceding line, being set equal to zero in line 1. The values for c and d are calculated for the table by equations (8) and (9). The seventh and eighth columns of the table represent the sums of $A + c$ and $B + d$, which, when plotted against the corresponding values of A, intersect at a point corresponding to 0.01030 for A. This figure serves for the calculations of line 7, from which the solubility m is calculated, c and d being taken from line 4, where the value of A is nearest that of line 7.

TABLE IX.

Solubility of TlCl in 2.023 Normal HNO_3.

	A.	B.	C.	D.	c.	d.	A+c.	B+d.
1.	0.01485	0.01485	1.558	1.558	0.04978	0.02014	0.06463	0.03499
2.	0.01200	0.01838	1.542	1.519	0.04124	0.02308	0.5324	0.04146
3.	0.01100	0.02005	1.540	1.526	0.03863	0.02443	0.04963	0.04448
4.	0.01000	0.02206	1.539	1.528	0.03587	0.02604	0.04587	0.04810
5.	0.00900	0.02451	1.538	1.531	0.03305	0.02794	0.04205	0.05245
6.	0.00800	0.02757	1.537	1.532	0.03014	0.03019	0.03814	0.05776
7.	0.01030	0.02142	1.539	1.528	0.03671	0.02552	0.04701	0.04694

$n = 2.023$

$a = 0.00165$

$m = A + a + c = 0.04866$

$m = B + a + d = 0.04859$

Mean solubility = 0.04863

c. Application of Theory to the Experimental Results.

The theory thus developed has been tested by comparison with the experimental results on the solubility of silver acetate and thallous chloride. Concerning these compounds, the necessary data may be had for calculation of all the constants necessary. For the tabulation below, the exponential constant n was found by the graphic method described by Bancroft,[2] using values for the dissociation of the compounds derived

---

[1] *Z. physik. Chem.*, **27**, 271 (1898).

[2] *Ibid.*, **31**, 189 (1899).

from their electrical conductivity between concentrations of one one-thousandth normal and normal. These values halved are the constants n_b, n_c, and n_d, to be substituted in equations (7), (8) and (9). The equilibrium constants k were found to hold with but negligible variation within the limits of concentrations mentioned. The solubility product for substitution in equation (5) has been calculated for the two insoluble salts.

TABLE X.

Constants for Dilution Law, $\frac{(C)^n}{C_s} = k$, at 25° C.

	Electrolyte.	n.	$n/2 = n_b, n_c, n_d$.	$k = k_b, k_c, k_d$.	Solubility product.
1[1].	HNO_3	1.46	0.73	4.100	....
2[2].	HCl	1.34	0.67	3.982	....
3[3].	$HC_2H_3O_2$	2.00	1.00	0.000018	....
4[4].	$AgNO_3$	1.56	0.78	1.165	....
5[5].	$AgC_2H_3O_2$	1.74	0.87	0.260	0.002261
6[6].	$TlNO_3$	1.58	0.79	1.025	....
7[7].	TlCl	1.58	0.79	0.642	0.0002206

In Table XI is given a comparison of the experimental and calculated values for the solubility of silver acetate in nitric acid. The calculation was carried out according to the method illustrated in Table VIII. The figures of column 3 are mean values of the solubilities calculated from

TABLE XI.

Solubility of $AgC_2H_3O_2$ in HNO_3 at 25° C.

	Concentration of HNO_3.	Solubility. found.	Solubility. Calculated.	Variation. Per cent.
1	0.4845	0.511	0.5079	—0.60
2	0.9506	0.970	0.9678	—0.22
3	1.789	1.841	1.783	—3.15
4	3.269	3.290	3.218	—2.24
5	3.923	3.929	3.845	—2.13
6	4.703	4.745	4.590	—3.26
			Mean,	—1.93

---

[1] Data from Kohlrausch and Holborn, *Leit. der Electrolyte*, pp. 160 and 200. The figures are founded on the conductivity at 18°, since the conductivity of HNO_3 at 25° has not been measured.

[2] Data from Ostwald, Lehr. 2, pp. 722–3; λ_∞ from Bredig, *Z. physik. Chem.*, **13**, 228 (1894).

[3] Constants from Ostwald, *Z. physik. Chem.*, **3**, 174 (1889).

[4] Data from Loeb u. Nernst, as given by Bredig, *Loc. cit.*

[5] Data from Loeb u. Nernst, *Z. physik. Chem.*, **2**, 959 (1888); Bredig, *Loc. cit.* Arrhenius (*Z. physik. Chem.*, **31**, 223 (1899), calculates n as 1.61 and K as 0.3569. Solubility product from measurements of Goldschmidt, *Z. physik. Chem.*, **85**, 95 (1898).

[6] Data from Franke, *Z. physik. Chem.*, **16**, 467 (1895), and Bredig, *Loc. cit.*

[7] Data from Franke, *Loc. cit.*, and Bredig, *Loc. cit.* Solubility product from measurements of Goodwin, *Z. physik. Chem.*, **13**, 608 (1894).

equations (1) and (2), which gave figures agreeing with each other within 0.2 per cent. or less. In order to attain results of this degree of accuracy within reasonable limits of time, it was found necessary to use a calculating machine.

It will be noted that there is a surprising agreement between the values of columns 2 and 3, when it is recalled that the constants used are those derived from conductivity measurements in comparatively dilute solution, here applied to solutions running up to a concentration of 792 grams of salt per liter. The results indicate clearly that the laws of dilute solutions, as given in the fundamental equations used, may be applied to a very concentrated solution of a salt of a weak acid in a very strong acid, with but small resulting error. The "neutral salt effect" in this case is apparently exceedingly slight, and one may fairly deduce that the dissociation relations of silver acetate in a nitric acid solution containing nearly 300 gms. of acid per liter are not fundamentally different from the dissociation relations in dilute aqueous solution. The agreement between experiments and theory is nearly as good as that found by Noyes[1] when working with silver benzoate in nitric acid and chloracetic acid solutions of one-fortieth normal concentration or less, whose results show an average variation in the two sets of experiments of ±1.43 per cent., with a maximum variation of +2.76 per cent.

A further set of calculated results is given in Table XII. Here the solubility of thallous chloride has been calculated by the simplified method illustrated in Table IX, since it is obvious that the presence of one-twentieth gram equivalent of the salt cannot greatly affect the dissociation of nearly four gram equivalents of nitric acid, which is the most extreme ratio considered in the calculations.

TABLE XII.

Solubility of TlCl in HNO_3 at 25° C.

	Concentration of HNO_3.	Solubility. Found.	Solubility. Calculated.	Variation. Per cent.
1	0.000	0.01650	....	......
2	0.497	0.02475	0.02948	+19.2
3	1.004	0.02875	0.03755	+30.5
4	2.023	0.03401	0.04863	+43.0
5	3.996	0.04145	0.06817	+64.3

Comparison of columns 2 and 3 shows that conditions are here radically different from those of Table XI. It is apparent that the dissociation of thallous chloride is very greatly affected by the solvent, since even in the comparatively dilute acid of line 2 the solubility is far below the calculated value. Whether the difference between the behavior of this salt and silver acetate is due to the fact that the ratio of solvent to solute is so much greater in the former case than in the latter, or whether

---

[1] *Z. physik. Chem.*, **27**, 283 (1898).

it is due to some cause connected with the nature of the salts, cannot here be determined.

It has not been possible to calculate the solubility of the other salts studied, since data on their dissociation relations are not at hand. It is intended to provide the measurements for these calculations at a later date, and to continue the study of the solubility of other salts in concentrated acids, with the hope of gaining further information on the extent to which the dissociation of these compounds, as calculated by the laws of dilute solution, is affected by the presence of other electrolytes.

The results of this investigation may be summarized as follows:

(1) The solubilities of silver acetate, chloracetate, oxalate, iodate and sulphate, and of thallous chloride, have been determined in solutions of nitric acid of high concentration.

(2) A mathematical solution of the known laws bearing on solubility relations has been proposed.

(3) Comparison of experimental and calculated results has shown that the laws of dilute solutions hold for extremely concentrated solutions of a salt of a weak acid in a strong acid, while the solubility of a salt of a strong acid has been shown to be greatly depressed under the same conditions by some factor presumably connected with the neutral salt effect, but not yet capable of quantitative expression.

It is a pleasure to express our indebtedness to Professor Arthur B. Lamb, of this department, for much helpful advice in the prosecution of this work, and to Professor T. W. Edmondson, of the Department of Mathematics, for kind assistance in the mathematical part of this work.

NEW YORK UNIVERSITY.

NOTE.

Constant-level Reservoir.—The writer has had trouble heretofore with liquids that would filter only with the greatest difficulty. The filter pump could not always be used to advantage on account of clogging, which necessitated the removal of the filtering medium and replacing it with another.

What seemed to be wanted was an apparatus that would supply to the funnel new liquid as fast as the filtration took place. The filter pump could then be used to an advantage or a funnel with its filter paper. With this object in view the writer proceeded to design an apparatus.

The illustration, which is almost self-explanatory, shows the survival of the fittest. It works the same as inverting a flask containing the liquid to be filtered over a funnel with its filter paper, having the opening of the flask a little below the edge of the paper.