

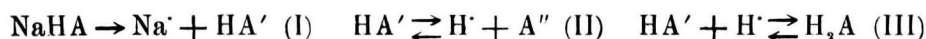
Chemistry. — ‘*The second dissociation constant of sulphoacetic and α -sulphopropionic acids.*’ By Prof. H. J. BACKER. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of January 27, 1923).

The determination of the second dissociation constant of a dibasic acid H_2A from the concentration of the hydrogen ions in the solution of an acid salt readily suggests itself.

However, A. A. NOYES¹⁾ has shown, that generally these data will not suffice.

Suppose that the ionisation of the acid sodium salt (reaction I) is nearly complete, and that the concentration of the HA' ions, which according to reaction II are partly split further, may be identified with the concentration of the acid salt dissolved, we must nevertheless remember that the number of hydrogen ions will decrease by combination with the ions HA' (reaction III).



This last reaction will be especially noticeable, when the acid is weak, which is indeed the case with all organic acids examined in this respect.

The sulphocarboxylic acids, however, are examples of strong dibasic acids, which at small dilutions are already well ionised. Therefore, we may expect, that the consumption of hydrogen ions for formation of the free acid will only have a small influence, so that from the concentration of the hydrogen ions the degree of dissociation of reaction II may be determined, and further the dissociation constants.

NOYES has given the following general formula for the acid salts of dibasic acids:

$$k_2 = \frac{(k_1 + c + H) H^2}{k_1 (c - H)}$$

k_1 and k_2 are the first and second dissociation constants of the acid, c is the original concentration of the acid salt (in gram molecules per litre) and H is the concentration of hydrogen ions (in gram ions per litre).

¹⁾ Z. f. physik. Chemie **11**, 495 (1893).

If k_1 is large compared with c and H , we may write:

$$k_2 = \frac{H^2}{c-H}.$$

Now, this expression is identical with OSTWALD's dilution law, $k = \alpha^2/(1-\alpha)v$, as shown by substitution of $\alpha = H/c$ and $v = 1/c$.

This simplification will be permissible in the case of sulphoacetic and sulphopropionic acids, for which, in a previous paper¹⁾ the first dissociation constants were found to be 0.58 and 0.57 respectively.

Now, the solutions of the acid salts of these compounds in various concentrations were compared, by the aid of indicators, at room temperature, with the buffer solutions of SÖRENSEN and of CLARK.

In the following table v is the number of litres, containing 1 gram molecule of the acid salt, p is the hydrogen exponent ($p = -\log H$) H is the concentration of the hydrogen ions in gram ions per litre, α is the degree of dissociation of reaction II ($\alpha = Hv$) and the equilibrium constant derived therefrom is $k_2 = \alpha^2/(1-\alpha)v$.

	v	p	H	α	k_2
Sulphoacetic acid	16	2.65	0.00224	0.0358	8.3×10^{-5}
	32	2.8	0.00158	0.0506	8.4
	64	2.95	0.00112	0.0717	8.5
	128	3.05	0.00089	0.114	11.5
	256	3.25	0.00056	0.143	9.4
	512	3.4	0.00040	0.205	10.3
Sulphopropionic acid	16	2.7	0.00200	0.0320	6.6×10^{-5}
	32	2.85	0.00141	0.0451	6.7
	64	3.0	0.00100	0.0640	6.8
	128	3.2	0.00063	0.0806	5.5
	256	3.4	0.00040	0.102	4.5
	512	3.55	0.00028	0.144	4.7

The concordance of the constants at various dilutions is very satisfactory, as the indicator method does not allow a great accuracy.

However, for great concentrations a correction might be made

¹⁾ These Proceedings 25, 359 (1922).

according to NOYES' formula. For this the values of k_2 must be multiplied by $(k_1 + c + H) / k_1$.

This correction only affects the dilutions 16, 32 and 64.

Thus, the following values are found:

	$v = 16$	32	64	128	256	512	mean value.
sulphoacetic acid	$k_2 = 9.1$	8.9	8.8	11.5	9.4	10.3	9.7
sulphopropionic acid	$k_2 = 7.2$	7.1	7.0	5.5	4.5	4.7	6.0

Little differences in the colorimetric determinations of p have in this method a great influence on the value of k_2 .

In a simpler way the second dissociation constant of a dibasic acid may be measured by examining a mixture of a neutral and an acid salt¹⁾.

If α'' is the degree of dissociation of the neutral salt Na_2A and α' the degree of dissociation of the acid salt NaHA , then the second dissociation constant of the acid may be represented by:

$$k_2 = \frac{\alpha'' \times [\text{Na}_2\text{A}]}{[\alpha' \times \text{NaHA}]}$$

Since these degrees of dissociation for salts are not much smaller than 1, the factor α''/α' may be neglected in a first approximation.

For the sake of simplicity a solution was taken containing an equal number of molecules of the acid and of the neutral salt, so that $k = H$, and this solution was examined at various dilutions.

The concentration of hydrogen ions was again determined by means of the indicator method.

In next table v is the number of litres containing one molecule of the neutral salt together with one molecule of the acid salt.

The variations of the constant due to dilution are not considerable, but it is remarkable that they are all in the same direction. By dilution the degree of acidity of the solution decreases.

This behaviour indeed agrees with the theory, since for the sodium salt of a dibasic acid the dissociation on diluting increases more than for the sodium salt of a monobasic acid. Therefore the value of α''/α' , which for infinite dilution must amount to 1, is smaller for the greater concentrations.

The value of α'' follows from the conductivity of the neutral sodium salt at various dilutions, published in the previous paper, and for α' the above mentioned values may be taken.

¹⁾ In this way I. M. KOLTHOFF has measured the second dissociation constants of a number of dicarboxylic acids. (Der Gebrauch von Farbenindikatoren, p. 102).

	v	p	$H = k_2$
Sulphoacetic acid	32	4.0	10.0×10^{-5}
	64	4.05	8.9
	128	4.1	7.9
	256	4.15	7.1
	512	4.25	5.6
Sulphopropionic acid	32	4.25	5.6×10^{-5}
	64	4.3	5.0
	128	4.35	4.5
	256	4.4	4.0
	512	4.4	4.0

When this correction is made, the following constants are found:

	$v = 32$	64	128	256	512	mean value :
sulphoacetic acid	$k_2 = 8.7$	7.9	7.3	6.7	5.4	7.2
sulphopropionic acid	$k_2 = 4.8$	4.4	4.1	3.7	3.8	4.2

In the preceding paper the second dissociation constants of both acids are calculated from measurements of the conductivity of the acid salts.

In the present paper these constants have been obtained colorimetrically first from the pH of the acid salt and then from the pH of mixtures of neutral and acid salts.

The mean results of the various methods are collected in the following table.

Methods	Sulphoacetic acid	Sulphopropionic acid
I. Conductivity of acid salts.	$k_2 = 7.4 \times 10^{-5}$	$k_2 = 4.8 \times 10^{-5}$
II. Hydrogen ion concentration of mixtures of acid and neutral salts.	7.2	4.2
III. Hydrogen ion concentration of acid salts.	9.7	6.0

In judging these figures it should be remembered, that each of the methods used here only gives approximative values, which is also evident from the deviations in each series of measurements.

However, the order of magnitude is the same for the constants determined in various ways.

Thus from this research we may conclude, that the second dissociation constant of sulphoacetic acid amounts to about 1×10^{-4} and that the constant of sulphopropionic acid is about one third smaller.

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*Organic chemical laboratory
of the University.*
