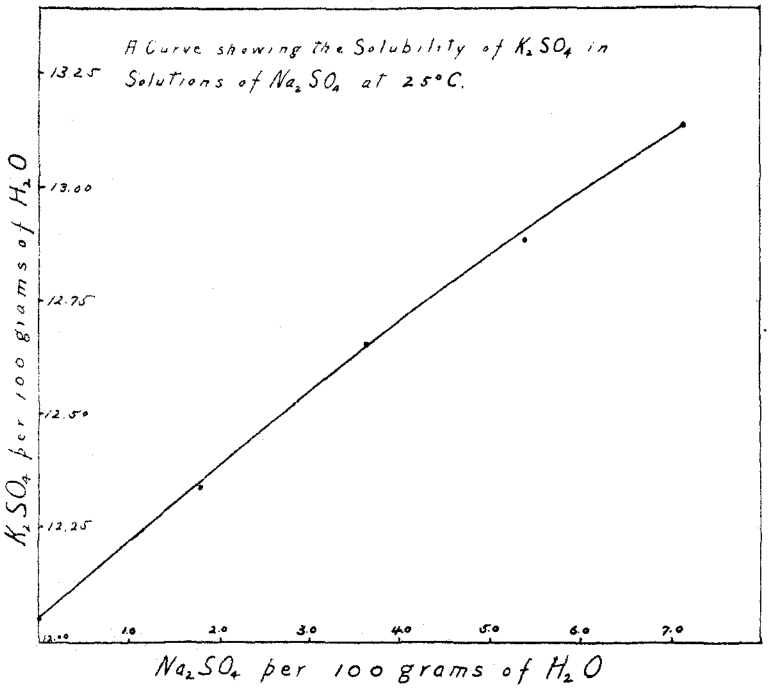

Fig. 4.

This method is open to the objection that sodium sulfate may to some extent have been removed from the solutions, owing to the presence of the solid potassium sulfate. It should be pointed out, however, that the solutions were at the start all far from saturation with respect to sodium sulfate; that if any sodium sulfate was removed it was probably removed in quantities increasing with the sodium sulfate concentration; and that the correction of any error arising from this cause would most likely result in exposing a still more marked rise in solubility of potassium sulfate with increasing amounts of sodium sulfate.

URBANA, ILL.

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THE INCONSTANCY OF THE SOLUBILITY PRODUCT. II.

BY ARTHUR E. HILL.

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In an earlier publication,[1] it was shown that the solubility product of thallous chloride decreases in value upon addition of acetic acid to the aqueous solution, and that tetramethyl ammonium iodide behaves in the same fashion when treated with potassium hydroxide. The present

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[1] Hill, THIS JOURNAL, 32, 1186 (1910).

publication contains experimental evidence bearing upon the same point. The solubility of the above mentioned salts has been re-determined, in solutions as dilute with respect to the second electrolyte as were found to have any measurable effect, and three additional series of solubility determinations have been added.

In the five cases investigated, the solubility of the salt was found to diminish either upon the slightest addition of the second electrolyte, or, in the case of lead chloride, to suffer a slight initial increase followed by a decrease in solubility on addition of further amounts of the second substance. This behavior is the opposite of that which would be predicted by the theory of electrolytic dissociation; the addition of a second electrolyte with no ion in common with the saturating electrolyte should cause an increase in solubility through the formation of the products of metathesis. It will be shown that the result here found, a decrease in solubility instead of an increase, points to a decreasing value of the solubility product, and that in cases where the drop in solubility is sufficient, rigid proof of a decrease in the solubility product can be given, without assumption as to dilution formulas for any of the substances present.

Experimental Part.

The solubility determinations were conducted in a thermostat, at a temperature of 25°, measured on a thermometer tested by the Bureau of Standards. The thermostat was found to control the temperature within one or two one-hundredths of a degree. Equilibrium was obtained from undersaturation and supersaturation, the latter condition having been attained by agitation at temperatures of 40° to 70° in the different cases. In some of the experiments the materials were rotated in stoppered bottles within the thermostat, and in others glass paddles were used to stir the substances in Florence flasks of suitable size. No decided advantage of the one procedure over the other has been noted, either in respect of accuracy or speed.

Silver Bromate and Acetic Acid.—The silver bromate was prepared by mixing approximately normal solutions of potassium bromate and silver nitrate. The precipitate thus obtained was washed by decantation and recrystallized from boiling water. In this case, and in other cases where the salts are quite insoluble and also more or less unstable, it has been found advisable to recrystallize by introduction of live steam through a glass tube into the mixture of solvent and solute, thus avoiding the use of a Bunsen flame, which is apt to cause superheating at the bottom of the vessel and bring about partial decomposition of the salt lying directly above it.

Analysis gave a silver content, weighed as silver chloride, of 44.97% and 45.00%; theory 45.75%.

The acetic acid used was a C. P. preparation; the concentration of the solutions used in the experiments was determined by titration against a potassium hydroxide solution, in turn standardized against gravimetrically analyzed hydrochloric acid. The flasks containing an excess of salt with the acetic acid solution were stirred in the thermostat for three days, and then allowed to stand for half a day to settle. The solution did not require filtration, but could be pipetted directly into platinum dishes. The silver bromate in the pipetted liquid (50. 13 cc.) was determined by evaporation on the water bath, under draft so as to prevent contamination by dust. The residue was then dried in an electric oven at 110° for an hour, and ultimately weighed against another platinum dish as tare. The accuracy of the method was tested by taking about 100 mg. of dried salt, covering it in the platinum dish with 50 cc. of normal acetic acid, evaporating and weighing as above. A loss in weight of but 0.2 mg. was found. Similar experiments with pure water showed no detectable change in weight. By interpolation from a straight line, corrections were established and used when amounting to 0.1 mg. or more. The results of the experiments are given in Table I, where U and S are symbols used to indicate that the equilibrium was approached from undersaturation and supersaturation, respectively. The measurements were made by Mr. William L. Engels.

TABLE I.—SOLUBILITY OF SILVER BROMATE IN ACETIC ACID SOLUTIONS AT 25°.

Normality of acetic acid.	G. $AgBrO_3$ in 50.13 cc.	Solubility in grams per liter.	Solubility in milli-equivalents per liter.
1....... 0.0000	0.0979 U	1.9493	8.2668
	0.0977 S		
	0.0977 U		
	0.0976 S		
2....... 0.0498	0.0975 U	1.9429	8.2398
	0.0973 S		
3....... 0.0997	0.0973 U	1.9379	8.2187
	0.0970 S		
4....... 0.1995	0.09625 U	1.9206	8.1451
	0.0963 S		
5....... 0.4988	0.09346 U	1.863	7.9041
	0.0934 S		
6....... 0.9975	0.0904 U	1.8013	7.6392
	0.0902 S		
7....... 1.8721	0.0804 U	1.6178	6.8608
	0.0818 S		

The solubility of the salt in pure water is not greatly different from that found by A. A. Noyes[1] at 24.5°. Noyes' figure is 1.92 g. per liter. The result is, however, not at all in accord with Longi's figure[2] at 25°, 1.66 g. per liter, nor with that found by Whitby,[3] 1.71 g. per liter at 27°.

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[1] *Z. physik. chem.*, 46, 603 (1903).

[2] *Gazz. Chim.*, 13, 87 (1883).

[3] *Z. anorg. Chem.*, 67, 108 (1910).

Tetramethyl Ammonium Iodide and Potassium Hydroxide.—The salt used was a commercial preparation which was purified by recrystallization.

Iodine by precipitation as silver iodide, 63.00% and 62.92%; theory, 63.13%.

The potassium hydroxide solution was made from a pure preparation, and analyzed for its carbonate content. A very slight excess of an analyzed barium hydroxide solution was then added and the liquid eventually decanted from the precipitated carbonate. The solution thus prepared showed presence of a trace of barium only. The chloride content was also determined analytically in order that the weight of silver iodide found in the solubility experiments might be corrected for the chloride likewise precipitated; the corrections amounted to 0.04 mg. in Expt. 1 and 0.8 mg. in Expt. 4. Equilibrium was obtained by stirring overnight. Samples of 9.564 cc. each were withdrawn from the flasks, and the iodide content determined by precipitation as silver iodide, filtering and weighing in platinum Gooch crucibles. The measurements were made by Mr. Oliver J. Teeple, Jr.

TABLE II.—SOLUBILITY OF TETRAMETHYL AMMONIUM IODIDE IN POTASSIUM HYDROXIDE SOLUTIONS AT 25°.

Normality of potassium hydroxide.	G. $(CH_3)_4NI$ in 9.564 cc.	Solubility in grams per liter.	Solubility in milli-equivalents per liter.
1....... 0.0000	0.5035 U	52.72	262.28
	0.5039 S		
	0.5054 U		
	0.5039 S		
2....... 0.057	0.5002 U	52.30	259.99
	0.4993 S		
3....... 0.112	0.4962 U	51.88	258.10
	0.4963 S		
4....... 0.251	0.4824 U	50.40	250.73
	0.4815 S		

The solubility of the salt in water is found to be about 0.7% lower than Walden's figure,[1] 53.1 g. per liter. It is still further divergent from the figure given in the earlier publication on this topic,[2] 53.70 g. per liter, where the result was unquestionably influenced by a thermometric error.

Tetramethyl Ammonium Iodide and Ammonium Hydroxide.—The sample of salt used in this experiment was found upon two analyses to contain 63.00% and 63.13% iodine, determined gravimetrically; theory, 63.13%. The ammonium hydroxide solution used was found to give a residue of 0.3 mg. in 10 cc. of 0.1 *N* solution, 0.45 mg. in 0.5 *N* solution, by which amounts the solubilities were corrected; the residue from the water amounted to 0.1 mg. After equilibrium was obtained by rotating in closed bottles for 24 hours, samples of 10.025 cc. were pipetted into platinum dishes, evaporated on the water bath, dried in the electric oven

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[1] *Z. physik. Chem.*, **55**, 708 (1906).

[2] THIS JOURNAL, **32**, 1186 (1910).

at 110°, and weighed against platinum tares. Trial showed the weight of salt was not affected by evaporating with ammonium hydroxide, except to the extent of the residue, for which correction was made. The experiments were performed by Mr. Howard F. Brownell.

TABLE III.—SOLUBILITY OF TETRAMETHYL AMMONIUM HYDROXIDE IN AMMONIUM HYDROXIDE SOLUTIONS AT 25°.

Normality of ammonium hydroxide.	G. $(CH_3)_4NI$ in 10.025 cc.	Solubility in grams per liter.	Solubility in milli-equivalents per liter.
1....... 0.0000	0.5290 U	52.758	262.48
	0.5290 S		
	0.5288 U		
	0.5289 S		
2....... 0.0494	0.5284 U	52.708	262.23
	0.5284 S		
3....... 0.1001	0.5279 U	52.863	262.00
	0.5280 S		
4....... 0.2102	0.5277 U	52.623	261.80
	0.5276 S		
5....... 0.5224	0.5269 U	52.579	261.58
	0.5273 S		
6....... 1.0149	0.5250 U	52.384	260.62
	0.5253 S		
7....... 2.1099	0.5213 U	52.025	258.77
	0.5218 S		

The solubility in water is in close agreement with that given in Table II. The ammonium hydroxide is much less effective in lowering the solubility than the stronger potassium hydroxide.

Thallous Chloride and Acetic Acid.—The thallous chloride was prepared from the metal and purified by recrystallization.

Det. of Cl, av. of four closely agreeing grav. analyses, 14.79%; theory, 14.80%.

The acetic acid did not give a weighable residue upon evaporation of 50 cc. of 0.1 *N* concentration. Equilibrium was attained by stirring for 24 hours; pipetted samples of 50.344 cc. were evaporated as described in previous experiments, after determining that evaporation of thallous chloride with 50 cc. of the most concentrated acid here used did not affect its weight. The experiments were performed by Mr. Oliver J. Teeple, Jr.

TABLE IV.—SOLUBILITY OF THALLOUS CHLORIDE IN ACETIC ACID SOLUTIONS AT 25°.

Normality of acetic acid.	G. TlCl in 50.344 cc.	Solubility in grams per liter.	Solubility in milli-equivalents per liter.
1....... 0.0000	0.1940 U	3.8515	16.085
	0.1938 S		
2....... 0.0501	0.1933 U	3.8375	16.027
	0.1931 S		
3....... 0.0958	0.1930 U	3.8326	16.006
	0.1929 S		
4....... 0.263	0.1894 U	3.7503	15.662
	0.1883 S		
5....... 0.524	0.1837 U	3.6539	15.258
	0.1842 S		

The solubility in water is in excellent agreement with the value found by Bray and Winninghoff,[1] which is 16.07 milliequivalents per liter.

Lead Chloride and Acetic Acid.—The samples of lead chloride used were prepared by addition of hydrochloric acid to lead nitrate solutions, and recrystallized from water. Several gravimetric analyses gave the chlorine content close to the theoretical 25.51%, the maximum variation being 0.08%. The acetic acid solutions were standardized volumetrically. The materials were stirred for 24 hours, and filtered at the temperature of the bath from a little suspended chloride. Pipetted portions were evaporated and weighed in platinum as described before. Two complete sets of experiments were made, one by Mr. Charles E. Roake and a second by Dr. Frank O. Amon. 25 cc. portions were used for analysis in both series. It was established that evaporation of lead chloride with acetic acid of the concentrations here used did not affect the weight measurably.

TABLE V.—SOLUBILITY OF LEAD CHLORIDE IN ACETIC ACID SOLUTIONS AT 25°.

Normality of acetic acid.	Solubility in grams per liter (Mr. Roake).	Solubility in grams per liter (Dr. Amon).	Solubility in milliequivalents per liter (average).
1....... 0.000	10.778 U	10.780 U	77.53
	10.766 S	10.784 S	
		10.772 U	
		10.776 S	
2....... 0.050	....	10.816 U	77.82
	....	10.816 S	
3....... 0.100	10.846 U	10.880 U	78.17
	10.864 S	10.868 S	
4....... 0.150	....	10.784 U	77.59
	....	10.784 S	
5....... 0.200	10.701 U	10.716 U	77.03
	10.687 S	10.724 S	
6....... 0.465	10.262 U		73.92
	10.284 S		
7....... 0.929	9.453 U		68.03
	9.457 S		
8....... 1.845	7.906 U		56.86
	7.900 S		
9....... 3.680	5.260 U		37.88
	5.271 S		

The determinations of the solubility in water agree well with each other and with the figure given by Harkins,[2] 77.76 milliequivalents per liter.

Discussion of the Results.

The measurements show that in four of the five cases addition of as small an amount as one-twentieth equivalent of the second electrolyte causes a measurable decrease in solubility. This is in qualitative dis-

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[1] THIS JOURNAL, **33**, 1665 (1911).

[2] *Ibid.*, **33**, 1816 (1911).

agreement with theory as usually accepted, in that a second electrolyte should, by metathesis, reduce the ion concentration of the saturating phase, and so bring about an increase in solubility. The decrease in solubility of the undissociated material, which has been shown by Arrhenius[1] to occur under these circumstances, would in all probability be a much smaller factor, since the salts used are all strong electrolytes in aqueous solution. It is therefore proper to look to the behavior of the ions for the chief cause of this decrease in solubility. This point will be developed further on.

The solubility curve of lead chloride offers especial interest. It is seen that there is a small but unmistakable increase in solubility upon addition of 0.05 equiv. of acetic acid; the solubility then becomes greater at 0.10 equiv., dropping again at 0.15 to nearly the same value as in water, and from that point on diminishing rapidly upon addition of acid. The factors causing the initial increase are evidently of but slight influence as compared with those which cause the decrease. This is the more remarkable since the pair of electrolytes chosen here is one which might be expected to show considerable metathetical change (at least in so far as acetate ion is present in acetic acid), since lead acetate, the product of the metathesis, has been shown to be an exception among salts, having a comparatively slight dissociation. From this low dissociation (22% only in 0.1 *N* solution) Noyes and Whitcomb[2] have concluded that the high solubility of lead sulfate (and presumably that of other lead salts) in ammonium and sodium acetate solutions is due mainly to the formation of un-ionized lead acetate. Reasoning by analogy, we should expect that lead chloride would, for the same reason dissolve rather freely in acetic acid, or at least, since the acid furnishes but a small concentration of acetate ions for the reaction, that it would dissolve more freely than in other solvents at equal ionic concentration. The case furnishes an example, on a reduced scale, of the use of a solvent capable of producing a weak electrolyte by reaction with an insoluble compound, such as the use of a strong acid upon the salt of a weak acid. It has been in cases of this order that the theory of electrolytic dissociation has been most conspicuously successful in giving a qualitative explanation of the facts; yet in this instance the solubility is raised less than 1% over a short range of concentration, and throughout the rest of the range is more and more strongly depressed.

A quantitative examination of the results throws additional light on the question of the constancy of the solubility product. The first quantitative evidence showing the change of this value with the concentration pointed definitely to the view that the solubility product decreases with

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[1] *Z. physik. Chem.*, **31**, 224 (1899).

[2] THIS JOURNAL, **27**, 747 (1905).

increased concentration of electrolytes present.[1] On the other hand, a very considerable amount of evidence has been presented by Noyes,[2] Bray, Harkins and others, who have calculated an increase in the value of the solubility product on the basis of a large number of very carefully conducted experiments. The evidence of the experiments described in this paper is in support of the view that the solubility product decreases; a discussion of the opposed view will be given later on.

It is possible to produce rigid proof of the decrease of this value in the experiments given. If in the case of any double decomposition,

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

we indicate the concentration of ions at equilibrium by the capital letters and that of the four molecular species by the small letters, we may express the total solubility m of the compound AB in two ways:

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

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

Multiplying Equation 1 by Equation 2 and extracting the square root, we have

$$(3)\ m = \sqrt{\mathrm{AB}} + \mathrm{X},$$

where X is used to indicate the various other terms, all of which have positive value. But AB is the solubility product; hence, if the solubility product be a constant or have an increasing value, m, the total solubility must always be greater than $\sqrt{\mathrm{AB}}$, as calculated for the salt in pure water. If the total solubility becomes under any conditions less in value than $\sqrt{\mathrm{AB}}$, it is demonstrated that the solubility product has neither a constant nor an increasing value.

The solubility data of Table VI will show that this condition has been reached. The results in more dilute solutions have been omitted, and the concentration of soluble electrolyte given in approximate value only; the exact figures are to be had in Tables I to V.

The table shows that in four of the five cases (that of tetra-methylammonium iodide with ammonium hydroxide being the exception) the total solubility becomes less than the square root of the solubility product, the point being reached at a concentration between normal and twice normal. In these cases, therefore, it is established that the solubility product has a decreasing value. No assumption is involved in the demonstration except that the substance in solution is present in the form of ions and of undissociated molecules, which is the fundamental assumption of the dissociation theory. In the calculation of the solubility product, the assumption is of course made that the ratio of equivalent conductance in saturated solution to the equivalent conductance at zero con-

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[1] Hill, *Loc. cit.*

[2] This Journal, 33, 1643 (1911), *et seq.*

centration represents the degree of dissociation; this assumption is, however, of but secondary importance here, since the direction of the five solubility curves indicates clearly that the total solubility will become less than the square root of the solubility product however this value be altered (within reasonable limits) by errors in the degree of dissociation assumed.

TABLE VI.—SOLUBILITY IN MILLI-EQUIVALENTS PER LITER.

Approximate conc. of soluble electrolyte.	$AgBrO_3$ in $HC_2H_3O_2$.	$(CH_3)_4NI$ in KOH.	$(CH_3)_4NI$ in NH_4OH.	TlCl in $HC_2H_3O_2$.	$PbCl_2$ in $HC_2H_3O_2$.
0.00	8.2668	262.28	262.48	16.085	77.53
0.20	8.1451	252.00	261.8	15.82	77.03
0.50	7.9041	232.7[1]	261.5	15.29	73.40
1.00	7.6392	204.6[1]	260.6	14.73[1]	67.00
2.00	6.75	139.4[1]	258.8	13.03[1]	54.30
3.68	....	....	...	....	37.88
$\sqrt{AB}$	7.73[2]	167.8[3]	167.8[3]	14.32[4]	42.50[5]

In Col. 4 of Table VI it appears that the solubility of the salt is decreased but slightly by the ammonium hydroxide, and never reaches the lower limit necessary to the argument. In this case we can only reason by analogy, and assume that the decrease in total solubility is here likewise caused largely by decrease in the value of the solubility product, although the value does not become low enough to make calculations possible without assuming some form of dilution formula. A comparison with Col. 3 shows that the decrease in solubility runs, in a very rough way, parallel to the alkalinity (hydroxyl-ion concentration) of the two bases. At concentrations of 0.2 *N*, the caustic potash has caused 16 times the change in solubility caused by the ammonia, whereas its ion content may be calculated to be about 96 times that of the ammonia; that is, its effect on the solubility is about one-sixth that of the ammonia for equal alkalinity. At 2.0 *N* concentration the solubility change due to caustic potash is about 36 times that due to ammonia, and its dissociation about 305 times as great; hence its effect on solubility is about one-eighth as great as that of the ammonia for equal alkalinity. It appears that over this rather wide range of concentrations, in which the solubility of the salt is decreased some 47%, the effect of the stronger base is always

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[1] From Hill, *Loc. cit.*

[2] Calculated by extrapolation from the figures of Böttger at 19.94° C. (*Z. phys. Chem.*, **46**, 603) and of Noyes at 24.5° C. (*Z. phys. Chem.*, **6**, 246).

[3] Hill, *Loc. cit.*

[4] Bray, THIS JOURNAL, **33**, 1673 (1911).

[5] Harkins, *Ibid.*, **33**, 1820 (1911). It is to be noted that in the case of the biunivalent salt $PbCl_2$, the lower limit is not the square root of the solubility product, but the square root of AB, A and B representing molecular concentrations of the two ions. The value is here changed into milli-equivalents, in conformity with the remainder of the table.

from one-sixth to one-eighth that of the weaker, when referred to hydroxyl-ion concentrations.

In the case of lead chloride, shown in Col. 6, the solubility curve does not reach the value for the square root of AB until a much higher concentration of electrolyte is reached than in the other cases. This abnormality does not lie in the solubility curve itself, but in the value of AB. Actually the solubility curve has a downward pitch almost as steep as the curves for silver bromate and for thallous chloride, and it may be argued by analogy therefore that the solubility product is also as sharply depressed as in the other cases. The value AB, however, is derived from the dissociation of the salt, and lead chloride, like other bi-univalent salts, has a much lower degree of dissociation than the uni-univalent salts; the value calculated by Harkins,[1] and here used, is 56.2% only. A complication comes in, also, in the interpretation of the term "solubility product" as applied to salts of this class, since the formation of intermediate ions, as $Pb^{+}Cl$, must be reckoned with, whose actual concentration cannot be determined exactly. Harkins calculates on the basis of complete dissociation into lead and chlorine ions. Whether this assumption be made, or whether it be assumed that the dissociation is exclusively into $Pb^{+}Cl$ and Cl^{-} ions, or whether both conditions exist, will affect, of course, the point at which the solubility curves reaches the critical value, but since the curve is almost exactly linear and slopes downward sharply there can be no question but that it will, at some concentration, reach whatever value is used.

If it is regarded as established that the solubility product decreases with concentration increase in these cases, it must necessarily be asked how the conclusion can be harmonized with the opposite view expressed by Noyes, Bray and Harkins and others in the publications cited, in which the work is characterized by the greatest possible experimental care and includes determinations upon a large number of salts. Bray[2] has thought it possible to disregard evidence compiled by me showing a decrease, on the ground that acetic acid is not a typical strong electrolyte and that the previously published results did not include determinations in dilute solution; he thinks it possible that the experiments indicate rather the mutual insolubility of acetic acid and thallous chloride, and of tetra-methyl-ammonium iodide and potassium hydroxide. To these objections may be answered that acetic acid and the other weak electrolytes are just those that obey the mass law most closely and would, therefore be expected to give normal results in solubility experiments; one can hardly throw acetic acid and ammonium hydroxide out of court in researches having to do with any phase of the dissociation

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[1] THIS JOURNAL, 33, 1820 (1911).

[2] *Ibid.*, 33, 1684 (1911).

theory, when one remembers that it is the particular electrolytes and their adherence to the law of mass action that first gave the theory standing. Moreover, the substance potassium hydroxide, a typically strong electrolyte, has the same effect as the weak electrolytes, differing only in degree from ammonium hydroxide. The question as to whether the experiments have been conducted in dilute solution must always remain open, subject to definition of the term dilute; it has been established however that in the cases given in this publication the solubility decreases in as dilute solutions as have any effect upon the solubility, a result which was to be expected in view of the fact that dilute solutions and concentrated differ in degree rather than in kind. The question of mutual insolubility, as raised by Bray, seems irrelevant in the absence of special data on the cases given; it would be no more relevant to hold that the increase in solubility measured by Bray might be due to mutual solubility of the pairs under investigation.

A complete reconciliation of the divergent conclusions does not seem possible at this time. It should be pointed out, however, that the calculations showing an increase in the solubility product are based upon an added assumption as to a dilution law, and that the results are highly dependent on the dilution law used. The form used in the calculations referred to[1] is

$$\frac{C_B \times C_A}{C_{AB}} = K(\Sigma C_1)^{2-n} \qquad (1)$$

in which the term ΣC_1, denotes the sum of all the positive or negative ions present in the solution. This equation, first given by Arrhenius,[2] is based upon the assumption that the deviations from the mass law shown by any electrolyte are dependent upon the concentration of other ionic species present to just the same extent as upon its own ions. The formula is doubtless correct in giving the direction of the change brought about by a second substance, and may be regarded as a first approximation to the truth; but it is seriously open to question as a quantitative expression for the dissociation equilibrium of one electrolyte in the presence of a second. Up to the present, it lacks probability as an exact expression, and also lacks such experimental evidence as would warrant its being adhered to quantitatively. The improbability lies in its assuming all ions to be equivalent in affecting the dissociation of electrolytes; it does not seem probable that ions of different charge, of different chemical composition, and of different mobility should have exactly the same influence upon the dissociation of a given salt. From the experimental side, the evidence in favor of the formula is not convincing. Data from experiments on catalysis can hardly be depended upon, so long as the rela-

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[1] Noyes, THIS JOURNAL, 33, 1644 (1911).

[2] *Z. physik. Chem.*, 31, 218 (1899).

tion between ionization and catalysis is so imperfectly known. Measurements of electrical conductance of mixtures also give evidence which it is not easy to weigh. As an example, the investigation of Bray and Hunt[1] indicates that considerable differences in the degrees of ionization may be assumed without betraying themselves in the conductivity measurements. For these reasons it may be fairly held that the quantitative accuracy of the Arrhenius dilution formula is as yet unproved.

It is of the utmost importance to note however that the calculations of Bray depend upon the accuracy of this dilution law, and that a change in the assumption will lead to conclusions quite different from those which Bray has drawn. In order to test this point, a recalculation of Bray's data has been made, using the closely related Storch-Bancroft[2] dilution law, in the form

$$\frac{(C_B \times C_A)^{n/2}}{C_{AB}} = K. \tag{2}$$

As applied to cases of mixtures, this equation differs from the Arrhenius formula in assuming that the dissociation of each electrolyte is independent of the other electrolytes present; its otherwise close relation to the Arrhenius equation may be shown by writing it in the following form (which is applicable, however, only when no second electrolyte is present).

$$\frac{C_B \times C_A}{C_{AB}} = K(C_A)^{3-n},$$

which differs from the Arrhenius form only in the correction term applied to the mass law constant.

If the Storch-Bancroft formula, as given in Equation 2, is substituted for the Arrhenius formula as used by Bray, an entirely different conclusion as to the change in the solubility product results, and a decrease in its value appears where an increase was previously calculated. Table VII has been prepared to show this contrast. The second and fourth columns contain the increasing values of the solubility product as calculated by Bray, and the third and fifth show that for the same salts decreasing values may be found, by calculating according to the method used by Bray in every detail, with the exception of the use of the Storch-Bancroft formula (Equation 2) in place of the Arrhenius formula (Equation 1).

It will be seen that the calculations on the basis of the Storch-Bancroft formula show a *decreasing* value of the solubility product. Similar calculations have been made for the other uni-univalent electrolytes treated by Bray (TlCl in presence of KNO_3 and $TlNO_3$); the decrease is found in these cases likewise, and is of the same order.

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[1] THIS JOURNAL, **33**, 781 (1911).

[2] *Z. physik. Chem.*, **31**, 188 (1899).

TABLE VII.—VALUES OF SOLUBILITY PRODUCT.

Conc. of KCl in milli-equivalents.	Solubility product of TlCl in presence of KCl.		Solubility product of $KClO_4$ in presence of KCl.	
	Bray.	Hill.	Bray.	Hill.
0.0	204.9	204.9	13290	13290
25.0	218.1	203.8	...	....
50.0	229.6	201.1	13590	12918
100.0	256.3	198.6	13890	12778
200.0	290.0	181.4	...	...

All the other salts in the series are salts with a bivalent ion; for these the calculations were not again made, since an added assumption would be necessary as to whether or not the salt dissociates in stages. It seems reasonably certain, however, that in all these cases where the Arrhenius ionization principle shows an increase in the solubility product, the assumption of no ion effect will show a decrease.

It is not intended to argue in favor of the use of the Storch-Bancroft formula for such cases. All the evidence seems to be that a second salt *does* affect the dissociation of the first, and that the change is in the direction indicated by the Arrhenius formula, but that the extent of the influence is in doubt. What Table VII does show very clearly, however, is that the conclusion as to the change in the solubility product is directly dependent on the dilution formula used. If we assume with Arrhenius that the total ion concentration should be included in the formula, we find the solubility product increases; if we go to the other extreme and assume that the ions of the second salt have no effect, and should be left out of the formula, we find that the solubility product decreases; and it would be a matter of no especial difficulty at all to put in some intermediate function of the ions of the second salt, and find that the solubility product is the constant that it was once believed to be. It is clear, therefore, that until dissociation relations in mixtures of salt solutions are definitely known, we must accept any conclusion as to the solubility relations with caution if the conclusion involves any form of the dilution law; and that the use of the Arrhenius form may lead to errors as to the extent of the changes, and possibly even as to their direction.

Summary.

(1) Solubility measurements at 25° have been made of five salts in aqueous solutions of varying concentration of soluble electrolyte; silver bromate with acetic acid, tetra-methyl-ammonium iodide with potassium hydroxide and with ammonium hydroxide, thallous chloride with acetic acid, and lead chloride with acetic acid.

(2) It has been shown that the solubility of these salts decreases upon the addition of the smallest effective quantity of the soluble electrolytes used, except in the case of lead chloride, which shows a slight initial increase, followed by a marked decrease.

(3) It is shown, by calculations free from assumption as to dilution laws, that the product of the ions of the saturating salt (the so-called solubility product) decreases in value in the cases mentioned with increase in total concentration.

(4) It is shown that in calculations assuming a dilution law, the formula assumed will determine whether the solubility product shows an apparent increase, an apparent decrease, or an apparent constancy.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS LABORATORY OF HARVARD UNIVERSITY.]

ON THE ABSENCE OF THERMAL HYSTERESIS IN THE COPPER-CONSTANTAN THERMOELEMENT BETWEEN 30° AND 100° C.

BY T. W. RICHARDS AND H. W. RICHTER.

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The internal upheaval caused in solid substances by rise of temperature often produces a slight shifting or thermal hysteresis in the properties of these substances, particularly in substances composed of more than one element in a state of solid solution. The shift of a zero point of a mercury-in-glass thermometer is a typical case in point. Although this particular irregularity has been carefully studied and a correction for it can be suitably applied, nevertheless it is a source of annoyance in the use of this type of thermometer.

During the last ten years W. P. White has developed the use of the highly sensitive copper-constantan multiple thermoelement, and has shown the necessary precautions which must be applied in order to solve the somewhat difficult task of measuring electromotive forces of the order of magnitude of 0.0000001 volt, needful to secure the full advantage of this instrument. It seemed desirable to test whether or not the copper-constantan alloy suffers any marked shift of thermoelectric effect on being subjected to rapid changes of temperature.[1] The following note recounts brief experiments, which show the performance of the thermoelement to be more satisfactory in this particular respect than are most other means of measuring small differences of temperature.

A twelve-junction copper-constantan thermoelement kindly made by Dr. White in 1910 was used for the tests. It embodied many refinements. For the present purpose a duplicate twelve-junction thermoelement to put in opposition with this was not necessary, although such a duplicate is highly desirable in ordinary temperature measurements, as White has pointed out.

The measuring apparatus was a 90 ohm Diesselhorst split-circuit potentiometer made by Otto Wolff. This instrument embodied a fixed resis-

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[1] On p. 140 of White's paper of August, 1910 (*Phys. Rev.*, 31), brief reference is made to tests of this nature, but further elaboration seemed to be desirable.