ment at our disposal the heats of dilution of the several solutions. The purity of the metals used preventing the employment of a less concentrated acid because of their slow rate of solution, the latter alternative is perhaps the easier of the two. It is hoped in the near future that the experience gained in this research may be applied in a more complete manner. In the meantime the results here given must be looked upon as merely preliminary. At least it is hoped that the present papers have succeeded in putting the subject of the heats of solution of metals upon a sound scientific basis, to which the future can add nothing more than perfection of detail.

In conclusion, it is a pleasure to express our indebtedness to the generosity of the Carnegie Institution of Washington for pecuniary assistance.

Summary.

There follows in a few words a statement of the outcome of this paper:

1. The heats of dilution of the acids $HCl.20H_2O$ and $HCl.8.808$ to $HCl.200H_2O$ were determined. The results are 0.556 and 1.330 Calories (2.32 and 5.56 kilojoules) respectively.

2. The heats of dilution of the several products obtained by dissolving four metals in excess of concentrated acid were determined. The substitution of salt for acid was found, especially in the cases of zinc and cadmium, to affect seriously the heat of dilution.

3. From these data the heats of solution of a gram atom of the several metals in exactly the theoretical quantity of $HCl.200H_2O$ have been calculated as follows:

THE HEAT OF REACTION OF METAL ON $HCl.200H_2O$ CALCULATED FOR 1 GRAM ATOM OF METAL.

Metal.	Heat of reaction in 18° Calories.	Heat of reaction in Kilojoules.
Zinc	36.6	153.1
Aluminium	127.0	531.0
Magnesium	110.2	460.6
Cadmium	17.2	71.9
Iron	20.8	87.0

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

THE INCONSTANCY OF THE SOLUBILITY PRODUCT.[1]

BY ARTHUR E. HILL.

Received July 11, 1910.

The various assumptions made by Nernst[2] and A. A. Noyes[3] in their earlier investigations on the solubility of electrolytes have been subjected

---

[1] Presented before the New York Section of the American Chemical Society, June 10, 1910.

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

[3] *Ibid.*, 6, 241 and subsequent papers.

to careful scrutiny by their many successors in this field of work. As in the case of most pioneer work done in theoretical chemistry, it has here developed that many of the assumptions have been too broad, and that they must be subjected to considerable modification if they are to be adopted as a basis for the quantitative study of solutions of electrolytes. Of these original assumptions, two have been almost entirely displaced from the minds of chemists. The belief in the constancy of the concentration of the undissociated molecules of a dissolved electrolyte in equilibrium with its solid phase was shown to be untenable by the experimental work of Arrhenius,[1] which proved beyond question of doubt that this concentration diminishes as the total concentration of salts present is increased. In a like manner, the simplifying assumption that the degree of dissociation is independent of the presence of other electrolytes can no longer be made against the experimental evidence which has been accumulated by Arrhenius,[2] MacGregor, McIntosh, Archibald and McKay,[3] and most recently by Sherrill,[4] all of which makes it reasonably certain that the total concentration of electrolytes present is here also a determining factor.

Of these early assumptions, that of the constancy of the solubility product seems to be the one from which there has been least dissent. It is incorporated in the majority of our elementary text-books as a convenient help in the explanation of solubility relations, and has not lacked advocates even within recent years. Stieglitz[5] has recalculated the experiments of Arrhenius, and finds that by assuming the degree of dissociation to be in accordance with Arrhenius' isohydric principle, it is possible to find a satisfactory constancy for the solubility product, which, he maintains, we may well consider for the present to be an approximate empirical principle, in the absence of theoretical grounds upon which it may stand. Such a theoretical basis Washburn[6] considers to exist in the laws of osmotic pressure, developed with reference to "normal solutes," and "ideal solutions."

Direct experimental proof of the constancy of this value can hardly be looked for, since the concentration of the ions of the solute cannot be directly measured; the calculations based on solubility experiments are complicated by the necessity of making other assumptions as to the state of dissociation and the concentration of undissociated molecules. On the other hand, there already exists, in the solubility experiments of

---

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

[2] *Ibid.*, 2, 284 (1888); 31, 218 (1899).

[3] *Trans. Nova Scot. Inst. Sci.*, 9–10 (1895–1899).

[4] THIS JOURNAL, 32, 741 (1910).

[5] *Ibid.*, 30, 946 (1908).

[6] *Ibid.*, 32, 487 (1910); 32, 669 (1910).

Cameron[1] and of Hill and Simmons,[2] good reason for the belief that the product of the ions diminishes in value with increase in total concentration of electrolytes. Cameron noted that the solubility of gypsum was increased by addition of sodium chloride up to a certain concentration, beyond which it suffered a decrease; the same phenomenon was found to occur when silver sulphate was acted on by nitric acid solutions.[2] In both these cases, we should expect a continuous increase in solubility, due to the formation of new compounds by chemical interaction. This factor would be opposed by a small decrease in the amount of undissociated salt present, as Arrhenius'[3] experiments clearly prove. This latter factor, however, could not be expected to counterbalance the increase caused by chemical action, since the quantity of undissociated salt is practically negligible in the case of highly dissociated substances such as gypsum and silver sulphate. In order, therefore, to account for the diminution in total solubility, we must assume that the ions of the solute have been lessened in concentration, and that the solubility product accordingly has been diminished in value.

The preceding experiments do not permit any calculations as to the value of the solubility product without the use of the other complicating assumptions. In the belief, however, that the qualitative discussion above was correct in principle, other experiments have been conducted in which, without the addition of any common ion, the solubility of certain salts has been so diminished in the presence of other electrolytes as to prove conclusively, without the introduction of assumptions as to the degree of dissociation or the concentration of undissociated salt, that the solubility product is not a constant, but diminishes in value in the presence of other electrolytes.

In selecting material for the experiments, such pairs of electrolytes were chosen as would be expected to show least chemical interaction, so that the increased solubility due to this action might cease to be the determining factor at a low concentration. Thallous chloride, a salt of a strong acid, was used with acetic acid as the second electrolyte; since the solubility of this salt is not greatly increased even by nitric acid,[4] it was to be expected that the weaker acetic acid would have but little effect in this direction. Tetramethylammonium iodide and potassium hydroxide were taken as the second pair. When each of these pairs was tested, it developed that under no conditions was an increase in solubility of the salt to be noted, while the decrease became clearly marked upon the addition of very moderate amounts of the second electrolyte.

---

[1] *J. Physic. Chem.*, 5, 556 (1910).

[2] THIS JOURNAL, 31, 821 (1909). *Z. physik. Chem.*, 67, 594 (1909).

[3] *Loc. cit.*

[4] Hill and Simmons, *Loc. cit.*

Experimental Part.

The thallous chloride used was prepared from metallic thallium and recrystallized from water. Analyses of the pure compound gave the chlorine content as 14.79 and 14.75 per cent.; calculated, 14.80. The acetic acid was Kahlbaum's c. p. preparation, whose strength was determined by titration against a standard potassium hydroxide solution; the ultimate standard was gravimetrically analyzed hydrochloric acid. The solubility equilibrium was approached from supersaturation and undersaturation. Stirring of the samples for eight hours proved to be sufficient. After equilibrium had been reached, samples were pipetted out and analyzed for their chloride content by Volhard's method, filtering off the silver chloride[1] in each case. In experiments (8) and (9), in which the chloride content was low, gravimetric analyses were made. The specific gravity of the acetic acid solution at the temperature of standardization and that of the saturated solution at 25° were determined by direct weighing of measured volumes.

Table I.—Solubility of TlCl in $HC_2H_3O_2$ at 25°.

	Normality of $HC_2H_3O_2$.	Spec. grav. of $HC_2H_3O_2$ at room temp.	Spec. grav. of solution at 25°.	Equivalents TlCl per liter.	Mean solubility per liter.
1.	0.000	....	....	0.01628 U 0.01630 S	0.01629
2.	0.5134	0.9996	1.0014	0.01573 U 0.01589 S	0.01580
3.	1.013	1.0010	1.0043	0.01485 U 0.01505 S	0.01495
4.	2.016	1.0104	1.0114	0.01319 U 0.01323 S	0.01321
5.	4.180	1.0238	1.0323	0.009938 U 0.009952 S	0.009945
6.	8.130	1.0495	1.0550	0.005385 U 0.005413 S	0.005399
7.	11.49	1.0623	1.0599	0.002573 U 0.002615 S	0.002594
8.	14.31	1.0657	1.0643	0.001221 U&S	0.001221
9.	16.01	1.0667	1.0667	0.000478 U&S	0.000478

The tetramethylammonium iodide used for the second set of experiments was a preparation of Kahlbaum's which was recrystallized from water. Analysis by Volhard's method gave the following figures for iodide content: found, 63.08 and 63.38 per cent.; calculated, 63.13. The potassium hydroxide was freed from carbonates by agitating a concentrated solution with slaked lime; when siphoned off and tested, it was found to be free from calcium. The alkali solutions were made up from this stock solution and titrated against a gravimetrically analyzed hydro-

---

[1] Rosanoff and Hill, This Journal, 29, 269 (1907).

chloric acid. Specific gravity and solubility determinations were made as in the case of the thallous chloride, the iodides being determined by the method of Volhard.

TABLE II.—SOLUBILITY OF $(CH_3)_4NI$ IN KOH AT 25°.

	Normality of KOH.	Spec. grav. of KOH at room temp.	Spec. grav. of solution at 25° C.	Grams $(CH_3)_4NI$ per liter.	Equivalents $(CH_3)_4NI$ per liter.
1	0.000	......	1.0163	53.67 U 53.74 S	0.2671
2	0.250	1.0107	1.0268	51.51 U 51.24 S	0.2556
3	0.5325	1.0264	1.0408	47.66 U 47.93 S	0.2377
4	0.9899	1.0474	1.0601	41.81 U 41.98 S	0.2084
5	2.0743	1.0955	1.1048	28.74 U 29.03 S	0.1437
6	8.2962	1.3450	1.3435	3.022 U 2.909 S	0.01475

The solubility of the salt in water is found to be about one per cent. higher than the value which Walden[1] obtained in the case of an equilibrium approached from undersaturation. Walden's figure where the approach was made from the direction of supersaturation (58.9 grams per liter) shows that a true equilibrium was not attained in his experiment.

Determinations of the conductivity of tetramethylammonium iodide were made for use in the calculations of this paper. A dip cell was used for the measurements, the capacity being determined by means of *N*/50 potassium chloride solution, whose conductivity was taken as 0.002768. The water used in the dilutions had a conductivity of 0.0000029. Experiments were conducted with a saturated solution and with the customary dilutions from *N*/8 to *N*/1024.

TABLE III.—CONDUCTIVITY OF $(CH_3)_4NI$ AT 25° (±0.03°).

	Volume.	Equivalent conductivity.
1	3.74	81.20
2	8.0	88.86
3	16.0	96.54
4	32.0	103.4
5	64.0	109.3
6	128.0	113.9
7	256.0	118.2
8	512.0	121.8
9	1024.0	123.8
—	∞	(129.2)

The value of the equivalent conductivity at infinite dilution was found

---

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

by extrapolation to zero concentration from the results of experiments 5 to 9, following the method of A. A. Noyes.[1]

The limiting value 129.2 is much higher than that which would be found by taking for the migration numbers the accepted value 76.8 for iodide ion and for the tetramethylammonium ion 46.5 as calculated by Bredig[2] from conductivity measurements of the chloride. This value for the tetramethylammonium ion is surely several units too low, as appears when it is used to calculate the dissociation of tetramethylammonium hydroxide from Bredig's measurements;[3] at a dilution of 256, the base appears to have a conductivity corresponding to more than complete dissociation. If the migration number is taken from the above measurements as 52.4, the base is seen to possess only the extent of dissociation common to strong electrolytes, and the anomaly disappears.

Discussion of Results.

It has been shown that a diminution in solubility such as appears in Tables II and III gives strong qualitative indication that the value of the solubility product has also diminished. The case is capable of quantitative treatment where the decrease goes far enough. If in the case of the double decomposition

$$\underset{a}{\mathrm{AB}} + \underset{b}{\mathrm{CD}} \rightleftarrows \underset{c}{\mathrm{AD}} + \underset{d}{\mathrm{CB}},$$

we use the capital letters to indicate concentrations of free ions and the small letters to indicate concentrations of undissociated molecules, we can express the total solubility m of the compound AB in two ways:

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

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

If we assume the solubility product to have a constant value, we have

$$(3)\ \mathrm{A} \times \mathrm{B} = \mathrm{K}.$$

Multiplying (1) by (2) and extracting the square root, we find

$$(4)\ m = \sqrt{\mathrm{A} \times \mathrm{B}} + \mathrm{X},$$

where X is used to indicate the various other terms, all of which must have a positive value, since a, b, c and d are positive numbers. Substituting from (3), we obtain

$$(5)\ m = \sqrt{\mathrm{K}} + \mathrm{X},$$

which indicates that, on the assumption of the constancy of the solubility product, the total solubility could never be less than the value $\sqrt{\mathrm{K}}$. A value of m less than $\sqrt{\mathrm{K}}$ proves therefore an error in the assumptions

---

[1] *Report of the Carnegie Inst.*, 63, 50. See also the paper of Johnston, THIS JOURNAL, 31, 1010 (1910). The value of the exponent n for this salt was found to be 1.48.

[2] *Z. physik. Chem.*, 13, 228 (1894). Bredig's numbers have been multiplied by 1.067.

[3] *Ibid.*, p. 299.

of equations 1, 2, or 3. Equations 1 and 2 express the fundamental assumption of the dissociation theory, that the substances present exist as ions and as undissociated molecules; unless we are prepared to deny this, we must grant that a value of m less than $\sqrt{K}$ constitutes rigorous proof that the value of the solubility product has decreased.

In the following tables the values of m have been arranged with reference to the concentration of other electrolytes present; the values of the solubility product have been calculated for each salt. The solubilities have been calculated with reference to the volume of the solution and to the weight of water present, so that the meaning of the term concentration shall not be in question:

TABLE IV.—SOLUBILITY OF TlCl IN $HC_2H_3O_2$.

Volumetric normality of $HC_2H_3O_2$.	Equivalents TlCl per liter of solution.	Equivalents TlCl per 1000 gms. of H_2O.
0.00	0.01629	0.01634
0.5134	0.01580	0.01628
1.013	0.01495	0.01585
2.016	0.01321*	0.01484*
4.180	0.009945	0.01273
8.130	0.005399	0.00952
11.49	0.002590	0.00702
14.31	0.001221	0.00595
16.01	0.000478	0.00453
	$\sqrt{K}$ = 0.01486[1]	$\sqrt{K}$ = 0.01490

TABLE V.—SOLUBILITY OF $(CH_3)_4NI$ IN KOH.

Volumetric normality of KOH.	Equivalents $(CH_3)_4NI$ per liter of solution.	Equivalents $(CH_3)_4NI$ per 1000 gms. of H_2O.
0.000	0.2671	0.2774
0.250	0.2556	0.2657
0.5325	0.2377	0.2466
0.9899	0.2084	0.2162
2.0743	0.1437*	0.1491*
8.2962	0.01475	0.01683
	$\sqrt{K}$ = 0.1678[2]	$\sqrt{K}$ = 0.1743

It appears in the foregoing tables that the point at which m is found to be less than $\sqrt{K}$ occurs where the solution is at a concentration between normal and twice normal with respect to the second electrolyte. When this latter concentration is increased sufficiently, the solubility is decreased to a value of entirely different magnitude from that in pure water. We are left, therefore, no alternative but to dismiss our belief in the constancy of the solubility product, together with the other early assump-

---

[1] Calculated from the conductivity measurements of Goodwin, *Z. physik. Chem.*, 13, 608 (1894).

[2] Calculated from the conductivity measurements of Table III.

tions of the theory of solutions, and to be satisfied for the present with the purely qualitative statement that the solubility product shows a diminishing value with increased concentration of other electrolytes.

Conclusion.

The results of the foregoing paper may be summarized as follows:

(1) Determinations have been made of the solubility of thallous chloride in acetic acid solutions of varying concentrations, and of tetramethylammonium iodide in potassium hydroxide solutions of varying concentrations.

(2) The electrical conductivity of tetramethylammonium iodide has been measured.

(3) The solubility product has been shown to have a value which diminishes with increase in the total concentration of electrolytes present.

I am indebted to Mr. George Barmeyer and to Mr. Charles E. Roake for the solubility determinations of Tables I and II.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 54.]

A VOLUMETRIC METHOD OF DETERMINING IODIDE IN THE PRESENCE OF CHLORIDE, BROMIDE, OR FREE IODINE.

BY W. C. BRAY AND G. M. J. MACKAY.

Received July 25, 1910.

The method here described of determining iodide depends upon its oxidation to iodine in acid solution by means of potassium permanganate, the removal of the liberated iodine from the aqueous phase by carbon tetrachloride, and the titration of this iodine with a standard sodium thiosulphate solution. When the iodide contains free iodine dissolved in it this titration gives the total iodine present in solution; the dissolved iodine is determined by direct titration of the original solution with thiosulphate, and the difference between the two results gives the iodine present as iodide.

This method was suggested and used by Sammet,[1] but he gave no specific directions and no indication of its accuracy. A similar method was developed long ago by Fresenius,[2] in which carbon disulphide took the place of carbon tetrachloride, excess of nitrous acid was used instead of an equivalent amount of permanganate, and the nitrous acid in contact with the carbon disulphide was removed by repeated decantations with water. Information with regard to the accuracy of this method appears to be lacking, but it is doubtful if it would have, even if modified, any advantages over the present method.

The possibility of determining iodide in the presence of chloride or

---

[1] Sammet; *Z. physik. Chem.*, 53, 684 (1905).

[2] Fresenius, *Quant. Anal. 4th reprint* (1900) of 6th edit. (1875), page 482.