[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

DISSOCIATION OF POLYVALENT SUBSTANCES
II. RELATION OF CONSTANTS TO CHEMICAL STRUCTURE

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I. Notation.—The notation used in this article is the same as in the first paper,[1] with the following additions.

Distances in Ångström units (10^{-8} cm.).

"r" = "Distance" calculated by Bjerrum's Formula 3.

$\Sigma \frac{1}{r}$ = Sum of the reciprocal distances in Equation 25.

r_u = Distance between the negative charges in an *undissociated* divalent acid.

r_m = Distance between the negative charges in a *mono-ion* of a divalent acid.

r_m' = Distance between the negative charge of the ionized group and the positive charge of the un-ionized group in the *mono-ion.*

r_d = Distance between the two negative charges in a *di-ion* of a divalent acid. (See Fig. 1.)

r_L = Distance between two *like* charges in any substance.

r_0 = Distance between two *opposite* charges in any substance.

Work terms (in ergs per mole).

$W_1 = RTP_{K1}$ = Work in first step of ionization.

$W_2 = RTP_{K2}$ = Work in second step of ionization.

$W_0 = RTP_{K0}$ = "Intrinsic" work in ionizing a given group in a given molecule. This work depends upon chemical constitution and does not involve electrostatic work between ionizable groups.

ϕ = Electrostatic work in removing a hydrogen ion from the attraction of a negatively charged (ionized) group.

θ = Electrostatic work performed by two groups of like charge in repelling each other to a greater distance.

Δ = "Distortional" (electrostatic) work done in altering the relative positions of the positive and negative charges in an un-ionized group, with respect to an ionized group.

Miscellaneous.

Y = "Substitution" coefficient, of a substituted group.

x = Position of substitution.

$F\Delta$ = "Index" of distortional work. (See Equations 10 and 12.)

F = A constant $= \frac{0.4343.10^8}{RT}$ = 0.00175 mole per erg.

J = A constant $= F\frac{\epsilon^2 N}{D}$ = 3.0 Ångström units (at 25° C., $D = 80$).

ϵ = Charge on one electron = 4.774×10^{-10} e.s.u.

N = Avogadro number = 6.06×10^{23} molecules per mole.

D = Dielectric constant. (For water $D = 80$.)

R = Gas constant = 8.35×10^7 ergs per mole per degree.

T = Absolute temperature = 298° abs.

L = Function of electrostatic work between groups (see Equation 25).

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[1] THIS JOURNAL, **48**, 1239 (1926).

n = Number of groups with K_0L values too large to be considered in Equations 22 to 24 and 26 to 28.

A and B = Subscripts referring to initial and final states in Equation 25a.

f_0, f_1, f_2, etc. = Activity coefficients when 0, 1, 2, etc. groups, have "dissociated."

$P_X = -\log X$, where X is any constant or quantity.

Chemical groups are indicated by Roman numerals.

"Dissociation" refers to the effect of ionization of the acid groups and hydrolysis of salts of the basic (amino) groups.

S, after the number of an equation, indicates that the equation applies to symmetrical acids only.

II. Introduction.—Every polyvalent acid, base or ampholyte has a number of dissociation constants equal to the number of ionizable groups. The numerical value of each constant in water solution depends, first, upon the *nature of the groups;* second, upon the *influence of other substitutes* on each group; and third, the *effect of electrostatic forces* between the ionizable groups.

The *first factor* (the nature of the groups) determines the general order of magnitude of each constant while the other two factors have an influence to an extent dependent upon conditions. Table I gives approximate *characteristic* constants (P_{Kc}) of a few groups when attached to an aliphatic hydrocarbon or to a benzene ring.

TABLE I

CHARACTERISTIC CONSTANTS

Group	Aliphatic	P_{Kc}	Aromatic	P_{Kc}
$-NH_2$	CH_3NH_2	10.6	$C_6H_5.NH_2$	4.6
$=NH$	$(CH_3)_2NH$	10.7		
$\equiv N$	$(CH_3)_3M$	9.7		
$-COOH$	$CH_3.COOH$	4.73	$C_6H_5.COOH$	4.2
$-OH$	CH_3OH	>14	$C_6H_5.OH$	9.
$-PO_4H_2$	$CH_3.PO_4H_2$	(2) and (7)		
$=PO_4H$	$(CH_3)_2.PO_4H$	(2)		

Other groups are $-SH$, $-SO_3H$, $-CN$, etc. The constants for the amines are expressed in terms of hydrogen-ion activity (hydrolysis constants).

Concerning the *second factor.*—Each substituent produces an effect upon an ionizable group, dependent upon the nature of the substituent and the position of its substitution. The effect of various substituents upon a —COOH group has been studied by Derrick, Flürscheim, Micheal, Walker and Wegscheider.[2] They concluded that the effect was *through the molecule* and was reduced to about *one-third* for each carbon atom through which it was propagated.

We may express this as follows (2.7 fits the data better than 3):

$$P_{K_0} = P_{Kc} + Y/(2.7)^x \qquad (1)$$

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[2] See review by Lowry, *Trans. Faraday Soc.*, 19, 497 (1923), and Lehfeldt, "Electrochemistry," Longmans, Green & Co., 1918, Part I, p. 111 and following pages.

where Y is a coefficient, constant for each substituent and x is the number of atoms separating the group from the carboxyl.

The effect seems to be additive; hence, for a number of substituents with Y values, Y_1, Y_2, Y_3, etc., and substituted in positions x_1, x_2, x_3, etc., the "intrinsic" constant (K_0) of the group would be

$$P_{K_0} = P_{K_c} + \frac{Y_1}{(2.7)^{x_1}} + \frac{Y_2}{(2.7)^{x_2}} + \frac{Y_3}{(2.7)^{x_3}} + \text{etc.} = P_{K_c} + \Sigma \frac{Y}{(2.7)^{x}} \qquad (2)$$

Approximate values of Y for various groups are given in Table II.

TABLE II

SUBSTITUTION COEFFICIENTS

Substituent	—Cl	—Br	—I	—OH	=O	$—NO_2$
Y	5.4	5.2	4.5	2.5	8.0	8.3
Substituent	—COOH	$—COOCH_3$	$—COOC_2H_5$	$—CH_3$	$—C_2H_2$	$—NH_2$
Y	2.7	(4.2)	(3.9)	(0)	(0)	(4)

If, as has been supposed, this effect is through the molecule, it would appear that a substituent performs a certain amount of work upon the valence electrons of the adjacent carbon atom and that this work is propagated to the other three valences and distributed approximately among them. It is not within the province of this article, however, to refute or propose any theories on the mechanism of this effect. We present Equations 1 and 2 to express observations of the above-named men. Although entirely empirical, these equations have practical utility in calculating "intrinsic" constants from chemical structure.

For a monovalent acid, the dissociation constant is identical with the intrinsic constant. However, for polyvalent acids the dissociation constants (of the steps of ionization) differ from the intrinsic constants (of the chemical groups) by an amount dependent upon the electrostatic work between the groups. This, the *third factor*, will now be discussed.

III. Influence of Electrostatic Forces between Groups.—A. *Formula of Bjerrum* for *symmetrical* divalent acids.

Adams (in 1916) showed that for a long symmetrical divalent acid, the ratio K_1/K_2 should equal 4, whereas actual acids have a ratio greater than 4, the deviation being due to electrostatic forces (which were not formulated).

Bjerrum[3] (in 1923) derived the following formula on the assumption that the deviation of $K_1/4K_2$ from unity is a measure of the work in removing the second hydrogen ion from the electrostatic attraction of the charge on the first group, in a mono-ion (or singly charged ion).

$$``r" = \frac{3.1}{\log (K_1/4K_2)} = \frac{3.1}{P_{K_2} - P_{K_1} - 0.60} \qquad \text{(3aS)}$$

or

$$P_{K_2} - P_{K_1} - 0.60 = \frac{3.1}{``r"} \qquad \text{(3bS)}$$

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[3] Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

The distance "r" is a vaguely defined distance expressed in Ångström units.

The distances calculated by this expression have been shown by Bjerrum and Larson to correspond (very roughly) with those computed from the chemical structure of a number of dibasic acids.

However, this formula does not involve the distortional work Δ between the charged group and the un-ionized group in the mono-ion and, hence, gives quite inaccurate values for some acids.

It is desirable to determine the magnitude of this distortional work and also to know the relation between the constants and the dimensions in higher polyvalent acids, in bases and in ampholytes.

B. More Accurate Formulas, for *all* divalent acids.

The *total* work, or free energy change, in the complete ionization of a divalent acid, must equal the algebraic sum of all the work terms in passing from the initial state (low *P*H) to the final state (high *P*H). Hence (see Notations)

$$W_1 + W_2 = W_0^{I} + W_0^{II} + \phi - \theta \qquad (4)$$

If Δ is the same for either group, the work in the first step of ionization is

$$W_1 = -\Delta - RT\,ln\,(K_0^{I} + K_0^{II}) = -\Delta + W_0 - RT\,ln\,P \qquad (5)$$

where $P = (1 + K_0^{II}/K_0^{I})$ is a probability factor (equal to 2 in a symmetrical acid).

Hence
$$W_2 = \Delta + \phi - \theta + W_0^{II} + RT\,ln\,P \qquad (6)$$

and
$$W_2 - W_1 = 2\Delta + \phi - \theta + W_0^{II} - W_0^{I} + 2\,RT\,ln\,P$$
$$= 2\Delta + \phi - \theta - RT\,ln\frac{K_0^{I}K_0^{II}}{(K_0^{I} + K_0^{II})^2} \qquad (7)$$

From the definitions of the distances r_m and r_d, the work ϕ and θ (of removing the second hydrogen ion from the charge of the other group, and of extending the molecule to the distance r_d) for a divalent acid should be

$$\phi = \frac{\epsilon^2 N}{D}\frac{1}{r_m} \text{ and } \theta = \frac{\epsilon^2 N}{D}\left(\frac{1}{r_m} - \frac{1}{r_d}\right) \qquad (8)$$

Hence
$$\phi - \theta = \frac{\epsilon^2 N}{D \cdot r_d} = \frac{J}{F \cdot r_d} \qquad (9)$$

Similarly, the distortional work Δ resulting from the effect of the charged group upon the un-ionized group in the mono-ion is equal to the work of attracting the positive hydrogen atom from its original distance r_u to its final distance r_m', *less* the work of moving the negative oxygen atom from r_u to r_m:

$$F\Delta = J\left(\frac{1}{r_m'} - \frac{1}{r_u}\right) - J\left(\frac{1}{r_m} - \frac{1}{r_u}\right) = J\left(\frac{1}{r_m'} - \frac{1}{r_m}\right) \qquad (10a)$$

If we assume $r_m - r_m' = 0.30$, the radius of the hydrogen ion, we get

$$F\Delta = 3.0\left(\frac{1}{r_m - 0.30} - \frac{1}{r_m}\right) \text{ (approximately)} \qquad (10b)$$

Hence, from Equation 7

$$P_{K_2} - P_{K_1} - 0.60 = \frac{J}{r_\mathrm{d}} + 2\,J\left(\frac{1}{r_\mathrm{m}'} - \frac{1}{r_\mathrm{m}}\right) + \log\frac{(K_0^\mathrm{I} + K_0^\mathrm{II})^2}{K_0^\mathrm{I}K_0^\mathrm{II}}$$

$$= \frac{J}{r_\mathrm{d}} + 2F\Delta + \log\frac{(K_0^\mathrm{I} + K_0^\mathrm{II})^2}{K_0^\mathrm{I}K_0^\mathrm{II}} \qquad (11)$$

Solving for the index of distortional work, gives:

$$F\Delta = \frac{1}{2}\left(P_{K_2} - P_{K_1} - 0.60 - \frac{3.0}{r_\mathrm{d}} - \log\frac{(K_0^\mathrm{I} + K_0^\mathrm{II})^2}{K_0^\mathrm{I}K_0^\mathrm{II}}\right) \qquad (12)$$

For a symmetrical acid these become:

$$P_{K_2} - P_{K_1} - 0.60 = \frac{3.0}{r_\mathrm{d}} + 2\,F\Delta \qquad (11S)$$

and

$$F\Delta = \frac{1}{2}\left(P_{K_2} - P_{K_1} - 0.60 - \frac{3.0}{r_\mathrm{d}}\right) \qquad (12S)$$

Compare Equations 11 with Bjerrum's Formula 3.

Equations 11 and 12 are used in conjunction with Equations 10.

Equations 4, 5 and 6, respectively, give the following equations for unsymmetrical divalent acids.

$$P_{K_1} + P_{K_2} = P_{G_1} + P_{G_2} = P_{K_0}{}^\mathrm{I} + P_{K_0}{}^\mathrm{II} + \frac{3.0}{r_\mathrm{d}} \qquad (13)$$

$$P_{K_1} = P_{K_0} - \log\left(1 + \frac{K_0^\mathrm{II}}{K_0^\mathrm{I}}\right) - F\Delta \qquad (14)$$

$$P_{K_2} = P_{K_0}{}^\mathrm{II} + \log\left(1 + \frac{K_0^\mathrm{II}}{K_0^\mathrm{I}}\right) + F\Delta + \frac{3.0}{r_\mathrm{d}} \qquad (15)$$

For symmetrical acids these become:

$$P_{K_1} + P_{K_2} = P_{G_1} + P_{G_2} = 2P_{K_0} + \frac{3.0}{r_\mathrm{d}} \qquad (13S)$$

$$P_{K_1} = P_{K_0} - 0.30 - F\Delta \qquad (14S)$$

$$P_{K_2} = P_{K_0} + 0.30 + F\Delta + \frac{3.0}{r_\mathrm{d}} \qquad (15S)$$

Equations 10 to 15 may be used to calculate distances when the constants are known, or constants when the distances are known. P_{K_0} values may be calculated from Equations 13 to 15.

IV. Application of the Above Formulas to Divalent Acids.—It has been often stated that, for a divalent acid, K_1 is greater than $4K_2$ *because* the negative charge on the first group hinders the removal of the second hydrogen ion. If this were the only work occurring between the two groups, then (in a symmetrical acid) K_1 would equal $2K_0$.[4] However, the data of *cis* and *trans* acids show that this work may amount to only 20–40% of the work between the groups in such acids as maleic, oxalic and malonic. The remaining 60–80% is "distortional" work in changing the relative positions of the electrostatic charges in mono-ion and in the di-ion. K_1 does not equal $2K_0$.

[4] This is the basis of Wegscheider's rule that $K_1 = 2Ke$, where Ke is the constant of the half ester. This rule can be valid only when the acid is symmetrical, when $K_e = K_0$ and when $F\Delta = 0$ (or when the errors compensate each other).

The above formulas include all these work terms. They involve the distances r_m and r_m' between the *like* and *opposite* charges, respectively, in the mono-ion; and the distance r_d between the *like* charges in the di-ion (see Fig. 1).

The distance r_u, in the undissociated molecule, is not included. It has no bearing upon the dissociation constants.

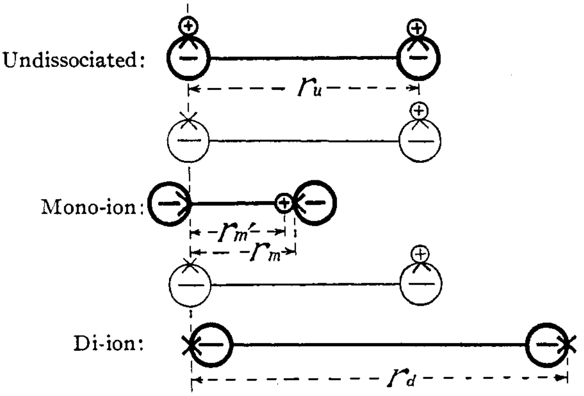

Fig. 1.—Distances in a dicarboxylic acid.

Only the ionizable hydrogen atoms (small circles) and the adjacent oxygen atoms (large circles) are shown. Crosses (x) indicate the position of the negative charge on the oxygen atoms. The carbon atoms (omitted) lie in an extended zigzag chain in the di-ion; and in irregular chains in the mono-ion and the undissociated molecule. The distances are approximately those of suberic acid. In Formula 25, $r_L = r_m$ and $r_0 = r_m'$ in the mono-ion; and $r_L = r_d$ in the di-ion.

In Table III are to be found the P_K values of the α,ω-dicarboxylic acids. In Col. 5 are the values of "r" according to Bjerrum's Formula 3. They

TABLE III

CALCULATION OF r_m (AND OF P_{K_0}) IN α,ω DICARBOXYLIC ACIDS

1	2	3	4	5	6	7	8	9	10
Equation	Found			(3)	Estimated		(11S)	(10b)	(15)
Acid	P_{K_1}	P_{K_2}	$P_{K_2}-P_{K_1}$	"r"	r_d	$\frac{3.0}{r_d}$	$F\Delta$	r_m	P_{K_0}
Carbonic	6.36	10.22	3.86	0.9	3	1.0	1.1	1.1	7.7
Oxalic	1.42	4.35	2.93	1.3	4.5	0.67	0.83	1.2	2.55
Malonic	2.79	5.38	2.59	1.5	5.7	.53	.73	1.3	3.82
Succinic	4.20	5.62	1.42	3.7	7.0	.43	.20	2.3	4.70
Glutaric	4.32	5.50	1.18	5.2	8.2	.37	.10	3	4.72
Adipic	4.43	5.62	1.19	5.1	9.4	.32	.13	3	4.86
Pimelic	4.49	5.59	1.10	6.0	10.6	.28	.11	3	4.9
Suberic	4.52	5.55	1.03	7.0	11.8	.25	.09	3	4.9
Azelaic	4.60	5.56	0.96	8.3	12.1	.25	.05	4	4.9
Sebacic	4.62	5.60	.98	7.9	14.3	.21	.08	4	5.0

Distances "r," r_d and r_m are in Ångström Units.

increase qualitatively with the length of chain—but have no quantitative significance.

In Col. 6 are values of r_d estimated from the chemical structure (see Section IV on molecular dimensions).

From these values and from the difference between the constants $(P_{K_2} - P_{K_1})$, the index of distortional work $(F\Delta)$ may be calculated (from 12S). From Equation 10b we then get the values of r_m in Col. 9 (under the assumption that $r_m' = r_m - 0.30$). These values are all reasonable and possible.

Due to thermal agitation, however, the di-ion may not extend to its greatest possible length. Then the values of r_d would be less than those given; $F\Delta$ would be smaller; and the distances r_m would be slightly greater. The high values of r_m in the longer acids indicates that, although the groups can touch each other, thermal agitation prevents them from remaining in this position.

Values of P_{K_0} (Equation 13S) are given in the last column. These agree approximately with values (not given) calculated from Equation 2.

TABLE IV

CALCULATION OF $P_{K_2} - P_{K_1}$ IN CIS AND TRANS ACIDS

1	2	3	4	5	6	7	8	9	10	11	12
	Equation	Found		(3)	Estimated			(10b)	(11S)	Found	(14S)
	Acid	P_{K_1}	P_{K_2}	"r"	r_d	r_m	$\frac{3.0}{r_d}$	$F\Delta$	$(P_{K_2} - P_{K_1})$		P_{K_0}
Cis	Maleic	1.92	6.30	0.8	6.0	0.9	0.50	1.67	4.44	4.38	3.89
Trans	Fumaric	3	4.6	3.0	6.5	3.5	.46	0.18	1.4	1.6	3.5
Cis	2,5-Anhydrosaccharic	1.98	4.94	1.3	7.0	1.2	.43	.83	2.69	2.96	3.11
	2,5-Anhydromucic	2.02	4.53	1.6	7.0	1.2	.43	.83	2.69	2.51	3.15
Trans	2,5-Anhydromanno-saccharic	2.81	3.80	7.9	7.5	4.0	.40	.06	1.12	0.99	3.17
	2,5-Anhydroidosaccharic	3.03	4.00	8.3	7.5	4.0	.40	.06	1.12	.97	3.39

Distances "r" r_d and r_m are in Ångström Units.

Let us now consider maleic acid (*cis*) and fumaric acid (*trans*) together with a group of isomeric *cis* and *trans* sugar acids (studied by Levene and Simms).[5] The "distances" calculated by Bjerrum's Formula 3 are given in Col. 5, Table IV. From structural models, based upon the chemical structure, we have estimated the values of r_d and r_m (Cols. 6 and 7) in the di-ions and mono-ions. From these distances, the values of $P_{K_1} - P_{K_1}$ in Col. 10 have been calculated by Equations 10b and 11S. These correspond very well with the experimental values in Col 11.

Still better proof of the validity of Equations 10 to 15 is found in the last column, in which isomeric *cis* and *trans* acids are found to have nearly the same intrinsic constants.

V. Molecular Dimensions.—In estimating the distances between parts of a molecule we may use the following values from Bragg[6] as giving

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[5] Levene and Simms, *J. Biol. Chem.*, **63**, 351 (1925).

[6] Bragg, *Phil. Mag.*, **40**, 169 (1920).

the diameters of the respective atoms (in Ångström units): C = 1.54; H = 0.60; O = 1.30.

We may assume that each atom is spherical; that the angle between any two valences in any element is about 109.5°; that adjacent atoms are free to rotate about the axis of a single bond (without work) and that a double bond is rigid.

Although these assumptions are not entirely justifiable, they give us a means for estimating the distances.

The distance r_d between ionized groups of like charge is the maximum distance compatible with the flexibility of the molecule and thermal agitation; while r_m is the minimum distance between the like charges in an ionized and an un-ionized group (see Fig. 1). We have taken $r_{m'}$ equal to $r_m - 0.30$, where 0.30 is the "radius" of the hydrogen ion. (This is somewhat arbitrary, since the "radius" does not necessarily have a constant value, and the difference between r_m and r_m' may not equal the radius.)

For a simple substance these distances may be estimated graphically. When there is a ring in the molecule, or when more than two groups are ionized, the various distances cannot be easily estimated except by use of a properly made structural model.[7] Such a model makes it possible to find the most probable shape of the molecule having certain positively charged or negatively charged groups, or both. The distances may then be measured.

VI. Trivalent Acids.—If $(HA^=)'$, $(HA^=)''$ and $(HA^=)'''$ represent the three types of di-ions produced by ionization of different pairs of groups in a trivalent acid, we may write for the first two steps in ionization:

$$K_1K_2 = \text{H}^2\,\frac{(HA^=)' + (HA^=)'' + (HA^=)'''}{H_3A} \tag{16}$$

Let $(HA^=)'$ be the concentration of the type of ion produced by ionizing Groups I and II (and not III); then the work will equal (see Equations 4 and 5)

$$W' = W_0^{\text{I}} + W_0^{\text{II}} + (\phi - \theta)^{\text{I II}} - \Delta^{\text{I III}} - \Delta^{\text{II III}} \tag{17}$$

where the roman numerals indicate the groups involved in each work term, Hence,

$$K_0^{\text{I}}K_0^{\text{II}}\cdot e^{\frac{\Delta^{\text{I III}} + \Delta^{\text{II III}} - (\phi - \theta)^{\text{I II}}}{RT}} = \text{H}^2\,\frac{(HA^=)'}{H_3A} \tag{18}$$

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[7] A structural model set is in use in this Laboratory, consisting of spherical mahogany balls (painted different colors for different elements) proportional to the above diameters, where 4 cm. represents 1 Ångström unit (10^{-8} cm.). They are held together by means of split brass pins (with a heavy coil spring at the center for ring compounds) which fit into brass lined holes in the balls. The holes are at an angle of 109.5° from each other for all elements. The number of holes equals the valence. Adjacent balls touch each other. Double bonded atoms are constructed specially.

Similarly for $(\mathrm{HA}^-)''$ and $(\mathrm{HA}^-)'''$; and we get Equation 20 (the second below). In a similar manner we derive (19) and (21):

$$K_1 = K_0^{\mathrm{I}} e^{\frac{\Delta^{\mathrm{I\,II}} + \Delta^{\mathrm{I\,III}}}{RT}} + K_0^{\mathrm{II}} e^{\frac{\Delta^{\mathrm{I\,II}} + \Delta^{\mathrm{II\,III}}}{RT}} + K_0^{\mathrm{III}} e^{\frac{\Delta^{\mathrm{I\,III}} + \Delta^{\mathrm{II\,III}}}{RT}} \tag{19}$$

$$K_1K_2 = K_0^{\mathrm{I}}K_0^{\mathrm{II}} e^{\frac{\Delta^{\mathrm{I\,III}} + \Delta^{\mathrm{II\,III}} - (\phi - \theta)^{\mathrm{I\,II}}}{RT}} + K_0^{\mathrm{I}}K_0^{\mathrm{III}} e^{\frac{\Delta^{\mathrm{I\,II}} + \Delta^{\mathrm{II\,III}} - (\phi - \theta)^{\mathrm{I\,III}}}{RT}} + K_0^{\mathrm{II}}K_0^{\mathrm{III}} e^{\frac{\Delta^{\mathrm{I\,II}} + \Delta^{\mathrm{I\,III}} - (\phi - \theta)^{\mathrm{II\,III}}}{RT}} \tag{20}$$

$$K_1K_2K_3 = K_0^{\mathrm{I}}K_0^{\mathrm{II}}K_0^{\mathrm{III}} e^{\frac{-(\phi - \theta)^{\mathrm{I\,II}} - (\phi - \theta)^{\mathrm{I\,III}} - (\phi - \theta)^{\mathrm{II\,III}}}{RT}} \tag{21}$$

K_2 equals Equation 20 divided by Equation 19 and K_3 equals Equation 21 divided by 20.

VII. Polyvalent Acids, Bases and Ampholytes.—In order to estimate the (uncorrected) dissociation constants[8] (K') for *any* polyvalent substance, we may write (as above)

$$K'_{n+1} = K_0^{\mathrm{I}}L^{\mathrm{I}}\left(\frac{f_0}{f_1}\right)^{\mathrm{I}} + K_0^{\mathrm{II}}L^{\mathrm{II}}\left(\frac{f_0}{f_1}\right)^{\mathrm{II}} + \text{etc.} \quad = \Sigma K_0L\left(\frac{f_0}{f_1}\right) \tag{22}$$

$$K'_{n+1}K'_{n+2} = K_0^{\mathrm{I}}K_0^{\mathrm{II}}L^{\mathrm{I\,II}}\left(\frac{f_0}{f_2}\right)^{\mathrm{I\,II}} + K_0^{\mathrm{I}}K_0^{\mathrm{III}}L^{\mathrm{I\,III}}\left(\frac{f_0}{f_2}\right)^{\mathrm{I\,III}} + \text{etc.} = \Sigma K_0K_0L\left(\frac{f_0}{f_2}\right) \tag{23}$$

$$K'_{n+1}K'_{n+2}K'_{n+3} = K_0^{\mathrm{I}}K_0^{\mathrm{II}}K_0^{\mathrm{III}}L^{\mathrm{I\,II\,III}}\left(\frac{f_0}{f_3}\right)^{\mathrm{I\,II\,III}} + K_0^{\mathrm{I}}K_0^{\mathrm{II}}K_0^{\mathrm{IV}}L^{\mathrm{I\,II\,IV}}\left(\frac{f_0}{f_3}\right)^{\mathrm{I\,II\,IV}} + \text{etc.} = \Sigma K_0K_0K_0L\left(\frac{f_0}{f_3}\right) \tag{24}$$

and so forth. Then, K'_{n+2} = Equation 23 divided by Equation 22; K'_{n+3} = Equation 24 divided by Equation 23, etc.

The subscript n refers to the number (known or unknown) of groups having values of K_0L too large to be considered. Only those groups are considered which have values of K_0L less than 1000 K_x and greater than 0.001 K_x, where K_x is the constant in question. For an acid in which all groups are considered, $n = 0$. The number of terms in each equation is equal to the number of possible combinations of the requisite number of K_0 constants.

The value of each L is such that

$$\log L = 3.0\left[\left(\Sigma\frac{1}{r_0} - \Sigma\frac{1}{r_L}\right)_B - \left(\Sigma\frac{1}{r_0} - \Sigma\frac{1}{r_L}\right)_A\right] \tag{25}$$

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[8] Up to this point in this article, we have discussed the K constants (corrected for activity) and the equations are applicable to very dilute solutions. In the Equations 22 to 24, involving the (uncorrected) K' constants, we have introduced the activity ratios $\left(\frac{f_0}{f_1}\right)$, $\left(\frac{f_0}{f_2}\right)$ and $\left(\frac{f_0}{f_3}\right)$ between the activities in the initial and final states, when one, two or three groups (designated by Roman numerals) have "dissociated." These may be neglected if the K constants are substituted for K' constants of polyvalent acids or bases—but not for ampholytes (except in very dilute solution; see previous article).

where A is the initial state (at a low P_H, where none of the acid groups under consideration have ionized and the basic groups have not hydrolyzed); and B is the final state (at a high P_H, where the indicated groups have ionized or hydrolyzed). $\Sigma(1/r_L)$ is the sum of all the reciprocal distances between *like charges*, while $\Sigma(1/r_0)$ is the sum of all reciprocal distances between *opposite charges*. This refers to *all* charges whether in ionized or non-ionized groups.

These distances must be estimated from the structural formula of the substance (as described in Section V).

When the initial state (A) is the neutral molecule (as in the case of a polyvalent acid, when $n = 0$) we may write

$$\log L = 3.0\left(\Sigma\frac{1}{r_0} - \Sigma\frac{1}{r_L}\right)_B \qquad (25a)$$

VIII. Summary of Constants.—The dissociation, the intrinsic and the titration constants, respectively, of *any* acid base or ampholyte are related as follows.

$$K'_{n+1} = \Sigma K_0 L\frac{f_0}{f_1} \qquad = \Sigma G' \qquad (26)$$

$$K'_{n+1}K'_{n+2} = \Sigma K_0 K_0 L\frac{f_0}{f_2} \qquad = \Sigma G'G' \qquad (27)$$

$$K'_{n+1}K'_{n+2}K'_{n+3} = \Sigma K_0 K_0 K_0 L\frac{f_0}{f_3} = \Sigma G'G'G' \qquad (28)$$

etc., where the intrinsic constant is related to the characteristic constant as follows.

$$P_{K_0} = P_e + \Sigma\,\frac{Y}{(2.7)^x} \qquad (2)$$

and the activity correction for acids (+), and bases(−) but not ampholytes, is approximately

$$P_K = P_K' \pm 0.30\sqrt{\Sigma iv^2} \qquad (29)$$

and

$$P_G = P_G' \pm 0.30\sqrt{\Sigma iv^2} \qquad (I, 31)$$

Summary

The dissociation constants of a polyvalent acid, base or ampholyte depend, first, upon the types of ionizable groups (Table I); second, upon the influence of all substituents (Equation 2 and Table II); and finally, upon the electrostatic forces between the ionizing groups.

These forces have been formulated (Equations 10–15) in terms of the distances between the like and unlike charges in the mono-ion (singly charged ion) and also in the di-ion (doubly charged ion) of a *divalent* acid. "Distortional" work plays a large role in some acids. By use of these formulas the distances (r_m) between the negative charges in the mono-ions of some divalent acids have been calculated (Table III). These formulas have also been used to calculate the values of $(P_{K_2} - P_{K_1})$ in certain *cis* and *trans* acids from distances estimated with structural models.

The agreement is close (Table IV). Isomeric *cis* and *trans* acids are shown to have nearly identical intrinsic constants.

Formulas 19 to 24 are given for calculating the dissociation constants of *higher* polyvalent acids, and of bases and ampholytes, where the intrinsic constants of the individual groups are known, and when the distances between the charges in the groups may be estimated. Formulas 26 to 29 summarize the relations between the "dissociation" $(K)_1$ the "intrinsic" (K_0), the "titration" (G) and the "characteristic"[1] (K_c) constants of a substance, and also give the activity correction.

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STUDIES ON THE SYSTEM CALCIUM OXIDE-FERRIC OXIDE-SILICA[1,2]

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Many of the oxide systems in which ferric oxide is one of the components are of especial interest to the Portland cement industry because all Portland cements contain iron oxide in some type of combination. The combinations in which this oxide occurs in cement, its precise role in the manufacturing, in the setting and in the hardening processes are not known.

Of the ferric oxide systems pertaining to Portland cement, the $CaO.Fe_2O_3$ system is the only one that has been studied extensively. This system was investigated by Sosman and Merwin.[4] Two compounds of calcium oxide and ferric oxide were found by these investigators having the compositions, respectively, $CaO.Fe_2O_3$ and $2CaO.Fe_2O_3$. It was found also that both compounds appear to melt incongruently, the first at 1216° and the latter at 1436°. Andersen[5] studied this system later and confirmed the work of Sosman and Merwin. More recently Martin[6] prepared these two compounds and studied their behavior with various reagents. In a later paper Martin[7] reports several other compounds of calcium oxide with ferric oxide. His criteria for the existence of these compounds, however, appear to be inadequate.

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] Paper No. 1 of the Portland Cement Association Fellowship at the Bureau of Standards.

[3] Microscopic examinations by F. W. Ashton.

[4] Sosman and Merwin, *J. Wash. Acad. Sci.*, **6**, 532 (1916).

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[6] Martin, 3me Congrès Chimie Industriel, **1924**, **406**.

[7] Martin, *Mon. sci.*, **15**, 97 (1925).