the industrial chemist and the metallurgist, since arsenic in a great number of cases is a constituent of the metallic sulphides, especially those of copper. Large amounts of arsenic are given off by the smelters of Salt Lake, Utah; Everett, Washington; Great Falls, and Butte, Montana; and from many of the smelters of Germany, England, and other countries. In 1854 and 1875, Haubner investigated the smelter smoke disease in the Freiburg district, and various other cases have been studied to a slight extent.

In the decision of Judge Marshall of the Circuit Court of the United States as made November 5, 1906, the conditions existing in the Salt Lake smelter district are described in such a way as to make an interesting comparison with the results of this series of papers. In speaking of the sulphur dioxide he says: "This gas is heavier than air, and when cooled, falls to the ground at a distance from the smelters dependent upon the air currents. When it is brought in contact with moisture, either in the form of rain, freshly irrigated ground, or the moisture present in growing plants and the foliage of trees, sulphurous or sulphuric acid is formed, which is destructive to vegetation. Besides the emission of gas, some flue dust is emitted from the smelters which contains perceptible quantities of arsenic resulting in the death of horses and cows."

In conclusion, the writers wish to thank Dr. John Maxson Stillman for the many suggestions which have been helpful in this work.

THE UNIVERSITY OF MONTANA AND STANFORD UNIVERSITY,
March 14, 1908.

NOTE ON THE SOLUBILITY PRODUCT.[1]

BY JULIUS STIEGLITZ.

Received April 2, 1908.

Nernst[2] was the first to advance the theory that at a given temperature the solubility of a difficultly soluble electrolyte in water or in aqueous solutions of other electrolytes is dependent on a constant called the solubility product, which is proportional to the concentrations of the ions of the salt, each raised to the power corresponding to the number resulting from one molecule. The constant is an important one in the theory of precipitation and solution and particularly useful in calculations of the solubility of a precipitate in mixtures that are not too concentrated. In Nernst's text-book on physical chemistry,[3] the relation for a difficultly soluble binary salt—such as silver acetate—in water and in solutions containing a salt with a common ion, is developed as follows: calling the total concentrations of the difficultly soluble salt m_0 and m in the saturated water solution and in the salt solution respectively,

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[1] Reported at the Chicago meeting of the American Chemical Society.

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

[3] Translation of the 4th German Edition (1904), p. 527.

and the corresponding degrees of ionization α_0 and α we have first by the application of the isotherm of dissociation, *i. e.*, on the basis of the law of mass action for the two cases:

$$(m_0\alpha_0)^2 = Km_0(l - \alpha_0) \qquad (1)$$

and

$$(m\alpha + x)\, m\alpha = Km\,(1 - \alpha), \qquad (2)$$

in which $(m\alpha + x)$ represents the total concentration of the common ion.

Then, on the basis of the theorem that the undissociated substance has a constant solubility—derived from the law of heterogeneous or physical equilibrium,

$$m_0(1 - \alpha_0) = m\,(1 - \alpha). \qquad (3)$$

Combining the three equations we have

$$(m_0\alpha_0)^2 = m\alpha\,(m\alpha + x),$$

and as $(m_0\alpha_0)^2$, the product of the concentrations of the ions in a saturated, pure aqueous solution at a given temperature, has a definite value, we have in general,

$$m\alpha\,(m\alpha + x) = K_{\text{Solubility product}}. \qquad (4)$$

Substituting the variable symbols C_{Ag}, C_{CH_3COO} and C_{CH_3COOAg}, we can express the first principle for silver acetate by

$$\frac{C_{Ag} \times C_{CH_3COO}}{C_{CH_3COOAg}} = K_{\text{Ionization}}. \qquad (5)$$

and the principle of the constant solubility of the undissociated silver acetate by

$$C_{CH_3COOAg} = k. \qquad (6)$$

Then for the constant solubility product we have simply

$$C_{Ag} \times C_{CH_3COO} = K_{\text{Solubility product}}, \qquad (7)$$

in which C_{Ag} and C_{CH_3COO} represent the concentrations of the silver and acetate ions in any saturated solution of silver acetate, whether in aqueous solution where $C_{Ag} = C_{CH_3COO}$ or in the presence of other salts, where they will usually have different values.

It has long been known, however,[1] that the ionization of strong electrolytes does not conform to the law of mass action—in other words that equations (1) and (2) as used above to develop the theory of the solubility product do not agree with the facts in the cases of such electrolytes, *e. g.*, salts, for which the theory of the solubility product is especially important. The real relation for a salt like silver acetate is that the proportion on the left side of equation (5) grows larger with increasing concentration.[2] This difficulty was recognized by A. A. Noyes,[3] to whom we owe a large part of the

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[1] Translation of the 4th German Edition (1904), p. 498.

[2] Rudolphi, *Z. physik. Chem.*, 17, 385 (1895).

[3] *Ibid.*, 6, 241 (1890); 9, 613 (1892); 16, 125 (1895); 26, 152 (1898); 42, 336 (1903)

most exact experimental work on the solubility product, and Noyes attempted to meet the difficulty by assuming that for all solutions in which the concentration of the undissociated substance was kept constant, the product of the ion concentrations is also a constant. Noyes calculated his results on the basis of this assumption and used it even as a method of determining the degrees of ionization of salts in the mixture. Arrhenius[1] showed the error of such an assumption, which cannot be reconciled with his principles of isohydric solution. The latter principle has been established on a safe basis by the work of Arrhenius, Manson, Barmwater, Archibald, McKay, Barnes and others, and has been found to hold, up to a concentration of at least half-normal, for mixtures of salts of the same type as well as for those of different types.[2] We find thus that the application of the law of mass action in equations (1) and (2) to the question of solubility is not justified by experience.

In an important paper published in 1899, Arrhenius[3] took up the investigation of the second fundamental principle involved in the solubility of electrolytes, the widely and generally accepted theory of the constant solubility of the undissociated molecules, as expressed in equations (3) and (6). Originally himself apparently inclined in common with practically all chemists to accept[4] it as a matter of course, as a consequence of the law of heterogeneous or physical equilibrium, but later led to question its correctness, he tested its validity by determining the solubility of silver salts of a number of organic acids in water and in solutions containing an increasing excess of the corresponding sodium salts. Calculating the proportion of ionized and non-ionized silver salt with the aid of the principle of isohydric solutions, he found that as a matter of fact the molecular solubility is not constant but decreases decidedly with the increasing concentration of the total electrolyte.[5] A similar fact has long been known for the relative solubility of gases like carbon dioxide, oxygen, etc., in water and in salt solutions and Arrhenius's result should not have been unexpected.[6]

We thus find that the two fundamental equations on which the theory of the constant solubility product originally was based, are both invalid and we may well ask if this result does not thoroughly discredit and dispose of the theory. Perhaps some such feeling led Arrhenius himself to refrain from calculating the values for the solubility products for the silver salts in his own experiments.

However, if we consider the true relations as now established for the two cases of chemical and physical equilibrium, we have for the

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[1] *Z. physik. Chem.*, **11**, 391 (1893) and **31**, 197 (1899).

[2] A. A. Noyes, Vol. IV, p. 311, *Reports of the Congress of Arts and Science, St. Louis.*

[3] *Z. physik. Chem.*, **31**, 197 (1899).

[4] *Ibid.*, **11**, 396 (1893).

[5] *Vide* also A. A. Noyes, Reports, etc., Vol. IV, p. 322 (1904).

[6] *Vide* also Nernst, *loc. cit.*, p. 476.

equilibrium between the ions and the undissociated substance of a binary electrolyte a proportion,

$$\frac{C_{\text{Pos. ion}} \times C_{\text{Neg. ion}}}{C_{\text{Mol}}},$$

which grows *larger* with increase of concentration,[1] and for C_{Mol} the molecular solubility resulting from the equilibrium between the solid phase and the solution, a value growing *smaller* with increasing concentrations of the total electrolyte present.[2] Now it is obvious that with a decreasing value for C_{Mol} and an increasing value for the whole proportion, the ion product, $C_{\text{Pos. ion}} \times C_{\text{Neg. ion}}$ possibly might remain constant or approximately constant after all: it is clearly a question for rigorous experiment and calculation to determine whether the ion product does or does not remain constant, that is, whether the values for the proportion and the molecular solubility are inversely porportionate, the proportion growing larger to the same extent as C_{Mol} grows smaller with increased concentrations. Even if it should not prove to be a real, *natural* constant, it might still be found to be sufficiently constant to be of practical value and assistance in the study of the reactions of precipitation and solution.

I have not found in the literature any discussion or investigation of the subject from this point of view; although Arrhenius's paper was published in 1899, even the new edition[3] of Nernst's text-book,[4] as well as other recent editions of books on physical chemistry, such as Jones's "Elements of Physical Chemistry," Mellor's "Chemical Statics and Dynamics,"[5] as well as text-books on the application of physical chemistry to analytical chemistry, do not even refer to it or its extremely important conclusions, but develop the solubility product as given above. I should except a statement made by A. A. Noyes in his address before the Congress of Arts and Science at St. Louis, in which the discrepancy shown to exist by Arrhenius between the principle of isohydric solutions and the old hypotheses concerning solubility is clearly pointed out and the need for further investigation on these lines emphasized.[6]

Considerations[7] of the above nature led me then to complete the calculations of Arrhenius's experimental data on the solubilities of organic silver

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[1] Rudolphi, *Loc. cit.*

[2] Arrhenius, *Loc. cit.*

[3] Translation of the 4th German Edition (1904).

[4] P. 595.

[5] 1904, p. 231.

[6] *Loc. cit.*, page 321. Since the presentation of this paper, Professor Noyes has informed me that work along these lines has been continued in his laboratory since 1904.

[7] The theory of the constant solubility product formed an essential element in a chemico-geological investigation carried out by me for Professor Chamberlin (*vide* a forthcoming report, Carnegie Institution), and this study has resulted from that investigation.

salts in the presence of an excess of the corresponding sodium salt, by calculating the value of the ion product in each experiment. To this end, the degrees of ionization of the sodium salts of the fatty acids in the mixtures used had to be calculated first, and this was done with the aid of the principle of isohydric solutions. On account of the form in which Arrhenius's data are presented, the following method was pursued: Arrhenius gives first a table showing the ion concentrations and degrees of ionization of isohydric solutions of silver and sodium acetate. From these data the corresponding total concentrations for the isohydric solutions of the two salts were first calculated and the results expressed in two curves in which the cube roots of the molar concentrations and the degrees of ionization were used as coordinates. The curve obtained for sodium acetate is rectilinear and that for silver nitrate only slightly curved, so the necessary interpolations for the further calculations were easily made. In his other tables, Arrhenius gives the solubility of the silver salts and their degrees of ionization, and the total concentration of the sodium salts, but not the corresponding degrees of ionization. For instance, in the presence of 0.2667 mol. sodium acetate, the solubility of silver acetate is 0.0203 mol., of which 50.4 per cent. is ionized. To find the degree of ionization of the sodium acetate in such a mixture, I found from the curve for the silver salt that an ionization of 50.4 per cent. corresponds to a value of 0.73 for $\sqrt[3]{m}$ and consequently the molar concentration of the silver salt is $(0.73)^3$ or 0.389 when it is considered to be *in its share of the water* according to the isohydric principle. Then its share of the liter of water must be 0.0203/0.389 or 52.2 cc. This leaves 948 cc. for the sodium acetate and its concentration in 948 cc. is 0.2667/0.948 or 0.2813 molar. Then its degree of ionization is 69.6 per cent., according to the curve. The concentration of the acetate ions in each of the isohydric solutions, considered separately, is 0.1961 and 0.1960 for the silver and the sodium acetate, respectively—showing that they were really isohydric. The agreement was not in all cases as close as this, but with one or two exceptions mentioned below, it was satisfactory, the concentrations of the common ion being usually within one per cent. of each other.

In the given case, the total concentration of the acetate ion in the mixture is therefore 0.196, that of the silver ion, as given by Arrhenius is 0.0102 and the value of the ion product in this experiment therefore:

$$C_{Ag} \times C_{CH_3COO} = 0.0102 \times 0.196 \text{ or } 0.00200.$$

All the calculations were made in this way and the following tables give all the results obtained for the acetate, propionate, butyrate, valerate and chloracetate of silver. In the calculations the curves for the acetates were always used to find the degree of ionization for all these salts, following Arrhenius's method.

In the tables the first column gives the molar concentration of the sodium salt used, column 2 its degree of ionization, calculated in the way just described, column 3 the concentration of the ionized part of the sodium salt. Column 4 gives the total solubility of the silver salt, column 5 its degree of ionization, column 6 the concentration of the ionized part of the silver salt and column 7 the concentration of the undissociated part, which represents therefore the molecular solubility of the silver salt. The last column gives the value for the solubility product, $C_{Ag} \times C_{CH_3COO}$. The value for C_{Ag} is found in column 6, and C_{CH_3COO} is the sum of the acetate concentrations given in columns 3 and 6.

TABLE 1.—SILVER ACETATE AT 18.6°.

Na·Acet.	100α.	10^3Acet.	Ag-Acet.	100α'.	10^3Acet.	10^3Mol.	10^5K.
0	..	...	0.0593	72.0	42.7	16.6	182
0.0333	80.0	26.6	0.0474	68.1	32.3	15.1	190
0.0667	78.0	52.0	0.0384	64.4	24.7	13.7	190
0.1333	75.0	100.0	0.0282	58.4	16.4	11.8	191
0.2667	69.6	186.7	0.0203	50.4	10.2	10.1	200
0.5000	63.0	315.0	0.0147	42.8	6.3	8.4	202

TABLE 2.—SILVER PROPIONATE AT 18.2°.

Na·Prop.	100α.	10^3Prop.	Ag·Prop.	100α.	10^3Prop.	10^3Mol.	10^5K.
0	..	..	0.0462	74.5	34.4	11.8	118.4
0.0167	82.0	13.69	0.0393	72.1	28.3	11.0	119.4
0.0333	81.0	27.00	0.0345	69.6	24.0	10.5	122.4
0.0667	78.9	52.63	0.0258	65.5	16.9	8.9	118.0
0.1333	75.3	100.37	0.0191	58.8	11.2	7.9	124.7
0.2667	69.8	186.2	0.0131	50.6	6.6	6.5	127.1
0.5000	63.2	316.0	0.0101	42.9	4.3	5.8	(137.7)

TABLE 3.—SILVER BUTYRATE AT 18.2°.

Na.Butyr.	100α.	10^3Butyr.'	Ag·Butyr.'	100α.	10^3Butyr.'	10^3Mol.	10^5K.
0	..	...	0.0224	81.1	18.2	4.2	33.0
0.0066	86.0	56.8	0.0199	79.6	15.8	4.1	(49.8)
0.0164	84.9	13.9	0.0169	77.3	13.1	3.8	35.4
0.0329	83.0	27.3	0.0131	73.5	9.6	3.5	35.4
0.0658	80.0	52.6	0.0091	67.7	6.2	2.9	36.4
0.1315	75.9	100.0	0.0060	59.9	3.6	2.4	37.3
0.2630	70.1	184.4	0.0040	51.1	2.0	2.0	36.8
0.4930	63.3	312.1	0.0027	43.2	1.2	1.5	37.6

TABLE 4.—SILVER VALERATE AT 18.6°.

Ag-Val.	100α.	10^2Val.'	Ag·Val.	100α.	10^3Val.'	10^3Mol.	10^5K.
0	..	...	0.0095	87.3	8.3	1.2	6.9
0.0175	86.5	15.1	0.0047	81.1	3.8	0.9	7.2
0.0349	84.0	29.3	0.0030	75.5	2.2	0.8	6.9
0.0689	80.1	55.9	0.0018	68.1	1.2	0.6	6.9
0.1395	75.8	105.7	0.0015	59.7	0.9	0.6	(9.6)

TABLE 5.—SILVER CHLORO-ACETATE AT 16.9°.

Na-ClAcet.	100α.	10^3ClAcet.′	Ag-ClAcet.	100α.	10^3ClAcet.′	10^3Mol.	10^5K.
0	..	..	0.0644	71.1	45.8	18.6	209.8
0.0333	79.8	26.6	0.0499	67.6	33.7	16.2	202.2
0.0667	78.1	52.1	0.0405	63.9	25.9	14.6	203.3
0.1333	74.8	99.71	0.0299	58.1	17.4	12.5	202.3
0.2667	69.4	185.1	0.0208	50.4	10.5	10.3	205.8
0.5000	63.2	316.0	0.0162	42.8	6.9	9.3	222.0

The experimental results of Nernst's determinations of the solubility of silver acetate in the presence of sodium acetate and silver nitrate, respectively, were also recalculated. Nernst used the isohydric principle in determining the degrees of ionization of the salts in the mixtures, but considered the salts to ionize with about equal readiness. Such is not the case, if we accept Arrhenius's determinations of the ionization of silver acetate, the values for which, it is true, were very largely obtained by extrapolation. But these same values having been used in bringing the proof that the molecular solubility decreases with the increasing concentrations of the total electrolyte, it seems most reasonable to use the values also for the determinations of the solubility product of the same salt. In Tables 6 and 7 the results of the recalculation of Nernst's data are tabulated, the degrees of ionization being determined by the application of the isohydric principle in the usual way—the two salts present being supposed to divide the water in such a way as to give solutions containing the same concentration of the common ion. The division of the water was rapidly ascertained by trial calculations with the help of the curves of dissociation for the third root of the concentrations. The columns in these tables have in part a different significance from the columns of the previous tables: column 1 gives the molar concentration of the sodium acetate (silver nitrate in Table 7) used in excess, column 2 gives the portion of the water, in cubic centimeters, in which all the sodium acetate (silver nitrate) is supposed to be dissolved to form a solution isohydric with the solution of silver acetate in the rest of the water. Column 3 gives the degree of ionization of the sodium acetate (silver nitrate), column 4 the concentration of the common ion in this solution, 5 the total concentration of silver acetate, 6 its degree of ionization, and column 7 the concentration of the common ion in the isohydric silver acetate solution. The last column gives the values for the solubility product.

TABLE 6.—SILVER ACETATE AT 16°.

Na-Acet.	cc. H_2O.	100α.	10^3Acet.′	Ag-Acet.	100α.′	10^3Acet.′	10^5K.
0	...	....	......	0.0603	70.8	0.0427	182.3
0.061	656	78.6	0.0731	0.0392	64.5	0.0735	185.4
0.119	843	75.8	0.1070	0.0280	59.7	0.1065	178.5
0.239	937	70.8	0.1738	0.0208	52.3	0.1727	188.2

TABLE 7.—SILVER ACETATE AT 16°.

$AgNO_3$.	cc. H_2O.	100α.	10^3Ag.'	Ag-Acet.	100α.'	10^3Ag.'	10^5K.
0	...	....	......	0.0603	70.8	0.0427	182.3
0.061	650	82.0	0.0770	0.0417	64.0	0.0763	204.4
0.119	825	78.4	0.1131	0.0341	58.6	0.1142	227.2
0.230	944	74.0	0.1803	0.0195	51.7	0.1809	182.1

Considering the data in the last columns of the tables, we find that the value of the solubility product increases at most from five to ten per cent. in mixtures down to a concentration of half-molar,[1] and in some of the experiments (Tables 4, 5, 6 and 7), it shows practically no variation of moment. All the variations may well be within the limit of errors of experiment and computation in an investigation in which a large part of the calculations are based on an extrapolated curve. Of the serious discrepancies, the bracketed value in Table 3 (line 2) corresponds to an experiment, the figures of which given by Arrhenius show, by the method of calculation used above, a decided divergence from the principle of isohydric solutions—so there must be an error of observation or record in it. The bracketed value in Table 4, last line, also corresponds to an experiment in which there is probably some error, as is indicated by a consideration of the values in the next to the last column of the table.

We find thus empirically that in the case of the silver salts of these organic acids the principle of the constant solubility product, faulty as its original theoretical basis was, is sufficiently in agreement with the observed facts to prove of some practical value. This conclusion confirms the results of the experimental data of others on the solubility of a salt in the presence of other electrolytes having a common ion. Nernst's results have already been mentioned. Findlay's[2] experiments on the relative solubility of lead iodide and sulphate, although the theoretical development is open to the same criticism made above, were nevertheless calculated correctly according to the isohydric principle and they agree with the theory of a constant solubility product. In this case, the condition of the equilibrium in the mixtures was determined not only on the basis of conductivities but also by measurements of electromotive forces. Bodländer's[3] work on the solubility of calcium carbonate in water containing carbon dioxide in equilibrium with varying partial pressures of carbon dioxide

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[1] A. A. Noyes, *loc. cit.*, p. 322, pointed out that in the case of a solution saturated simultaneously with thallous chloride and bromate, the product of the ion concentrations of each is increased by about five per cent. Each salt gives an approximately $^1/_{40}$ molar solution. This case was considered *typical.*

[2] *Z. physik. Chem.*, 34, 409 (1900).

[3] *Ibid.*, 35, 23 (1900). *Vide* also a paper by Stieglitz to be published in the report of the Carnegie Institute of Washington, in which the data presented by Bodländer are recalculated on the basis of more recent determinations of the constants involved.

led to excellent constants: the theoretical treatment started from the assumption of a constant solubility product for calcium carbonate. In the address referred to, A. A. Noyes[1] mentions two or three other cases, such as the solubility of lead iodide in the presence of potassium iodide and of lead chloride in the presence of potassium chloride, and of calcium hydroxide in the presence of ammonium chloride, in which cases the theory is said to be sustained approximately.

In view of these facts and also in view of the results of the complete calculation of Arrhenius's data on the solubility of the silver salts, which removed the last *theoretical* foundation for the solubility product constant, we may well consider it for the present to be an approximate empirical principle, much in the same way as so many other important principles concerning electrolytes are still simply empirical, such as the isohydric principle itself, and the various rules—Rudolph's, van't Hoff's, Kohlrausch's—expressing the equilibrium between strong electrolytes and their ions. A great deal more exact work on the extent of the reliability of the solubility principle will obviously be necessary to determine what the true relations are. If it should be confirmed still further and firmly established, the question of its theoretical bearing will become an interesting one—particularly in its relation to the other empirical principles of solutions of electrolytes.

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[CONTRIBUTION FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY OF THE HARVARD MEDICAL SCHOOL.]

A DIAGRAMMATIC REPRESENTATION OF EQUILIBRIA BETWEEN ACIDS AND BASES IN SOLUTION.

BY LAWRENCE J. HENDERSON.

Received March 27, 1908.

During a series of investigations concerning the adjustment of neutrality in the animal organism,[2] it has been found convenient to construct diagrams representing the equilibria between bases and acids of different ionization constants in solution of varying acidity and alkalinity. These diagrams, simple consequences of the concentration law, and of the principle of isohydric solutions, seem to possess certain advantages over other methods of presentation of the somewhat involved conditions. Especially are they useful to indicate immediately the adjustment of all possible equilibria of this sort, with at least a moderate degree of accuracy, and on account of such practical usefulness they are here presented.

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[1] *Loc. cit.*, p. 322.

[2] For general conclusions and the literature see Henderson, *American Journal of Physiology*, May, 1908.