$k_b = 0.00155$, in accordance with the measurements of Ostwald, and determining c from conductivity measurements.

In the following tables are given the experimental and the theoretical values, together with the percentage differences between them.

SOLUBILITY OF THE SILVER BENZOATE IN NITRIC ACID.

Experiment No.	Concentration of the nitric acid.	Found solubility.	Calculated solubility.	Percentage difference.
I	0.00	0.01144	......	......
II	0.004435	0.01395	0.01406	+0.78
III	0.008870	0.01698	0.01703	+0.29
IV	0.008915	0.01715	0.01706	—0.53
V	0.01774	0.02324	0.02390	+2.76
VI	0.01783	0.02351	0.02396	+1.89
VII	0.02674	0.03071	0.03159	+2.79

SOLUBILITY OF THE SILVER BENZOATE IN CHLORACETIC ACID.

Experiment No.	Concentration of the chloracetic acid.	Found solubility.	Calculated solubility.	Percentage difference.
I	0.00	0.01144	......	......
II	0.003935	0.01385	0.01368	—1.24
III	0.00785	0.01612	0.01588	—1.51
IV	0.01574	0.02093	0.02117	+1.13

The agreement between the found and the calculated values is very satisfactory, especially considering the large number of dissociation values used in the calculation; consequently the solubility principles and the validity of the theoretical laws of dissociation in the case of weakly dissociated acids are again confirmed. It is specifically shown by this investigation that the solubility of silver benzoate is increased both by nitric acid and chloracetic acid in such a way that the product of the concentrations of the Ag and the $C_6H_5CO_2$ ions remains constant.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE SOLUBILITY OF ACIDS IN SOLUTIONS OF THE SALTS OF OTHER ACIDS.[1]

BY ARTHUR A. NOYES AND EDWARD S. CHAPIN.

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I. PURPOSE OF THE INVESTIGATION.

IN an article published elsewhere by one of us,[2] the theory of the influence of one di-ionic electrolyte on the solubility of

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[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

[2] *Ztschr. phys. Chem.*, 27.

another with different ions, was developed for the different cases actually occurring. Certain experiments made with the object of testing the theoretical equations so derived have been presented in the preceding paper; but there remains an especially important case to which the application of the theory has not yet been experimentally tested,—that involving the effect of a neutral salt of a partially dissociated acid on the solubility of another acid, likewise only partially dissociated. An example of this kind would be the effect of sodium acetate or of sodium formate on the solubility of benzoic acid, and we have in fact investigated this case, using each of the salts at different concentrations.

2. DESCRIPTION OF THE EXPERIMENTS.

In the first place the preparation of the substances and of the solutions employed will be described. The benzoic acid was prepared from a commercial sample by dissolving in the sodium carbonate solution, *partially* precipitating with dilute hydrochloric acid, and twice recrystallizing from boiling-water. As powdered benzoic acid probably saturates a solution much more quickly than does the crystallized form, the acid was then melted and finely pulverized. It was shown by qualitative test to be free from chlorine.

The sodium acetate and sodium formate used were prepared by twice recrystallizing the commercial salts. Solutions of these were made up by weighing out roughly the air-dried salts; and their concentrations were then accurately determined by evaporating measured portions with hydrochloric acid in platinum dishes, moistening the residue with the acid, and igniting gently until a constant weight was obtained. The three check determinations made in each case agreed within three-tenths per cent.

The solubility determinations were made by rotating for about sixteen hours at 25° in the previously described apparatus[1] bottles containing pure water or the solutions of sodium acetate or sodium formate and an excess of the solid benzoic acid. In one-half of the experiments the state of saturation was approached by cooling the solutions from a higher temperature,

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[1] *Ztschr. phys. Chem.*, 9, 606.

and in the other half by warming from a lower temperature. Portions of the solution were quickly filtered, and twenty-five cc. measured out with a pipette and titrated, using phenolphthalein as an indicator, with a barium hydroxide solution which had been standardized by means of calcium carbonate and succinic acid, and which was 0.02936 normal.

3. THE EXPERIMENTAL RESULTS.

The following tables contain the results of all the solubility experiments. The numbers express the quantity of dissolved benzoic acid in millimols per liter. Those values which were obtained by cooling the solutions down to 25° are placed under the heading "supersaturated;" while those obtained by heating up to 25° are designated as "undersaturated."

SOLUBILITY OF BENZOIC ACID IN PURE WATER.

No.	Supersaturated.	Undersaturated.
1	27.92	28.02
2	27.80	27.79
3	28.10	27.88
4	28.22	27.80
5	27.96	27.81
Mean	28.00	27.86
	±0.058	±0.032

SOLUBILITY OF BENZOIC ACID IN SODIUM ACETATE SOLUTIONS.

	Concentration of the salt. 13.21 millimols.		Concentration of the salt. 26.41 millimols.		Concentration of the salt. 52.82 millimols.	
Experiment number.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.
1	38.84	38.71	48.55	48.32	64.92	64.58
2	....	....	48.44	48.28	64.90	64.70
Mean..	38.84	38.71	48.50	48.30	64.91	64.64

SOLUBILITY OF BENZOIC ACID IN SODIUM FORMATE SOLUTIONS.

	Concentration of the salt. 14.14 millimols.		Concentration of the salt. 28.28 millimols.		Concentration of the salt. 56.57 millimols.	
Experiment number.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.
1	34.65	34.65	38.85	38.83	45.36	45.24
2	34.52	34.42	39.00	38.84	45.33	45.27
Mean..	34.59	34.54	38.93	38.84	45.35	45.26

It will be seen from an examination of the tables that the supersaturated values are, in general, from three-tenths to five-tenths per cent. higher than the undersaturated values, a result which may be regarded as very satisfactory, in view of the difficulty in this respect often experienced in solubility experiments with organic substances.[1] In the subsequent calculations and summary of results, the averages of the supersaturated and undersaturated mean values are adopted as most probably correct.

4. COMPARISON OF THE EXPERIMENTAL WITH THE CALCULATED VALUES.

It remains now to determine to what extent the values found as above described agree with the requirements of the theory of solubility effect. In order to determine this, we have calculated the solubility of the benzoic acid in the various salt solutions from its solubility in pure water and the dissociation relations of the substances involved, using the equation applicable to this case, derived in the preceding article of Noyes and Schwartz. This equation is

$$x^3 + (r - 2c)x^2 + (c^2 - rc - rn + rb - k_a)x + (rcn - rcb + k_a c - k_a r) = 0,$$

in which

$$x = m - m_0(1 - a_0) \text{ and } k_a = m_0^2 a_0^2,$$

where m_0 and m are the solubilities of the benzoic acid in pure water and in the salt solution of the concentration n, and where a_0 is the dissociation corresponding to the concentration m_0; in which, further, $r = \frac{k_a}{k_d}$, where k_d is the dissociation-constant of the acetic or formic acid; and in which b and c represent the undissociated portions of sodium acetate or formate and of sodium benzoate respectively.

The data in the calculations by this formula are the following: The solubility in pure water m_0 was found by our experiments to be 0.02793; the dissociation a_0 corresponding to this was calculated from the dissociation constant $0.0_4 60$, determined by Ostwald, and found to be 0.0453, from which it follows that $k_a = 0.0_5 1601$. The dissociation constants k_d of acetic and formic acids are respectively $0.0_4 18$ and $0.0_3 214$. The values of b and c varied in the different cases and were determined as described in the article just referred to from the electrical con-

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[1] Compare Paul; *Ztschr. phys. Chem.*, 14, 112, and the preceding article.

ductivity of the salts and measured by Ostwald; they were in the case of the sodium acetate as follows: For

(1) $n = 0.01321 \quad b = 0.00028 \quad c = 0.001737$
(2) $n = 0.02641 \quad b = 0.00138 \quad c = 0.00448$
(3) $n = 0.05282 \quad b = 0.00508 \quad c = 0.001142$

and in the case of the sodium formate, for

(4) $n = 0.01414 \quad b = 0.00081 \quad c = 0.00133$
(5) $n = 0.02828 \quad b = 0.00278 \quad c = 0.00309$
(6) $n = 0.05657 \quad b = 0.00886 \quad c = 0.00714$

By substituting these values and the values of the constants just preceding in the algebraic equation given above, the following six numerical equations were obtained:

(1) $x^3 + 0.08547\,x^2 - 0.001303\,x + 0.0_51859 = 0$
(2) $x^3 + 0.0800\,x^2 - 0.002606\,x + 0.0_5985 = 0$
(3) $x^3 + 0.0661\,x^2 - 0.005134\,x + 0.0_44835 = 0$
(4) $x^3 + 0.004830\,x^2 - 0.0001095\,x + 0.0_61224 = 0$
(5) $x^3 + 0.001296\,x^2 - 0.0002059\,x + 0.0_65787 = 0$
(6) $x^3 - 0.006802\,x^2 - 0.0003625\,x + 0.0_52549 = 0$

Estimated values of x were substituted in these equations till the roots were found; and from the latter the solubility was calculated by the equation: $m = x + m_0(1 - a_0)$. The solubility values so calculated are placed in the following table by the side of the mean values experimentally determined. In the last column the percentage differences between the two series of values are given.

SOLUBILITY OF BENZOIC ACID IN SODIUM ACETATE SOLUTION.

Number.	Concentration of the salt.	Calculated solubility.	Found solubility.	Percentage difference.
1	0.00000	0.02793	0.02793	.....
2	0.01321	0.03846	0.03878	+0.82
3	0.02641	0.04783	0.04840	+1.19
4	0.05282	0.06380	0.06480	+1.52

SOLUBILITY OF BENZOIC ACID IN SODIUM FORMATE SOLUTION.

Number.	Concentration of the salt.	Calculated solubility.	Found solubility.	Percentage difference.
1	0.00000	0.02793	0.02793	.....
2	0.01444	0.03423	0.03456	+0.96
3	0.02828	0.03858	0.03888	+0.77
4	0.05657	0.04553	0.04530	—0.50

The tables show that the agreement between the found and the calculated solubility is satisfactory. The correctness of the principles of solubility-effect and of the laws of dissociation involved in the equation used for the calculation is therefore demonstrated.

As the equation given above is quite complicated, and as the determination of the values of b and c involved is a laborious operation, it is important to show that approximately accurate results can be obtained when these quantities are neglected. In this case equation (1) becomes simplified to the following equation:

$$x^3 + rx^2 - (rn + k_a)x - k_a r = 0. \tag{2}$$

The values of the solubilities calculated by the equation are given in the following table, together with those calculated by equation (1), and with the percentage differences between the two values. The first three columns of figures show the solubility in the three sodium acetate solutions, the last three that in the sodium formate solutions.

Calculated Solubilities.

By equation (1)·····	0.03846	0.04783	0.06380	0.03423	0.03858	0.04553
By equation (2)·····	0.03844	0.04798	0.06392	0.03384	0.03801	0.04391
Percentage difference	0.05	0.30	0.20	1.14	1.48	3.60

It will be seen that in the case of the sodium acetate solutions the solubility values calculated by the simpler formula are almost identical with those obtained by means of the exact formula. In the case of the formate the differences are greater, but only for the greatest concentration is it at all considerable (three and six-tenths per cent.). Therefore for acids not more soluble than benzoic acid, when dissolved in salt solutions of corresponding concentrations, the simpler equation would be sufficiently exact for most purposes.