

Dissociation Constants of Multibasic Acids and Their Application to the Calculation of Molecular Dimensions

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1. It is the aim of the present work to develop a theory of the ratio between the dissociation constants of multibasic acids.

Firstly, it will be shown in which way it is possible from this ratio to calculate the effect exerted by the ionization of one hydrogen atom on the state of the other hydrogen atoms.

Subsequently, a theoretical explanation of this effect will be given and it is assumed that this effect is due to the attraction of the hydrogen atoms by the free charge produced through ionization. In the case of multibasic acids with carboxyl groups which are *not too close to each other*, this electrostatic theory can explain the total effect. However, the latter becomes greater than expected from the theory when the ionizable hydrogen atoms are situated *very closely to each other*. In these cases we must assume a special effect through the *atom chain*.

2. Dissociation of a *dibasic acid* follows the equations



In the corresponding expressions of the law of mass action

$$\frac{[\text{HS}^-] \cdot [\text{H}^+]}{[\text{H}_2\text{S}]} = K_1 \quad \text{and} \quad \frac{[\text{S}^{--}] \cdot [\text{H}^+]}{[\text{HS}^-]} = K_2$$

the symbols in brackets represent concentrations (more exactly: activities) of the respective substances. K_1 and K_2 are the first and the second dissociation constant of the acid.

As a measure for the strength of the acid it is advantageous in many cases to use instead of the dissociation constants rather their negative logarithms¹, which we will call *dissociation exponents* or *dissociation numbers of the acid* (p):

$$p_1 = -\log K_1 \quad \text{and} \quad p_2 = -\log K_2 .$$

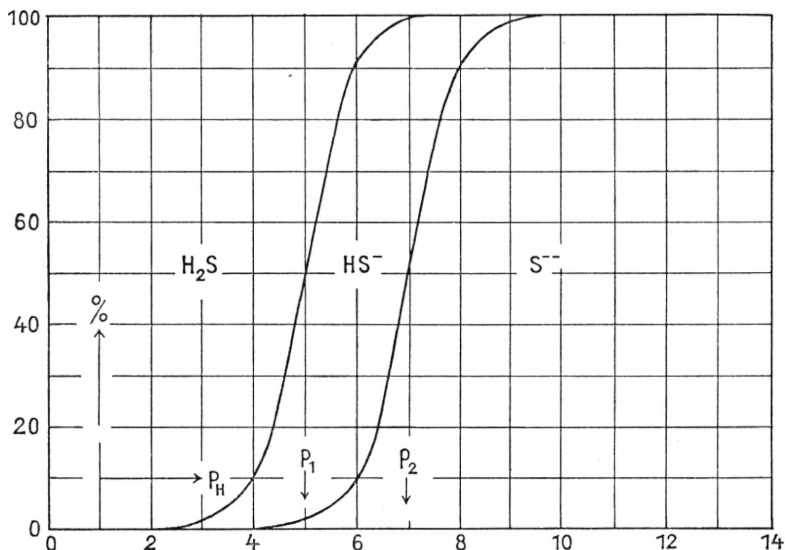


Fig. 1.

The latter denotation is in agreement with the name "Reaktionstal" (*reaction number*) proposed by Hasselbalch² for the hydrogen-ion exponent ($pH = -\log [H^+]$).

In equimolar mixtures of a free acid and the corresponding acid salt, or of an acid salt and the corresponding neutral salt, the dissociation numbers and the reaction numbers are almost identical. However, this does not hold when the dissociation numbers fall closely together. Exactly speaking, dissociation numbers mean those reaction numbers where the concentrations (activities) of H₂S and HS⁻, or HS⁻ and S²⁻, respectively, are equal.

The state of a dibasic acid at different reaction numbers may be illustrated very clearly in the following graphical way (fig. 1).

As the abscissa are plotted the reaction numbers increasing, as is well known, from zero to 14 from strongly acid to strongly alkaline solutions. The ordinate at each different reaction number is divided into parts, one over the other, which indicate in per cent how much of the acid is present as S²⁻, HS⁻, and H₂S, respectively. The areas between the curves of fig. 1 thus correspond to the forms S²⁻, HS⁻, and H₂S. The pieces of the ordinate situated in the different areas show the quantity of the respective form of the acid in per cent at the hydrogen-ion concentration in question. The points of inflection of the two S-shaped curves fall approximately at those points of the reaction scale which correspond to the dissociation numbers p_1 and p_2 .

The graphical method described here deviates from the usual one (*cf.* for

example³). It illustrates much better the relative amounts of the three forms, but it shows less clearly the maximum of the form HS^- .

3. Table 1 given below comprises the first and second dissociation numbers of the normal homologues of oxalic acid. If not otherwise indicated, the values

Table 1. Normal Dicarboxylic Acids

	p_1	p_2	$p_2 - p_1$	n
Oxalic acid C ₂	1.42	4.35	2.93	2.33
Maleic acid C ₃	2.80	5.69 ^{a)}	2.89	2.29
Succinic acid C ₄	4.20 ^{a)}	5.62 ^{b)}	1.42	0.82
Glutaric acid C ₅	4.32	5.50	1.18	0.58
Pimelic acid C ₇	4.49	(5.36) ^{c)}	(0.87)	(0.27)
Suberic acid C ₈	4.52	5.55	1.03	0.43
Azelaic acid C ₉	4.60	5.56	0.96	0.36
Sebacic acid C ₁₀	4.62	5.60	1.02	0.42

^{a)} 18° C. Larsson, E. private communication.

^{b)} 18° C. Larsson, E. *Z. anorg. Chem.* **125** (1922) 281.

^{c)} Determined only by shaking out. For the homologous acids, this method gives lower values than does the conductivity measurement on the acid salt also applied by Chandler.

were calculated from those given by Chandler⁴ for the dissociation constants at 25° C. Larsson's figures are valid at 18° C. Since for the dissociation of a carboxyl group the heat of ionization Q is rather small (varying from -1600 to +1100 calories according to the heats of neutralization found by Jul. Thomsen), the dissociation numbers change at the most by 0.03 between 18 and 25° C according to the formula

$$\frac{d \ln K}{dt} = -\frac{Q}{RT^2}.$$

For all acids given in the table, the second dissociation number is larger than the first, the difference being the more significant, the closer the carboxyl groups are to each other.

The dissociation number of acetic acid and its unibasic homologues is approximately 4.8. The first dissociation number of the acids given in the table is always smaller, the second one larger than this value. It follows from this that the strength of a fatty acid is increased by introduction of a carboxyl group, and is reduced by introduction of an ionized carboxyl group.

This difference between $-\text{COOH}$ and $-\text{COO}^-$ has already been observed by Ostwald⁵, who interpreted it as the effect of attraction of the negative charge on the hydrogen ion. Ostwald has emphasized that this hypothesis also explains

why the second hydrogen atom of a dibasic acid is the more difficult to split off, the closer the two charges of the divalent ions are to each other.

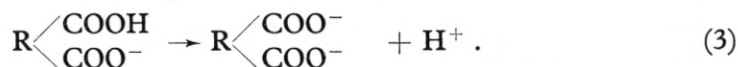
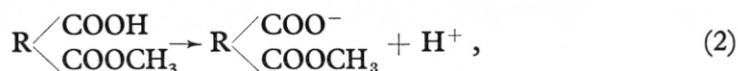
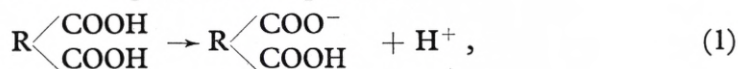
4. A difference between p_1 and p_2 may be caused in different ways.

In an *unsymmetrical* acid, such as malic acid, the more acid carboxyl group will start dissociating, so that we already for this reason must expect $p_2 > p_1$. In a *symmetric* acid, such as succinic acid, this point is lacking, but even though, and owing to the *Ostwald electrostatic action*, p_2 will be greater than p_1 .

However, even if the ionizable hydrogen atoms of a dibasic symmetrical acid are so far apart that electrostatic forces no longer play a part, we must expect for statistical reasons that K_1 will exceed the value of K_2 by a factor of 4, i.e. that

$$p_2 - p_1 = \log 4.$$

Let us consider the following dissociation processes:



Assuming the carboxyl groups so far apart that their ionizations do not affect each other, their dissociation according to scheme 1 will occur just as easily as will the dissociation of the acid methyl ester according to scheme 2. Since, however, in the latter only one and in the former two carboxyl groups dissociate, K_1 must, for statistical reasons, be twice the dissociation constant K_{CH_3} of the acid ester.

These considerations originate from Wegscheider⁶, who found them confirmed by Walden's and Walker's measurements of the dissociation constants of acid methyl- and ethyl esters of those dibasic acids whose carboxyl groups are not closer together than those of succinic acid.

Comparing, furthermore, the dissociation of the acid methyl ester according to scheme 2 with that of the acid ion according to scheme 3, and taking into account that the carboxyl groups far apart from each other do not influence each other we come to the result that, for statistical reasons, K_2 must be the half of K_{CH_3} . In the doubly charged anion formed according to scheme 3, there are two places for the re-entrance of hydrogen ions, while the singly charged ion formed according to scheme 2 has only one.

From

$$K_1 = 2 K_{\text{CH}_3} \quad \text{and} \quad K_2 = \frac{1}{2} K_{\text{CH}_3}$$

it follows that

$$K_1 = 4 K_2 \quad \text{and} \quad p_2 = p_1 + \log 4.$$

For a dibasic acid with carboxyl groups close to each other, it naturally holds that

$$K_1 > 4 K_2 \quad \text{and} \quad p_2 > p_1 + \log 4.$$

This statistical effect on the ratio of the two constants has been discussed by Adams⁷. He considers it a support of his views that in the oxalic acid series always $K_1/K_2 > 4$, even when the carboxyl groups are far apart. The value of 4 has never been reached here. However, *phenolphthalein* is a dibasic acid where the ratio K_1/K_2 is exactly 4.

According to Adams, this is due to the fact that the acid hydroxyl groups are very far apart, namely at the farthest ends of a diphenyl-methane group. However, we shall see that also in phenolphthalein the ratio of the *true* dissociation constants exceeds 4 and that it is only accidental that the found, apparent constants have the ratio 4 to 1.

In an attempt to find a *measure* (n) for the *mutual influence* of the ionization processes of the carboxyl groups in a symmetrical, dibasic acid, $\log 4 = 0.60$ must be subtracted from $p_2 - p_1$ in order to eliminate the statistical effect. We then obtain

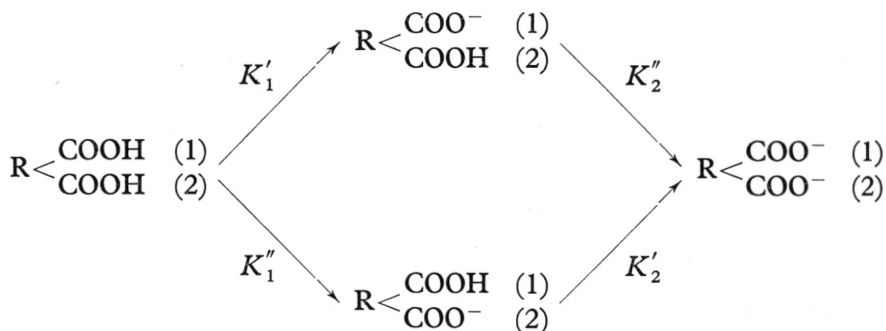
$$n = p_2 - p_1 - 0.60. \quad (4)$$

5. In *dibasic, unsymmetrical carboxylic acids* it is less simple to calculate the mentioned mutual influence of the carboxyl groups from the dissociation numbers. However, this can be done with approximation as follows (in close connection with Wegscheider's considerations⁸ concerning the dissociation-in-steps of dibasic acids).

On ionization of a dibasic unsymmetrical acid



two different singly charged ions and one doubly charged ion are formed



The constants corresponding to these four partial processes be K'_1 , K''_1 and K'_2 , K''_2 , where the suffices (1 and 2) denote the first and the second dissociation

constant, respectively, and the dashes denote the number of the dissociating carboxyl group.

The gross constants of the ionization process found experimentally (for example from conductivity measurements or measurements of the degree of hydrolysis) are related to the mentioned four fundamental constants as expressed in the following equations:

$$K_1 = K'_1 + K''_2$$

and

$$\frac{1}{K_2} = \frac{1}{K'_2} + \frac{1}{K''_2} . \quad (5)$$

This appears directly from the respective expressions of the law of mass action.

The ratio to be determined is K'_1/K'_2 or the corresponding logarithm. This fraction actually determines in which way the dissociation of carboxyl group (1) is influenced by that of carboxyl group (2). The analogous ratio K''_1/K''_2 , characterizing the effect of ionization of the COOH-group (1) on the state of the other carboxyl group, is of course equally interesting: however, introducing mass action expressions for the constants, it becomes evident that these two ratios are identical.

As a *measure for the inequality of the carboxyl groups* we introduce

$$K'_1/K''_1 = q . \quad (6)$$

Taking into account the expressions from the law of mass action, through which the constants are defined, we also get

$$K'_2/K''_2 = q . \quad (7)$$

From the equations 5, 6, and 7 follows

$$\frac{K'_1}{K'_2} = \frac{K''_1}{K''_2} = \frac{K_1}{K_2} \cdot \frac{q}{(1+q)^2} . \quad (8)$$

For the logarithmic term n , representing the measure for the mentioned mutual influence of the carboxyl groups, we obtain

$$n = \log \frac{K'_1}{K'_2} = \log \frac{K''_1}{K''_2} = p_2 - p_1 - \log \frac{(1+q)^2}{q} . \quad (9)$$

For a *symmetrically* built acid ($q = 1$), this expression becomes, as was to be expected,

$$n = p_2 - p_1 - \log 4 .$$

For an *especially unsymmetrical* acid (q very small or very large), it holds that

$$n = p_2 - p_1 - \log q$$

or

$$n = p_2 - p_1 + \log q .$$

Here, the statistical effect can be completely disregarded, and a correction is required only for the different strengths of the acid groups.

Equation 9 takes a more symmetrical form if, as a measure for the inequality of the carboxyl groups, two numbers α' and α'' are used instead of q . These two numbers give the fractions of K_1 falling on K'_1 and K''_1 , respectively (and also the distribution of the singly charged ion over its two isomeric forms). We have

$$\alpha' = \frac{K'_1}{K_1}, \quad \alpha'' = \frac{K''_1}{K_1};$$

and

$$\alpha' + \alpha'' = 1 \quad \text{and} \quad \frac{\alpha'}{\alpha''} = q. \quad (10)$$

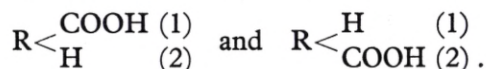
It follows from equations 9 and 10:

$$n = p_2 - p_1 + \log \alpha' \alpha''. \quad (11)$$

In order to calculate n , we must find a way of determining q or α' and α'' .

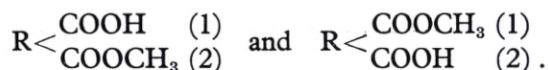
Ostwald⁹ has shown that introduction of a substituent in a certain position relative to the carboxyl group changes the dissociation constant by a definite factor, rather independent of the presence of other substituents in the acid molecule. This so-called *factor law* was investigated more thoroughly by Wegscheider¹⁰. He has given a survey of factors which correspond to the substitution with different radicals in different positions. Later, Derick¹¹ used the factor law in a slightly modified form, without giving any proof of the necessity of this change.

On the basis of the factor law, the ratio K'_1/K''_1 (and thus q) is equal to the ratio of the constants of the two unibasic acids



Consequently, we can compute q for malic acid from investigations of α - and β -oxypropionic acid, and q for pyrotartaric acid from investigations of butyric acid and isobutyric acid, etc.

In a similar way, q can also be calculated as the ratio of the constants of two isomeric acid esters, for example



6. In tables 1-4 the values of p_1 , p_2 , and n are given for a number of dibasic acids.

Table 1 shows n decreasing from 2.3 to 0.4 with increasing distance between the carboxyl groups so that the latter are gradually withdrawn from interaction.

Table 2. Glutaric Acids

	p_1	p_2	$p_2 - p_1$	n
Glutaric acid	4.32	5.50	1.18	0.58
Thiodiglycolic acid	3.31 ^{a)}	4.46 ^{b)}	1.15	0.55
Camphoric acid	4.65 ^{c)}	5.8 ^{a)}	1.15	0.55
<i>m</i> -phthalic acid	3.54	4.60	1.06	0.46

Table 3. Symmetric Succinic Acids

	p_1	p_2	$p_2 - p_1$	n
Succinic acid	4.20 ^{a)}	5.62 ^{b)}	1.42	0.82
<i>d</i> -tartaric acid	3.02 ^{a)}	4.39 ^{b)}	1.37	0.77
Dibromosuccinic acid	1.47	2.80	1.33	0.73
Fumaric acid	3.03	4.47 ^{b)}	1.44	0.84
Phthalic acid	2.92	5.45 ^{a)}	2.53	1.93
Maleic acid	1.93	6.29 ^{a)}	4.36	3.76

Table 4. Unsymmetric Succinic Acids

	p_1	p_2	$p_2 - p_1$	q	n
Pyrotartaric acid	4.13 ^{a)}	5.63 ^{b)}	1.50	1.07	0.90
<i>l</i> -malic acid	3.48 ^{a)}	5.11 ^{b)}	1.63	4.45	0.80
Monobromosuccinic acid	2.56	4.50	1.94	11.0	0.82
Aspartic acid	1.98 ^{d)}	3.82 ^{d)}	1.84	(14.8)	(0.61)

^{a)} 18° C. Larsson, E. private communication.

^{b)} 18° C. Larsson, E. *Z. anorg. Chem.* **125** (1922) 281.

^{c)} 18° C. Ostwald, W. *Z. physik. Chem.* **3** (1889) 369.

^{d)} 25° C. Bjerrum, N. *Z. physik. Chem.* **104** (1923) 152.

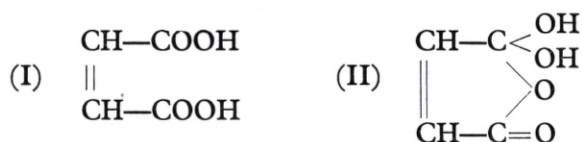
It appears from tables 2–4 that the value of n actually depends on the distance between the carboxyl groups, as indicated in “glutaric acids” and “succinic acids” (with 3 and 2 atoms, respectively, between the carboxyl groups).

Thiodiglycolic acid (table 2), where one methylene group of the glutaric acids is replaced by sulfur, and also *camphoric acid* behave like glutaric acid. However, n is somewhat smaller for *m*-*phthalic acid* (by 0.14), the carbocyl groups of the latter influencing each other to a less extent, maybe because the stiff benzene ring keeps them further apart.

Among the *symmetric succinic acids* (table 3), tartaric acid, dibromosuccinic acid, and fumaric acid are very much like succinic acid. However, the value for

phthalic acid deviates considerably (by 1.11) from these n -values, and still more does that for *maleic acid* (by 2.94). It is tempting in this connection to think of the *stereochemical* effect causing that here the carboxyl groups come still closer to each other than in succinic acid. In the case of *phthalic acid*, the deviation can be explained completely in this manner. In the case of *maleic acid*, this explanation may be insufficient, since the high value of $n = 3.76$ even markedly exceeds the values for malonic and oxalic acid, although the charges of the divalent ions of oxalic acid and malonic acid are just as close to each other as in *maleic acid*.

Possibly, for *maleic acid*, apart from the usual symbol (I) also the old Anschütz formula (II) may be taken into consideration, and we may assume that solutions of the acid contain both forms.



If 50–100 per cent of the undissociated acid and the doubly charged ion were present as (I), and 90 per cent of the singly charged ions as (II), the anomalous value of n would be understandable. However, this hypothesis claims a higher strength of the Anschütz acid than ordinarily expected.

Among the *unsymmetrically* built succinic acids, *pyrotartaric acid*, *malic acid*, and *monobromosuccinic acid* follow completely succinic acid (mean value $n = 0.84$; for succinic acid $n = 0.82$). *Aspartic acid* has a somewhat deviating value of n ; however in this case the determination of q is rather uncertain because the constants of the β -amino propionic acid are unknown and q has to be calculated indirectly.

Already in 1893, Noyes¹² stated that the introduction of new groups into a dibasic acid influences the dissociation constant of the acid and its acid salt “in the same direction”. Later Wegscheider¹³ showed in greater detail why the factor law leads to this result; moreover, he has shown the approximate validity of the rule on several examples.

7. It is easy *outside the group of carboxylic acids* to find multibasic acids, the ionizable hydrogen atoms of which are still closer to each other than those of oxalic acid. Such atoms are present in carbonic acid, sulphurous acid, and phosphoric acid in the hydroxyl groups, which are bound to the same metalloid atom. In hydrogen sulphide, they are even directly bound to the same metalloid atom.

Owing to anhydride formation, the usual figures for the first dissociation constant of carbonic acid and sulphurous acid are not the true values. According

Table 5. Inorganic Acids

	p_1 (uncorr.)	p_1	p_2	$p_2 - p_1$	n
Carbonic acid	6.51 ^{a)}	abt. 4	10.34 ^{b)}	6.34	5.74
Phosphoric acid		1.96 ^{f)}	7.26 ^{b)}	5.30	4.82
Sulphurous acid	1.77 ^{c)}		5.30 ^{c)}		
Hydrogen sulphide		7.04 ^{d)}	14.92 ^{e)}	7.88	7.28

a) 18° C. Warburg, E. J. *Biochem. J.* **16** (1922) 233.

b) 18° C. Unmack, A. unpublished.

c) 25° C. Jellinek, K. Z. *physik. Chem.* **76** (1911) 257.

d) 18° C. Auerbach, F. Z. *physik. Chem.* **49** (1904) 220.

e) 25° C. Knox *Trans. Faraday Soc.* (1908) 43. Cited from reference f).

f) 18° C. Abbot, G. A., and Bray, W. C. *J. Am. Chem. Soc.* **31** (1909) 729.

to Thiel and Strohecker¹⁴ and to Faurholt¹⁵, we must ascribe a p_1 about 4 to the real *carbonic acid*.

In the calculation of n for *phosphoric acid*, log 3 instead of log 4 has been subtracted from $p_2 - p_1$ in view of the tribasic nature of this acid. This point will be discussed later.

The not very different n -values for carbonic acid and phosphoric acid indicate that here the mutual effect of the ionizable hydrogen atoms is of the same order of magnitude and — as was to be expected — even stronger than in any of the dicarboxylic acids.

In the case of *sulphurous acid*, n cannot be calculated because the degree of hydration is still unknown. If we assume that n is the same as in carbonic acid and that the acid is built symmetrically, we obtain — 1.04 as the true value of p_1 . This means that in aqueous solution only the fraction $10^{-1.04-1.77} = 0.0016$ of the sulphur dioxide is present as H_2SO_3 (obviously the solution also contains larger quantities of ionized H_2SO_3). The value becomes still smaller if the sulphurous acid has an unsymmetrical structure. Since the value already is very low, it is impossible from the dissociation constants to derive any support for the unsymmetrical structure of H_2SO_3 .

The highest value of n , namely 7.28, is found for *hydrogen sulphide*, as was to be expected.

8. If it is assumed that n for *water* is the same as for the analogously built hydrogen sulphide, the *number of doubly charged oxygen ions* O^{--} in water can be calculated. Their existence has frequently been assumed, for example by Nernst¹⁶, in order to explain certain phenomena during electrolysis of water. However, concerning the quantity of such ions not even a rough estimate has been possible so far.

For water we can put $p_1 = 14 + \log 55.5 = 15.7^*$. Adding 7.3 to $\log 4$ we find $p_2 = 23.6$. Consequently, we get for the concentration of the oxygen ion

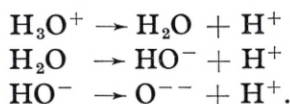
$$[\text{O}^{--}] = \frac{[\text{H}_2\text{O}]}{[\text{H}^+]^2} \cdot 10^{-p_1-p_2} = \frac{10^{-37.6}}{[\text{H}^+]^2}.$$

The concentration of O^{--} thus amounts to

$$\begin{array}{ll} \text{In 1 } N \text{ alkali} & ([\text{H}^+] = 10^{-14}) : 10^{-9.6} \\ \text{At the neutral point} & ([\text{H}^+] = 10^{-7}) : 10^{-23.6} \\ \text{In 1 } N \text{ acid} & ([\text{H}^+] = 1) : 10^{-37.6}. \end{array}$$

The reliability of this calculation suffers from the fact that the dissociation numbers of hydrogen sulphide are not exactly known and, especially, that the equality of n for all acids of the H_2S type is only an approximation. An investigation into the dissociation properties of hydrogen selenide and telluride would be most instructive.

9. It must be assumed that in aqueous solution the hydrogen ion is *hydrated with about 8 H_2O* ¹⁷. According to Fajans¹⁸, one water molecule is combined with the ion in a special way, forming the complex H_3O^+ ; the other 7 molecules must therefore be bound more loosely, similarly as in the hydrated hydroxyl ion and in the associated molecules of water proper. If we disregard these loosely bound H_2O molecules, the following dissociation processes occur in water



The ion H_3O^+ can therefore be considered a *tribasic acid*. Similar considerations hold for the first and second dissociation constants as for the constants of the ordinary tribasic acids. Here, the ratio between the two constants is

$$\frac{K_2}{K_1} = \frac{[\text{H}_3\text{O}^+][\text{HO}^-]}{[\text{H}_2\text{O}]^2} = \frac{K_{\text{H}_2\text{O}}}{55.5^2} = 10^{-17.4}.$$

Hence, it follows that: $p_2 - p_1 = 17.4$. If H_3O^+ contains three equivalent hydrogen atoms, n becomes = 16.9 because we must correct for the statistical effect by subtraction of $\log 3$ (possibly $\log 3/2$, which is unimportant in this connection). The fact that this n -value is so much higher than that for hydrogen sulphide (7.28) seems to indicate that the assumption of equivalency of all three hydrogen atoms in the ion H_3O^+ is far from being justified.

10. Concerning *acids of an basicity higher than 2*, similar considerations can be put forward. We confine ourselves to the discussion of the phenomena in

* The dissociation constant of water ($[\text{H}^+] \cdot [\text{OH}^-]$) is, as is well known, about 10^{-14} .

the case of a *tribasic* acid. However, the expressions can be formulated in such a way that generalization for acids of higher basicity becomes directly possible.

The (equivalent or non-equivalent) positions of the three hydrogen atoms in a tribasic acid H_3R be denoted by 1, 2, and 3. In solutions of the acid and its salts the following 8 types of molecules can thus be present:

the undissociated molecule	: H_3R ;
the three singly charged ions	: H_2R^1, H_2R^2, H_2R^3 ;
the three doubly charged ions	: $HR^{1\cdot2}, HR^{1\cdot3}, HR^{2\cdot3}$;
the triply charged ion	: $R^{1\cdot2\cdot3}$.

The dissociation constants determined in the usual way are then defined as follows:

$$K_1 = \frac{[H^+] \cdot ([H_2R^1] + [H_2R^2] + [H_2R^3])}{[H_3R]}, \quad (12)$$

$$K_2 = \frac{[H^+] \cdot ([HR^{1\cdot2}] + [HR^{1\cdot3}] + [HR^{2\cdot3}])}{[H_2R^1] + [H_2R^2] + [H_2R^3]}, \quad (13)$$

$$K_3 = \frac{[H^+] \cdot [R^{1\cdot2\cdot3}]}{[HR^{1\cdot2}] + [HR^{1\cdot3}] + [HR^{2\cdot3}]} \quad (14)$$

In addition to these three gross dissociation constants we have 12 partial dissociation constants, viz.

three first dissociation constants:

$$K_1^1 = \frac{[H^+] \cdot [H_2R^1]}{[H_3R]} \text{ and the two analogues } K_1^2 \text{ and } K_1^3; \quad (15)$$

six second dissociation constants:

$$K_2^{2(1)} = \frac{[H^+] \cdot [HR^{1\cdot2}]}{[H_2R^1]} \text{ and the five analogues } K_2^{a(b)}; \quad (16)$$

three third dissociation constants:

$$K_3^{3(1\cdot2)} = \frac{[H^+] \cdot [R^{1\cdot2\cdot3}]}{[HR^{1\cdot2}]} \text{ and the two analogues } K_3^{2(1\cdot3)} \text{ and } K_3^{1(2\cdot3)}. \quad (17)$$

Of these symbols the first upper index number denotes the H atom whose ionization is discussed. The other indices (in brackets) denote those hydrogen atoms which are already ionized. The lower suffices indicate whether the constant is a first, second, or third dissociation constant. a and b are arbitrarily chosen numbers of 1, 2, and 3.

The 12 elementary constants are not independent of one another. However, it is practical to use a system of independent, if possible symmetrical constants.

This is most suitably done by introducing 7 constants each of which is connected with one of the ions present.

Firstly, the following relations hold:

$$K_1^1 \cdot K_2^{2(1)} = K_1^2 \cdot K_2^{1(2)} \text{ and the two analogous equations.} \quad (18)$$

This is due to the fact that the concentration of the $\text{HR}^{1,2}$ -ion can be expressed by

$$[\text{HR}^{1,2}] = \frac{[\text{H}_3\text{R}]}{[\text{H}^+]^2} \cdot K_1^1 \cdot K_2^{2(1)},$$

as well as by

$$[\text{HR}^{1,2}] = \frac{[\text{H}_3\text{R}]}{[\text{H}^+]^2} \cdot K_1^2 \cdot K_2^{1(2)}.$$

Thus, if three constants are introduced:

$$K_{1,2}^{1,2} = K_1^1 \cdot K_2^{2(1)} \text{ and the two analogous } K_{1,2}^{a,b}, \quad (19)$$

the six elementary second dissociation constants can be dispensed with, since they can be expressed by

$$K_2^{1(2)} = K_{1,2}^{1,2} / K_1^2 \text{ and the five analogues } K_2^{a(b)} = K_{1,2}^{a,b} / K_1^b. \quad (20)$$

Moreover, it holds that

$$K_{1,2}^{1,2} \cdot K_3^{3(1,2)} = K_{1,2}^{2,3} \cdot K_3^{1(2,3)} = K_{1,2}^{1,3} \cdot K_3^{2(1,3)}. \quad (21)$$

This follows from the fact that the concentration of the $\text{R}^{1,2,3}$ -ion can be formulated as the product of any one of these expressions and $[\text{H}_3\text{R}] / [\text{H}^+]^3$. Generally, the product

$$K_1^a \cdot K_2^{b(a)} \cdot K_3^{c(a,b)}$$

has always the same value, independent of the order in which the numbers 1, 2, 3 are distributed over a , b , and c . If we therefore introduce a new constant

$$K_{1,2,3} = K_{1,2}^{1,2} \cdot K_3^{3(1,2)} = K_{1,2}^{a,b} \cdot K_3^{c(a,b)} = K_1^a \cdot K_2^{b(a)} \cdot K_3^{c(a,b)} \quad (22)$$

we can dispense with the three third dissociation constants which can be expressed as follows:

$$K_3^{1(2,3)} = K_{1,2,3} / K_{1,2}^{2,3}, \text{ generalized: } K_3^{a(b,c)} = K_{1,2,3} / K_{1,2}^{b,c}. \quad (23)$$

By means of the four new constants $K_{1,2}^{a,b}$ and $K_{1,2,3}$, and the three K_1^a , thus altogether seven constants, the three gross constants can be written as follows:

$$K_1 = K_1^1 + K_1^2 + K_1^3 \quad (24)$$

$$K_1 K_2 = K_{1,2}^{1,2} + K_{1,2}^{2,3} + K_{1,2}^{1,3}. \quad (25)$$

Thus we have

$$K_2 = \frac{K_{1.2}^{1.2} + K_{1.2}^{2.3} + K_{1.2}^{1.3}}{K_1^1 + K_1^2 + K_1^3} \quad (26)$$

$$K_1 \cdot K_2 \cdot K_3 = K_{1.2.3}, \quad (27)$$

and consequently,

$$K_3 = \frac{K_{1.2.3}}{K_{1.2}^{1.2} + K_{1.2}^{2.3} + K_{1.2}^{1.3}} \quad (28)$$

We now wish to express the ratios between $K_{1.2}$, $K_{2.3}$, and K_3 firstly by means of numbers (α) characterizing the difference in the hydrogen atoms of the acid, in other words their unsymmetry, and secondly by means of numbers (β) indicating the effect of ionization of one or several hydrogen ions on the dissociation constants of the others. Putting

$$\alpha_1 = \frac{K_1^1}{K_1}; \quad \alpha_2 = \frac{K_1^2}{K_1}; \quad \alpha_3 = \frac{K_1^3}{K_1}; \quad (29)$$

$$\beta_{1.2} = \frac{K_2^{1(2)}}{K_1^1} = \frac{K_2^{2(1)}}{K_1^2}; \quad \text{generally: } \beta_{a.b} = \frac{K_2^{a(b)}}{K_1^a} = \frac{K_2^{b(a)}}{K_1^b}; \quad (30)$$

$$\beta_{1(2.3)} = \frac{K_3^{1(2.3)}}{K_1^1}, \quad \text{generally: } \beta_{a(b.c)} = \frac{K_3^{a(b.c)}}{K_1^a}; \quad (31)$$

$$\beta_{1.2.3} = \beta_{1(2.3)} \cdot \beta_{2.3} = \beta_{2(1.3)} \cdot \beta_{1.3} = \beta_{3(1.2)} \cdot \beta_{1.2}. \quad (32)$$

α_1 , α_2 , and α_3 , whose sum equals 1, are proportional to the dissociation constants for the three hydrogen atoms. $\beta_{1.2}$ and its analogues give the effect of the ionization of the first hydrogen atom on the dissociation constant for the second atom (or the identical counter effect of the second atom on the constant for the first).

$\beta_{1(2.3)}$ characterizes the influence of the second and third ionized hydrogen atom on the constant for the first. Since, however, $\beta_{a(b.c)} \cdot \beta_{b.c}$ always has the same value, independent of the way in which 1, 2, 3 are substituted for a , b , c , it is sufficient to use the constant $\beta_{1.2.3}$ if the effect of dissociation of two hydrogen atoms on the constant for the third has to be expressed.

From equations 26, 19, 29, and 30 it follows that

$$\frac{K_2}{K_1} = \alpha_1 \alpha_2 \beta_{1.2} + \alpha_1 \alpha_3 \beta_{1.3} + \alpha_1 \alpha_2 \beta_{2.3}. \quad (33)$$

From equations 27, 22, 29, 31, and 32 we obtain

$$\frac{K_3}{K_2} = \frac{\alpha_1 \alpha_2 \alpha_3 \cdot \beta_{1.2.3}}{(\alpha_1 \alpha_2 \beta_{1.2} + \alpha_1 \alpha_3 \beta_{1.3} + \alpha_2 \alpha_3 \beta_{2.3})^2}. \quad (34)$$

11. The formulae obtained for K_2/K_1 and K_3/K_1 will now be applied to *citric acid*



The carboxyl groups (1) and (3) are stronger than butyric acid, as 1 β -hydroxyl, 1 β -carboxyl, and 1 γ -carboxyl group have been introduced. Carboxyl group (2) is stronger than isobutyric acid, taking into account the presence of 1 α -hydroxyl and 2 β -carboxyl groups. The factor 4.4 (derived from lactic acid and hydracrylic acid) corresponds to the difference between α - and β -hydroxyl groups, — the factor 1.35 (from succinic acid and glutaric acid) corresponds to the inequality of the β - and γ -carboxyl groups. Butyric and isobutyric acid can be regarded as equally strong.

The carboxyl group (2) of citric acid is thus $4.4 \cdot 1.35 = 6.0$ times as strong as the other carboxyl groups. We therefore have

$$\alpha_1 = \alpha_3 = \frac{1}{8}$$

and

$$\alpha_2 = \frac{6}{8}.$$

The carboxyl group (2) is in a β -position to the others, just as the carboxyl groups of succinic acid. We may consequently put

$$-\log \beta_{1.2} = -\log \beta_{2.3} = n_{\text{succinic acid}} = 0.82.$$

The carboxyl groups (1) and (3) are in γ -position to each other, just as in glutaric acid. We may therefore put

$$-\log \beta_{1.3} = n_{\text{glutaric acid}} = 0.58.$$

It can be calculated from this according to equation 33

$$\log (K_1 / K_2) = 1.49.$$

For the *dissociation numbers of citric acid* Miss A. Unmack found by means of electrometric measurements at 18° C (in a yet unpublished work)

$$p_1 = 3.23 \quad p_2 = 4.85 \quad p_3 = 6.40,$$

from which we obtain

$$\log (K_1 / K_2) = 1.62.$$

The calculated value is only 0.13 too high, which is a rather satisfactory result.

For $\log (K_2 / K_3)$ these measurements lead to 1.55. From this value and equation 34 together with the mentioned α - and β -values we obtain

$$-\log \beta_{1.2.3} = 2.59,$$

where $\beta_{1.2.3}$ is equal to $\beta_{1.2} \cdot \beta_{3(1.2)}$. If it is assumed that the total effect of ionization of the hydrogen atoms (1) and (2) equals the product of the single effects of these ionization processes, it holds that

$$\beta_{3(1.2)} = \beta_{1.3} \cdot \beta_{2.3},$$

thus

$$\beta_{1.2.3} = \beta_{1.2} \cdot \beta_{1.3} \cdot \beta_{2.3}.$$

In the case of citric acid,

$$-\log \beta_{1.2.3} = 2 n_{\text{succinic acid}} + n_{\text{glutaric acid}} = 2.22$$

and

$$\log (K_2 / K_3) = 1.18.$$

The value found directly from the measurements is, however, 0.37 higher. The ionization of both of the two hydrogen atoms has thus a somewhat stronger effect than indicated by the product of the single effects.

It is not improbable that the deviation of the value found for K_2 / K_1 from that calculated can, at least partly, be ascribed to the application of α -values, the incorrectness of which is due to the inaccuracy of the factor law. If we use in the computation of $-\log \beta_{1.2.3}$ such α -values ($\alpha_1 = \alpha_3 = 0.087$; $\alpha_2 = 0.826$) that the figures obtained for K_2 / K_1 are in agreement with experience, we arrive at $-\log \beta_{1.2.3} = 2.50$, a value which is somewhat closer to 2.22 than is the earlier value of 2.59.

The value of K_2 / K_1 for citric acid (and other tribasic acids) does not reveal considerably more than can be found out much more easily from a dibasic acid. However, K_3 / K_2 gives some additional information. This term tells us how the ionization of two hydrogen atoms affects the dissociation constant for a third hydrogen atom.

12. For a *symmetrical tribasic acid* we have

$$\alpha_1 = \alpha_2 = \alpha_3 = \frac{1}{3}$$

and

$$\beta_{1.2} = \beta_{1.3} = \beta_{2.3} = \beta,$$

whereby equations 33 and 34 can be reduced to

$$\frac{K_2}{K_1} = \frac{\beta}{3} \quad (35)$$

and

$$\frac{K_3}{K_2} = \frac{\beta_{1.2.3}}{3\beta^2}. \quad (36)$$

Owing to the statistical effect, K_2 thus becomes three times, and K_3 nine times, smaller than K_1 . The term denoted above as n is equal to $-\log \beta$. Taking the logarithms thus leads from equation 35 to

$$n = p_2 - p_1 - \log 3 \quad (37)$$

and from equation 36 to

$$-\log \beta_{1.2.3} = p_3 - p_2 - \log 3 + 2n. \quad (38)$$

In the case of *phosphoric acid* we have^{19, 20}

$$p_1 = 1.96 \quad p_2 = 7.26 \quad p_3 = 12.44.$$

Subsequently, we obtain from equation 37

$$n = 4.82$$

and from equation 38

$$-\log \beta_{1.2.3} = 14.34.$$

If we have

$$\beta_{1.2.3} = \beta_{1.2} \cdot \beta_{2.3} \cdot \beta_{1.3} = \beta^3$$

we must obtain

$$-\log \beta_{1.2.3} = 3n,$$

and consequently $-\log \beta_{1.2.3} = 14.46$. The fair agreement with the value found above shows that in the case of phosphoric acid, the effect of ionization of two hydrogen atoms on the dissociation constant for the third must be almost identical with the square of the single effects.

13. The influence of the ionization of one hydrogen atom on that of another may probably arise in two ways.

Firstly, the negative charge liberated through dissociation will attract the hydrogen ions. This *electrostatic* effect will increase the hydrogen-ion concentration in the proximity of that hydrogen atom whose dissociation we consider above that prevailing in the solution. If the value of this deviation is estimated and taken into consideration in the calculation, we arrive at a theory of the electrostatic effect.

Secondly, there must exist an effect *through the atom chain*. During the ionization process intramolecular displacements of electrons take place, which propagate (with decreasing strength) over the chain of linked atoms and cause an increase of those forces which bind the other hydrogen atom. It is impossible to calculate this effect theoretically, but experimental data indicate how far into the atom chain this effect is noticeable.

The *electrostatic effect* can be calculated in the following way. Let r be the distance between the dissociating hydrogen atom and the negative charge already present, and D be the dielectric constant, which we assume does not vary.

In a given place, the concentration of one type of molecules is, according to Boltzmann,

$$c \cdot e^{\frac{\varphi N}{RT}}$$

(φ = the work to be performed in order to move one molecule from the respective place to another place with the concentration c . R is the gas constant, T the absolute temperature, and N Avogadro's constant).

The electric work required to move a hydrogen ion from a negative charge is

$$\varphi = \frac{\varepsilon^2}{Dr}$$

(where ε = the charge of the electron). A negative ion is therefore surrounded by a condensed hydrogen-ion "atmosphere", in which the hydrogen-ion concentration (c_r) depends on the distance r from the charge according to the following formula

$$c_r = c \cdot e^{\frac{\varepsilon^2 N}{DRT r}}$$

If r is the distance between the charge and the hydrogen atom remaining in the singly charged ion, the dissociation constant (K) must be reduced, owing to electrostatic attraction, by the factor

$$e^{\frac{\varepsilon^2 N}{DRT r}}$$

while the following term must be added to the dissociation number (p)

$$\log_{10} e^{\frac{\varepsilon^2 N}{DRT r}}$$

Putting $\varepsilon = 4.774 \cdot 10^{-10}$, $N = 6.06 \cdot 10^{23}$, $D = 80$, $R = 8.35 \cdot 10^7$, and $T = 291$, the increase of the dissociation number is found to be

$$\frac{3.1}{r \cdot 10^8}$$

14. If it is assumed that the value of n (the total effect of ionization on the dissociation number) originates exclusively from the electrostatic effect, we have

$$n = \frac{3.1}{r \cdot 10^8}$$

Table 6 shows the figures for r calculated according to this formula. In order to estimate their validity, table 7 presents a number of recent data concerning molecular distances, showing that the order of magnitude of the r -values given in the table is rather satisfactory.

Table 6. Distance between Acid Hydrogen Atoms in Some Acids

	n	r	a
Dibasic acids C ₈ -C ₁₀	0.40	$7.8 \cdot 10^{-8}$ cm	$14.0 \cdot 10^{-8}$ cm
Glutaric acid C ₅	0.58	5.3	8.0
Succinic acid C ₄	0.82	3.8	6.5
Malonic acid C ₃	2.29	1.35	5.0
Oxalic acid C ₂	2.33	1.33	3.5
Carbonic acid	5.74	0.54	
Phosphoric acid	4.87	0.64	
Hydrogen sulphide	7.28	0.43	

Table 7. Distance between the Centres of :

K ⁺ and Cl ⁻ in the potassium chloride crystal	$3.1 \cdot 10^{-8}$ cm
C - C - diamond	1.52
C - C - graphite	{ 1.45
	{ 3.41
H - Cl in HCl	1.28
N - N - N ₂	1.12
O - O - O ₂	0.85
H - H - H ₂	0.60
Radius of the hydrogen atom according to Bohr	0.55

The values found for succinic acid and higher dicarboxylic acids must be considered very good.

If the charge of the carboxyl group is at a distance of about 10^{-8} cm from the centre of the carbon atom, and the distance between neighbouring links of the carbon chain (as in diamond) is $1.5 \cdot 10^{-8}$ cm, then the distance between the two charges of a dicarboxylic acid (measured through the atom chain) can be calculated (a in table 6).

In succinic acid and the higher acids, the difference between a and r reaches such a value that it can easily be explained by the curved shape of the carbon chain. Here, we thus have none or only a weak effect through the atom chain.

For malonic acid and oxalic acid, and still more for carbonic acid, phosphoric acid, and hydrogen sulphide, the r -values (table 6) are too low (*cf.* table 7). For malonic acid and oxalic acid $r =$ about $1.34 \cdot 10^{-8}$ cm, while at least 3 or 4 times 10^{-8} should be expected. Here, a noticeable effect through the atom chain must be prevailing.

The fact that the atom chain effect is marked only when ionization takes place at an α - or β -carbon atom, is in best agreement with well-known observations concerning the influence of substituents on the dissociation of organic acids. If

the strength of an acid is increased by introduction of — OH, — COOH, — Cl, this must be due to an effect through the atom chain. In any case, an electrostatic effect is lacking here. These substituents have a strong effect only in the α - or β -position. If the introduction of a new carboxyl group in a δ -, ϵ -, or even in a still more remote position reduces the dissociation number of a fatty acid from about 4.9 to about 4.6 (*cf.* p_1 in table 1), this must be ascribed to the statistical effect (presence of *two* carboxyl groups: 0.3) rather than to the effect through the atom chain.

15. The above considerations have shown that removal of a hydrogen ion from a carboxyl group causes electron displacements which propagate from the carboxyl group through the atom chain and which are of a magnitude similar to the displacements due to the introduction of — OH, — COOH, or — Cl in an organic acid. It follows from this that the bonding of the hydrogen ion is far from being exclusively of an electrostatic nature (as suggested by Kossel). This binding must be accompanied by a very considerable *deformation* (*cf.* Fajans¹⁸) of the carboxyl group; it seems to me that the atom chain effect is so large that it gives the binding of the hydrogen ion in the carboxyl group almost a homopolar character. In favour of this speak also the fundamental optical changes accompanying ionization of carboxylic acids according to Hantzsch and Schäfer.

16. The dibasic nature of *phenolphthalein* is due to the presence of two phenolic hydroxyl groups — in a *p*-position to the same carbon atom — in different benzene rings. Putting the diameter of these rings equal to $3 \cdot 10^{-8}$ cm, the distance between two singly bound carbon atoms to $1.5 \cdot 10^{-8}$ cm, the distance between C and O to $1 \cdot 10^{-8}$ cm, and taking into account the curved shape of the carbon chain, we can estimate the distance between the acid hydrogen atoms to be $8 \cdot 10^{-8}$ cm, that is the same as in dicarboxylic acids with C_9 and C_{10} . From this it follows that

$$n = \text{about } 0.4; \quad p_2 - p_1 = n + \log 4 = 1.0.$$

Although Rosenstein's²¹ measurements are in disagreement with these estimations (he found $p_2 - p_1 = 0.61$), we should not (as Adams⁷ did) draw the conclusion of a mutually independent dissociation of the two hydrogen atoms. However, it should be taken into consideration that the doubly charged phenolphthalein ion has suffered a transformation appearing as a red colour of the ion. The approximate quantity of the doubly charged ion transformed into the red coloured form can be calculated from the difference between 1.0 and 0.61. If it is assumed that 60 per cent have been transformed and 40 per cent remained unchanged, the value of p_2 for the untransformed form increases by $-\log 0.4 (= 0.40)$ and we have

$$n = 0.61 + 0.40 = 1.01,$$

a value which is in good agreement with expectation (1.0).

17. It follows from our considerations that the effect of ionization of a hydrogen atom on the dissociation of another hydrogen atom can be calculated, using the *ordinary dielectric constant of water*, 80, when it is assumed that the hydrogen atoms are so far apart that no atom chain effect is noticeable. This result is of considerable interest.

A calculation with the ordinary dielectric constant is *theoretically* permissible only when numerous water molecules are present between the charges whose mutual effect has to be derived. The above result shows *empirically*, however, that the procedure is permissible also when the distance between the charges is only of molecular size, i.e. if only a few water molecules find room in the interspace.

In more recent works, a *complete* ionization of strong electrolytes is generally assumed. The effects interpreted in earlier works as being due to incomplete dissociation are now regarded as the consequences of interionic electric forces.

In a work recently²² concluded, I have found that correct results are obtained when calculating with the ordinary dielectric constant of water, even when the ions touch each other, which means under circumstances where no water is present in the interspace. Under these presuppositions, the diameter of the ions could be calculated from the decrease in osmotic effect of the ions with increasing concentration; it turned out to be in good agreement with the results of X-ray spectroscopy on crystal lattices. The result obtained through the study of multi-basic acids offers a valuable support for the validity of this method of calculation.

A theoretical explanation of these conclusions will not be given here, only the following may be pointed out. The decrease in the dielectric constant to be expected for very small distances may be more or less compensated by the fact that the repelling forces that appear when the ions come very close to each other have not been taken into account. If the ions touch each other, these forces become so strong that they completely compensate the electrostatic attraction. Such a consideration certainly makes the admissibility of the mentioned method understandable, indicating at the same time that the method has only the character of a rough approximation.

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