

2. This efficiency was maintained in some experiments until the distillate amounted to as much as 176 times the original volume of sulfuric acid, or till the ether produced reached 40 times the volume or 16 times the weight of acid used.

3. The efficiency fell off abruptly when there remained in the generating flask a charred and semi-solid residue weighing only about one-twentieth as much as the original acid.

4. The decrease in efficiency is not due to accumulation of water, for the reaction proceeds normally when dilute sulfuric acid is employed.

5. From 15 to 20% of the sulfuric acid used could be accounted for as sulfur dioxide.

PURDUE UNIVERSITY, LAFAYETTE, INDIANA.

DISSOCIATION CONSTANT OF WEAK ACIDS AND BASES FROM SOLUBILITY DATA.

BY NILRATAN DHAR.

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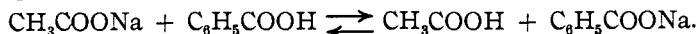
It is well known that magnesium hydroxide is markedly more soluble in solutions of ammonium chloride than in pure water, and according to a current explanation¹ this is due to the combination of the ammonium and hydroxyl ions which are brought together. The smallness of the dissociation constant of ammonium hydroxide involves the removal of a considerable quantity of hydroxyl ions in this way, and the quantity so removed must be made good by the solution of more solid magnesium hydroxide. Similarly much more calcium hydroxide dissolves in a solution of ammonium chloride than in pure water.²

Thus it is evident that a base will dissolve in greater amount in a solution of a salt of a weak base and a strong acid. Now assuming the dissociation constant of the dissolving base, the calculation of the dissociation constant of the base of which the salt is taken, is possible.

Exactly in the same way, the solubility of an acid is increased by the addition of a neutral salt solution of a weak acid and a strong base to it.

Thus much more benzoic acid dissolves in a solution of sodium acetate than in the same volume of water at the same temperature.

Since in the acetate solution, there is hydroxide ion (OH') (due to hydrolysis) which combines with the hydrogen ion (H') of the acid, forming water and also benzoate ion is formed at the same time. Moreover, benzoic acid partly decomposes the sodium acetate solution and the following reaction takes place:



¹ Loven, *Z. anorg. Chem.*, 11, 404 (1896).

² Cf. Noyes and Chapin, *Z. physik. Chem.*, 28, 520 (1899).

Now assuming the dissociation constant of benzoic acid, we can determine the dissociation constant of acetic acid in the following way.

Let a be the solubility of benzoic acid in water and b be the solubility of the same acid in a solution of sodium acetate of concentration c . Therefore, the concentration of benzoate ion in the solution = $(c - a)$; this must also be equal to the concentration of undissociated acetic acid in the solution. Therefore, the concentration of the hydrogen ion (H^+) in the solution is obtained from the following relation:

$$\frac{H^+ \times C_6H_5COO'}{HC_6H_5COO} = 6 \times 10^{-5}$$

or

$$H^+ = \frac{6 \times 10^{-5} \times H \cdot C_6H_5COO}{C_6H_5COO} = \frac{6 \times 10^{-5} \times a}{b - a}$$

The concentration of the acetate ion (CH_3COO') = $c - (b - a)$.

∴ The dissociation constant of acetic acid

$$= \frac{(6 \times 10^{-5} \times a)(c - b + a)}{(b - a)^2}$$

That the solubility of sparingly soluble acids is increased in this way is known. Some measurements were made by Noyes and Chapin.¹ Philip² has determined the solubility of cinnamic acid, benzoic acid, salicylic acid, and nitrobenzoic acid in solutions of sodium acetate, sodium butyrate, sodium formate, sodium monochloroacetate, and sodium salicylate. In this paper, the calculations are made from Philip's data. In the cases of salicylic and nitrobenzoic acid, difficulty in calculation arises due to ionization, since they are fairly strong acids.

With cinnamic and benzoic acids fairly concordant results are obtained, as seen in the following tables. Similar results are obtainable also from potassium salts:

TABLE I.—SODIUM BUTYRATE SOL.

A.—With cinnamic acid ($K = 3.55 \times 10^{-5}$).

Original salt conc.	Conc. of butyrate ion.	Conc. of cinnamate ion.	Conc. of H^+ .	Diss. conc. K .
0.0103	0.0046	0.0057	2.36×10^{-5}	1.90×10^{-5}
0.0513	0.0345	0.0168	0.803×10^{-5}	1.64×10^{-5}

The value is slightly higher than the ordinary value ($K = 1.5 \times 10^{-5}$).

B.—With benzoic acid ($K = 6 \times 10^{-5}$).

Original salt conc.	Conc. of butyrate ion.	Conc. of benzoate ion.	Dissociation constant.
0.0459	0.0036	0.0323	2.1×10^{-5}
0.0513	0.0136	0.0377	1.6×10^{-5}

In this case, also, the dissociation constant of butyric acid is slightly higher.

¹ *Z. physik. Chem.*, **27**, 442 (1898).

² *Trans. Chem. Soc.*, **87**, 987 (1905); also Philip and Garner, *Ibid.*, **95**, 1466 (1909).

TABLE II.—SODIUM ACETATE SOLUTION.

A.—With cinnamic acid.

Original salt conc.	Conc. of acetate ion.	Conc. of cinnamate ion.	K.
0.0096	0.0042	0.0054	1.93×10^{-5}
0.0192	0.0099	0.0093	1.54×10^{-5}
0.0480	0.0327	0.0153	1.88×10^{-5}

In the case of acetic acid, almost the standard value 1.8×10^{-5} is obtained.

B.—With benzoic acid.

Original salt conc.	Conc. of acetan ion.	Conc. of benzoate ion.	K.
0.0198	0.0041	0.0157	2.8×10^{-5}
0.0493	0.0139	0.0354	1.9×10^{-5}

In this case, slightly higher values are obtained.

TABLE III.—SODIUM FORMATE SOL.

A.—With cinnamic acid.

Original salt conc.	Conc. of formate ion.	Conc. of cinnamate ion.	K.
0.0244	0.0209	0.0035	2.3×10^{-4}
0.0610	0.0554	0.0056	2.38×10^{-4}

In this case, almost exact values are obtained.

B.—With benzoic acid.

Original salt conc.	Conc. of formate ion.	Conc. of benzoate ion.	K.
0.0244	0.0147	0.0097	2.7×10^{-4}
0.0610	0.0431	0.0179	2.3×10^{-4}

Here also good values are obtained.

TABLE IV.—SODIUM MONOCHLOROACETATE WITH BENZOIC ACID.

Original salt conc.	Conc. of chloroacetate ion.	Conc. of benzoate ion.	K.
0.0118	0.0093	0.0025	24.0×10^{-4}
0.0294	0.0241	0.0053	14.0×10^{-4}
0.0587	0.0502	0.0085	11.5×10^{-4}
0.0176	0.1049	0.0127	10.7×10^{-4}

The standard value for monochloroacetic acid from molecular conductivity determinations is 15.5×10^{-4} . Thus, in this case also, fairly concordant results are obtained.

TABLE V.—SODIUM SALICYLATE SOLUTION.

A.—With cinnamic acid.

Original salt conc.	Conc. of salicylate ion.	Conc. of cinnamate ion.	K.
0.0108	0.0100	0.0008	21.0×10^{-4}
0.0216	0.0203	0.0013	16.0×10^{-4}
0.0538	0.0512	0.0026	10.2×10^{-4}

The last value exactly equals the standard value.

The general applicability of this method will be discussed in a subsequent paper, in which the dissociation constants of other weak acids and bases will be calculated.