

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

THE ELECTRON-SHARING ABILITY OF ORGANIC RADICALS

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Ostwald¹ pointed out that certain elements or radicals, when substituents in organic acids, affected the dissociation constant in a uniform manner. Those elements, or radicals, which when substituted into acetic acid caused an increase in the dissociation constant, he called negative, and those which caused a decrease, positive. Wegscheider² summarizes the available data and puts them into a tabulated form from which it is possible to calculate the dissociation constant of various substituted acids. Many limitations to these generalizations, such as those of Bader³ and Hantzsch⁴ have been pointed out.

In 1901, Noyes and Lyon⁵ pointed out that if all reactions involving the decomposition of molecules are preceded by an ionization of the parts of the molecules, it would follow that elementary molecules as well must ionize into positive and negative parts. A few years later, Abegg⁶ stated that all elements are amphoteric, that is, exhibit both positive and negative electricity. We may interpret the generalizations of these pioneers to mean that the electron-sharing ability of any atom depends upon the strength of the other groups to which it is linked.

This generalization is involved in all of the recent theories⁷ which attempt to explain the distribution of affinity in the carbon compounds. All of these theories are qualitative in nature and the success of the manipulation depends upon reading into them a degree of stress or strain which can only be acquired by experience. The introductory statement used by Fry⁸ to one of his papers is especially significant. "The present series of papers is a further extension of the electronic principles of valence in an endeavor to interpret only a few of the many stereochemical problems now confronting us and concerning which Cohen tersely remarks: 'It must be confessed that we are still profoundly ignorant of the change which substituents effect in the character of the molecule as a whole, the causes which determine the rules of orientation—and a host of other phenomena of a similar nature.' "

¹ Ostwald, *J. prakt. Chem.*, **31**, 433 (1885); *Z. physik. Chem.*, **3**, 170, 418 (1889).

² Wegscheider, *Monatsh.*, **23**, 287 (1902).

³ Bader, *Z. physik. Chem.*, **6**, 295 (1890).

⁴ Hantzsch, *Ber.*, **32**, 3071 (1899).

⁵ Noyes and Lyon, *THIS JOURNAL*, **23**, 460 (1901).

⁶ Abegg, *Z. anorg. Chem.*, **39**, 330 (1904).

⁷ A general summary of these theories is given by Henrich, Johnson and Hahn in "Theories of Organic Chemistry," John Wiley and Sons, New York, 1922, pp. 75-168.

⁸ Fry, *THIS JOURNAL*, **36**, 248 (1914).

The confusion is due mostly to the lack of a quantitative measure of the "electron-sharing ability" of the various carbon radicals. Derick⁹ attempted to establish such a standard by means of the acidic and basic dissociation constants of the various hydroxides. We may use the following electronic explanation for Derick's reasoning. (a) In water, hydrogen and oxygen are balanced. There is an equal tendency for the formation of hydrogen and hydroxyl ions. (b) If one hydrogen is replaced by an element or radical R with a greater tendency than hydrogen to take on an electron, the compound tends to ionize into $RO^- + H^+$. Furthermore, the degree of the ionization would be a measure of the "negativity" of R. (c) If one hydrogen is replaced by an element or radical R with a greater tendency than hydrogen to give up an electron, the compound tends to ionize into $R^+ + OH^-$. Furthermore, the degree of this ionization would be a measure of the "positivity" of R. He then uses the following mathematical value for these terms. Positivity = $-1000/\log K_{\text{basic}}$; negativity = $-1000/\log K_{\text{acidic}}$. Ostwald had previously considered this standard but had rejected it in favor of the standard mentioned above, based on acetic acid, because the "non-ionization" of such a large group of compounds makes this standard impossible to apply experimentally. For this very reason, Derick's treatment of the subject is limited to the organic acids.

An Activity Series of Organic Radicals.—This difficulty which limits the applicability of Derick's work can easily be avoided by the following reasoning. If the electron theory of valence holds, then the polar properties of any series of compounds such as $R(OH)$, $R(COOH)$, $R(CH_2COOH)$, $R(CH_2CH_2COOH)$, RNH_2 , RSH , $RAso(OH)_2$, etc., must be a function of the "electron-sharing ability" of R if we exclude from consideration under R all groupings which themselves have polar linkages.

An examination of all of the values given in Landolt-Börnstein for the dissociation constants of the acids and amines makes possible the comparison shown in Table I for the dissociation constants of $R(NH_2.H_2O)$, $R(COOH)$, $R(CH_2COOH)$, $R(CH_2CH_2COOH)$ and ROH .

Representative values from Table I are plotted in Fig. 1 against an arbitrary abscissa designated as "electron-sharing ability of various radicals." In plotting these results, it was observed that the curves were exponential no matter what units were chosen for the x axis. Accordingly, an arbitrary curve $y = \log K^{10} = -20(e^{0.05x} - 0.75)$ was drawn and the dissociation constants for the various amines $R(NH_2.H_2O)$ were located on the curve, thereby fixing the position of R along the x axis. The corresponding values for the other derivatives of R were then located and a smooth

⁹ Derick, *THIS JOURNAL*, **33**, 1152, 1162, 1181 (1911); **34**, 74 (1912).

¹⁰ In Fig. 1 $y = \log K$. This value may be quickly approximated from the exponent given in Table I for the dissociation constant K .

TABLE I
DISSOCIATION CONSTANTS OF CORRESPONDING POLAR COMPOUNDS OF VARIOUS
RADICALS IN WATER AT 25°

Radical	Amine R.NH ₂ .H ₂ O	Acid R.COOH	Acid R.CH ₂ COOH	Acid R.CH ₂ .CH ₂ COOH	Hy- droxide ROH
(CH ₃) ₃ C—	3 × 10 ⁻⁴	1 × 10 ⁻⁵			
CH ₃ —	5 × 10 ⁻⁴	1 × 10 ⁻⁵	1 × 10 ⁻⁵	1 × 10 ⁻⁵	
CH ₃ CH ₂ —	5 × 10 ⁻⁴	1 × 10 ⁻⁵	1 × 10 ⁻⁵	1 × 10 ⁻⁵	10 ⁻¹⁵
CH ₃ CH ₂ CH ₂ —	5 × 10 ⁻⁴	1 × 10 ⁻⁵	1 × 10 ⁻⁵	1 × 10 ⁻⁵	
CH ₃ CH=CHCH ₂ —	4 × 10 ⁻⁴	5 × 10 ⁻⁵	3 × 10 ⁻⁵		
C ₆ H ₅ CH ₂ —	2 × 10 ⁻⁵	5 × 10 ⁻⁵	2 × 10 ⁻⁵		
CH ₂ =CH—	6 × 10 ⁻⁵	6 × 10 ⁻⁵	4 × 10 ⁻⁵	2 × 10 ⁻⁵	
H—	2 × 10 ⁻⁵	2 × 10 ⁻⁴	2 × 10 ⁻⁴	1 × 10 ⁻⁵	10 ⁻¹⁴
C ₆ H ₅ CH ₃ - <i>p</i>	2 × 10 ⁻⁹	5 × 10 ⁻⁵			
C ₆ H ₄ OCH ₃ - <i>p</i>	6 × 10 ⁻⁹	3 × 10 ⁻⁵			
C ₆ H ₄ CH ₃ - <i>m</i>	6 × 10 ⁻¹⁰	5 × 10 ⁻⁵			
C ₆ H ₄ OCH ₃ - <i>o</i>	2 × 10 ⁻¹⁰	8 × 10 ⁻⁵			
C ₆ H ₆ —	3 × 10 ⁻¹⁰	7 × 10 ⁻⁵	5 × 10 ⁻⁵	2 × 10 ⁻⁵	10 ⁻¹⁰
C ₆ H ₄ CH ₃ - <i>o</i>	3 × 10 ⁻¹⁰	1 × 10 ⁻⁴			
C ₆ H ₄ Br- <i>p</i>	2 × 10 ⁻¹⁰				
C ₆ H ₄ Cl- <i>p</i>	1 × 10 ⁻¹¹	9 × 10 ⁻⁵			10 ⁻¹⁰
C ₆ H ₄ Br- <i>m</i>	9 × 10 ⁻¹¹	1 × 10 ⁻⁴			
C ₁₀ H ₇ - <i>α</i>	9 × 10 ⁻¹¹	2 × 10 ⁻⁴			
C ₆ H ₄ Cl- <i>m</i>	6 × 10 ⁻¹²	2 × 10 ⁻⁴			
C ₆ H ₄ NO ₂ - <i>p</i>	1 × 10 ⁻¹²	4 × 10 ⁻⁴			10 ⁻⁸
C ₆ H ₄ NO ₂ - <i>m</i>	4 × 10 ⁻¹²	3 × 10 ⁻⁴			
H ₂ IC—		7 × 10 ⁻⁴	9 × 10 ⁻⁵	2 × 10 ⁻⁵	
C ₆ H ₄ Cl- <i>o</i>	9 × 10 ⁻¹³	1 × 10 ⁻³			10 ⁻⁹
CH ₃ CHCl—		2 × 10 ⁻³	9 × 10 ⁻⁵		
H ₂ CBr—		1 × 10 ⁻³	1 × 10 ⁻⁴	3 × 10 ⁻⁵	
H ₂ CCl—		1 × 10 ⁻³	9 × 10 ⁻⁵	3 × 10 ⁻⁵	
C ₆ H ₄ NO ₂ - <i>o</i>	1 × 10 ⁻¹⁴	6 × 10 ⁻³			
H ₂ C(NO ₂)—			2 × 10 ⁻⁴		
CH ₃ —C≡C—		3 × 10 ⁻³			
H ₂ C(CN)—		4 × 10 ⁻³			
C ₂ H ₅ OOC—			5 × 10 ⁻⁴	3 × 10 ⁻⁵	
HCCl ₂ —		5 × 10 ⁻²			
I—			8 × 10 ⁻⁴	9 × 10 ⁻⁵	
Br—			1 × 10 ⁻³	1 × 10 ⁻⁴	
Cl—			1 × 10 ⁻³	9 × 10 ⁻⁵	10 ⁻⁸
CN—			4 × 10 ⁻³		
NO ₂ —				2 × 10 ⁻⁴	

curve was drawn through them. It was found that the following mathematical expressions held for the dissociation constants of the various polar compounds listed.

$$R(\text{NH}_2 \cdot \text{H}_2\text{O}), y = \log K_b = -20(e^{0.05x} - 0.75) \quad (1)$$

$$R(\text{COOH}), y = \log K_a = 20(e^{0.5x-5.6} - 0.24) \quad (2)$$

$$R(\text{CH}_2\text{COOH}), y = \log K_a = 20(e^{0.5x-6.6} - 0.24) \quad (3)$$

$$R(\text{CH}_2\text{CH}_2\text{COOH}), y = \log K_a = 20(e^{0.5x-7.6} - 0.24) \quad (4)$$

Since the slope of the ROH curve is questionable, no equation has been derived.

For any reaction in which we start with the reactants at unit concentration and finish with the resultants at unit concentration, the thermodynamic expression $-\Delta F = RT \ln K$ or $-\Delta F = 2.3 RT \log K$ holds for the relationship between the "free-energy change" and the equilibrium constant. The application of this expression¹¹ to the present data will be as precise as the Ostwald dilution law. It would follow that the free energy of ionization of any polar derivative of the series of radicals

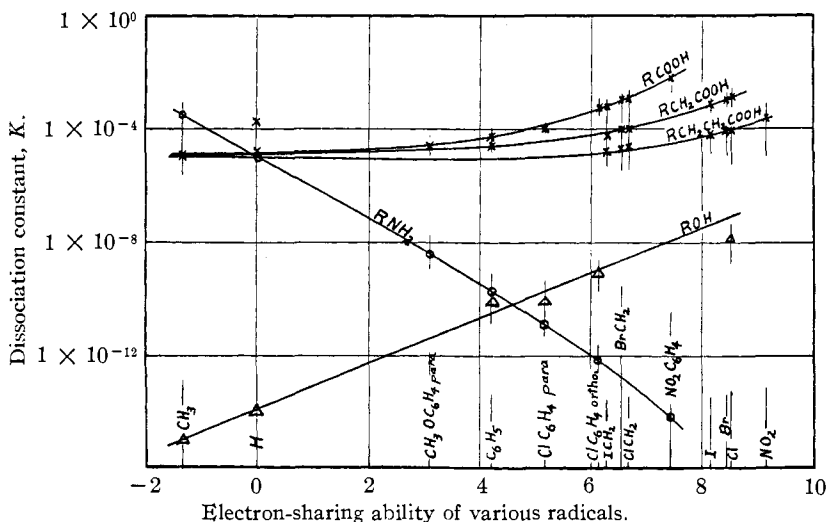


Fig. 1.—Relation between the dissociation constants of different polar derivatives of various radicals.

R could be expressed as a function of the electron-sharing ability x ; for example,

$$R-(\text{NH}_2, \text{H}_2\text{O}), -\Delta F = -46 RT(e^{0.05x} - 0.75) \quad (5)$$

$$R(\text{COOH}), -\Delta F = 46 RT(e^{0.5x-5.6} - 0.24) \quad (6)$$

$$R(\text{CH}_2\text{COOH}), -\Delta F = 46 RT(e^{0.5x-6.6} - 0.24) \quad (7)$$

$$R(\text{CH}_2\text{CH}_2\text{COOH}), -\Delta F = 46 RT(e^{0.5x-7.6} - 0.24) \quad (8)$$

For each series this may be put into the general form

$$-\Delta F = k RT(e^{ax-b} - c) \quad (9)$$

from which may be derived the expression for x

$$x = \frac{1}{a} \ln \left(c - \frac{\Delta F}{kRT} \right) + \frac{b}{a} \quad (10)$$

The free-energy change represents the work required to separate by means of the hypothetical equilibrium box, one mole of the undissociated acid

¹¹ Acknowledgment is made to Professor Anson Hayes for suggesting this method of treating the "free-energy change."

or base into the normal solutions of the two respective ions. If this is expressed in electrical units, the number of faradays, nF , per mole will be unity in all of the above cases and the potential E only will vary. Equations 9 and 10 could then be written

$$E = \frac{kRT}{nF} (e^{ax-b} - c) \quad (11)$$

$$x = \frac{1}{a} \ln \left(c - \frac{EnF}{kRT} \right) + \frac{b}{a} \quad (12)$$

where E represents the potential of the ions of the normal acid or base and is the only variable in each series, the temperature being kept constant. It will be seen that E is an exponential function of the electron-sharing ability of the substituent group R . The term "electron-sharing ability" receives a mathematical expression but its mechanical significance is not clear. It is also apparent that the free energy of ionization, or the ionic potential of a member of any series can be calculated from the corresponding member of any of the other series; that is, combining Equations 5 and 6

$$\frac{-\Delta F_{\text{acid}}}{\Delta F_{\text{base}}} = \frac{E_{\text{acid}}}{-E_{\text{base}}} = \frac{e^{0.5x-5.6} - 0.24}{e^{0.05x} - 0.75} \quad (13)$$

The Effect of Intervening CH_2 Units upon the Properties of Polar Groups.—Derick has stated a "rule of thirds" for the relationship of the dissociation constants of the acids substituted in α , β , γ , δ positions. This generalization holds very well for the acids substituted by the strongly negative groups but does not hold for the less negative substituents.

TABLE II

OBSERVED AND CALCULATED VALUES FOR $-\text{LOG } K$ OF SUBSTITUTED ACIDS WHEN VARIOUS SUBSTITUENTS "R" ARE REMOVED UNIFORM DISTANCES FROM THE CARBOXYL GROUP

The distance is measured by the number of intervening CH_2 units

Interven- ing CH_2 units = z	R = (Cl)		R = (Br)		R = (I)		R = (CH_2Cl)		R = (CH_2Br)		R = (CH_2I)		
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	
RCOOH	0	(0.4) ^a	0.21	(0.5) ^a	0.21	(1.0) ^a	0.80	2.81	2.85	2.86	2.85	3.12	3.12
RCH_2COOH	1	2.81	2.85	2.86	2.85	3.12	3.12	4.07	4.03	4.01	4.03	4.05	4.16
$\text{R}(\text{CH}_2)_2\text{COOH}$	2	4.07	4.03	4.01	4.03	4.05	4.16	4.52	4.57	4.58	4.57	4.64	4.62
$\text{R}(\text{CH}_2)_3\text{COOH}$	3	4.52	4.57	4.58	4.57	4.64	4.62	4.70	4.80	4.72	4.80	4.77	4.82
$\text{R}(\text{CH}_2)_4\text{COOH}$	4	4.70	4.80	4.72	4.80	4.78	4.82						
$\text{R}(\text{CH}_2)_5\text{COOH}$	6												
$\text{R}(\text{CH}_2)_6\text{COOH}$	8		5.00		5.00		5.00		5.00		5.00		5.00

		R = ($\text{C}_2\text{H}_5\text{OOC}-$)		R = (C_6H_5)		R = ($\text{CH}_2=\text{CH}$)		R = (CH_3)		R = (H)	
		Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
RCOOH	0	(1.70) ^a	1.80	4.16	4.10	4.25	4.23	4.73	4.80	3.67	3.52
$\text{R}(\text{CH}_2)\text{COOH}$	1	3.35	3.56	4.28	4.46	4.42	4.50	4.84	4.82	4.73	4.70
$\text{R}(\text{CH}_2)_2\text{COOH}$	2	4.52	4.36	4.64	4.66	4.68	4.66	4.81	4.84	4.84	4.94
$\text{R}(\text{CH}_2)_3\text{COOH}$	3							4.80	4.85	4.81	4.95
$\text{R}(\text{CH}_2)_4\text{COOH}$	4							4.84	4.86	4.80	4.97
$\text{R}(\text{CH}_2)_5\text{COOH}$	6	4.84	4.96					4.84	4.88	4.84	4.98
$\text{R}(\text{CH}_2)_6\text{COOH}$	8	4.85	5.00		5.00		5.00	4.95	4.92	4.84	5.00

^a This value is extrapolated from the curves in Fig. 1.

The more general exponential Equation 9 fits all cases for which data are at present available.

Table II presents the measured and calculated values for $-\log K$ when various substituents "R" are removed uniform distances¹² from the carboxyl group, the distance being measured by the number of intervening CH_2 units.

Designating the number of intervening CH_2 units by z , the formulas used for the calculated values in Table II are as follows.

For	$\log K =$	For	$\log K =$
Cl	$20(e^{-0.8z-1.43} - 0.25)$	CH_2I	$20(e^{-0.8z-2.36} - 0.25)$
Br	$20(e^{-0.8z-1.43} - 0.25)$	$\text{C}_2\text{H}_5\text{OOC}$	$20(e^{-0.8z-1.83} - 0.25)$
I	$20(e^{-0.8z-1.56} - 0.25)$	C_6H_5	$20(e^{-0.5z-3.1} - 0.25)$
CH_2Cl	$20(e^{-0.8z-2.23} - 0.25)$	$\text{CH}_2=\text{CH}$	$20(e^{-0.4z-3.3} - 0.25)$
CH_2Br	$20(e^{-0.8z-2.23} - 0.25)$	CH_3	$20(e^{-z-4.6} - 0.25)$
		H	$20(e^{-1.6-2.6} - 0.25)$

These equations are of the same general form as Equations 1, 2, 3 and 4 and there would be the same general relationships between free energy of ionization and z as that expressed in Equation 10 for x

$$z = \frac{1}{a} \ln \left(c - \frac{\Delta F}{kRT} \right) + \frac{b}{a} \quad (14)$$

The equations developed can be combined to give a three-dimensional figure as shown in Fig. 2. The model for this photograph was constructed

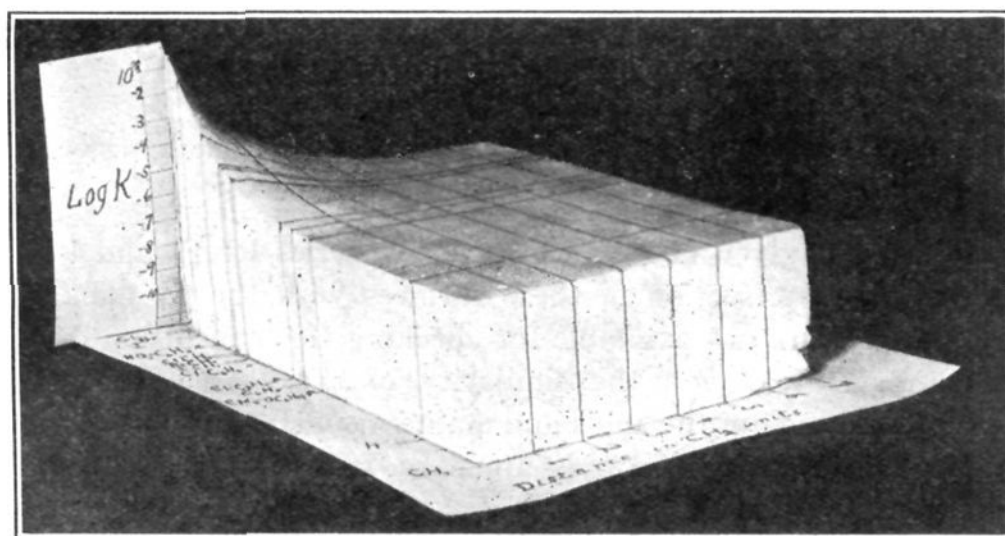


Fig. 2.—The systematic change in the dissociation constant of the acids as the substituting radical is moved varying distances, measured by number of intervening CH_2 units, from the carboxyl group.

to scale from the equations already given; the location of the substituents R along the x -axis is the same as that in Fig. 1 and in fact the curve in the

¹² See discussion regarding this treatment under the heading, Surface Tension as a Measure of Polarity.

$x\gamma$ plane and the two succeeding curves are the same as those shown in Fig. 1 for the relationship between the dissociation constants of RCOOH , RCH_2COOH and $\text{RCH}_2\text{CH}_2\text{COOH}$. The only outstanding abnormality found so far is that of formic acid or the point where $\text{R} = \text{H}$. From the comparison between the homologous series of alkyl acids and amines given below, this would appear to be the characteristic "abnormality of the first member of the series." This is treated later.

From the mathematical relationship previously pointed out for the dissociation constants of the acids and amines, it would be expected that a plane similar to that shown in Fig. 2 for the dissociation constants of the acids could also be constructed for the corresponding amines.

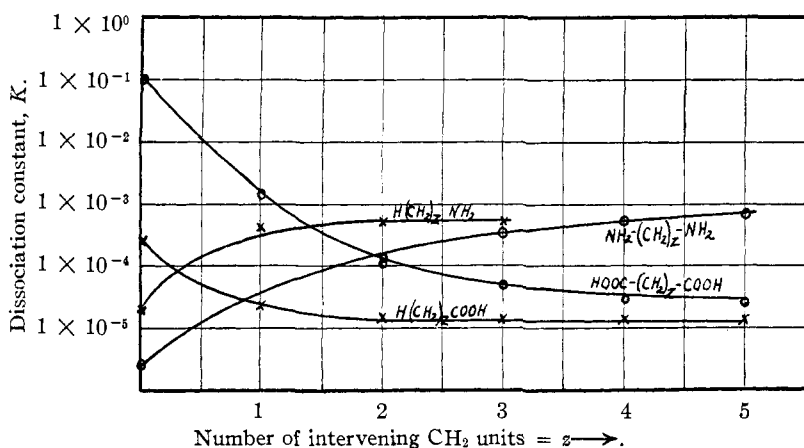


Fig. 3.—The similarity of the effect of intervening CH_2 units on the dissociation constants of corresponding acids and amines.

In fact the curves given in Fig. 1 for the two series RNH_2 and RCOOH would show the intersection of these surfaces with the $x\gamma$ plane. Unfortunately, data are not available for checking this conclusion over any extended range. However, the similarity of the change between the dissociation constants of the acids and amines as CH_2 units are interposed between R and the polar group is apparent from a comparison of the following pairs of equations for $\log K$ of

- (a) the alkyl amines $\text{H}(\text{CH}_2)_z\text{NH}_2$ $\log K = -20(e^{-1.6z-2.57} + 0.16)$
 the alkyl acids $\text{H}(\text{CH}_2)_z\text{COOH}$ $\log K = 20(e^{-1.6z-2.6} - 0.25)$
 (b) the alkyl diamines $\text{H}_2\text{N}(\text{CH}_2)_z\text{NH}_2$ $\log K = -20(e^{0.6z-2.05} + 0.15)$
 the alkyl diacids $\text{HOOC}(\text{CH}_2)_z\text{COOH}$ $\log K = 20(e^{0.6z-1.61} - 0.25)$

The similarity is more clearly seen by comparing the two pairs of curves in Fig. 3 for these equations. The agreement between the measured and calculated values is given in Table III for all except the alkyl acids, which were given in Table II.

TABLE III

Number of intervening CH ₂ units = <i>z</i>	Alkyl amines H(CH ₂) _z NH ₂		Alkyl diamines H ₂ N(CH ₂) _z NH ₂		Alkyl diacids HOOC(CH ₂) _z COOH	
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
0	4.73	4.72	5.52	5.58	1.00	1.00
1	3.30	3.50		4.42	2.80	2.79
2	3.25	3.26	4.07	3.98	3.80	3.80
3	3.33	3.22	3.46	3.42	4.34	4.33
4		3.20	3.29	3.24	4.64	4.43
5		3.20	3.14	3.14	4.85	4.50

A limited number of values are also available for testing this relationship by means of the dissociation constants of the corresponding substituted benzoic acids and anilines. The previous data, Table I, have

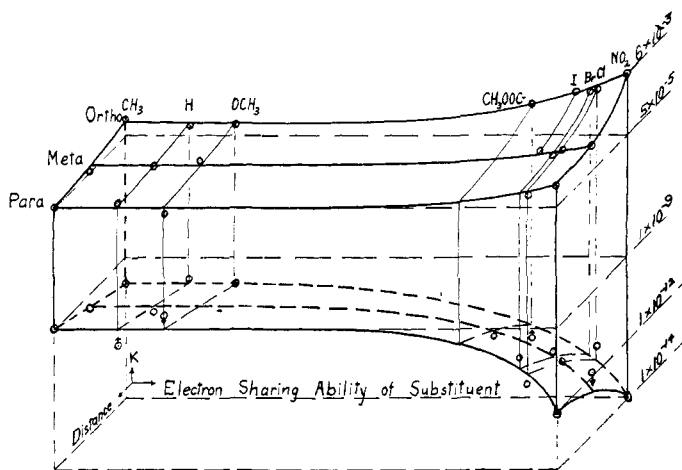


Fig. 4.—The relationships of the dissociation constants of correspondingly substituted benzoic acids and anilines.

treated the *ortho*, *meta*- and *para*-substituted phenyl derivatives merely by their individual electron-sharing ability. These values are grouped

TABLE IV

EFFECT OF POSITION OF VARIOUS RADICALS UPON THE DISSOCIATION CONSTANT OF SUBSTITUTED BENZOIC ACID AND ANILINE

Radical	Position of radical in—					
	Benzoic acid ring			Aniline ring		
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
CH ₃ —	1 × 10 ⁻⁴	5 × 10 ⁻⁵	5 × 10 ⁻⁵	3 × 10 ⁻¹⁰	6 × 10 ⁻¹⁰	2 × 10 ⁻⁹
H—	7 × 10 ⁻⁵	7 × 10 ⁻⁵	7 × 10 ⁻⁵	4 × 10 ⁻¹⁰	4 × 10 ⁻¹⁰	4 × 10 ⁻¹⁰
CH ₃ O—	8 × 10 ⁻⁵	9 × 10 ⁻⁵	3 × 10 ⁻⁵	2 × 10 ⁻¹⁰		6 × 10 ⁻⁹
CH ₃ OOC—	6 × 10 ⁻⁴			1 × 10 ⁻¹²	5 × 10 ⁻¹¹	3 × 10 ⁻¹²
I—	1 × 10 ⁻³	2 × 10 ⁻⁴				
Br—	1 × 10 ⁻³	1 × 10 ⁻⁴			9 × 10 ⁻¹¹	2 × 10 ⁻¹⁰
Cl—	1 × 10 ⁻³	2 × 10 ⁻⁴	9 × 10 ⁻⁵	9 × 10 ⁻¹³	6 × 10 ⁻¹²	1 × 10 ⁻¹¹
NO ₂ —	6 × 10 ⁻³	3 × 10 ⁻⁴	4 × 10 ⁻⁴	1 × 10 ⁻¹⁴	4 × 10 ⁻¹²	1 × 10 ⁻¹²

together in Table IV for comparison of effect of relative position. A perspective drawing is shown in Fig. 4, the substituting groups being spaced as to their electron-sharing ability on the same scale as in Figs. 1 and 2. The *ortho*, *meta* and *para* positions are plotted along the *z*-axis as of equal distance from the polar group, for the lack of any other standard. In spite of the rather large experimental error involved in the determination of these values, the only outstanding discrepancy is the value for the *p*-methylcarboxylic-substituted aniline.

Surface Tension as a Measure of Polarity.—The work of Langmuir¹³ regarding the structure of adsorbed films on the surface of liquids supports the generalizations advanced in this paper. After showing that the polar group causes orientation of the molecule in the surface film formed by an insoluble body on water, he calculated from Traube's data for the surface tensions of aqueous solutions of organic compounds, the loss in potential energy λ , when a gram molecule of the solute passes from the interior to the surface of the solution. Quoting from Langmuir, ". . . λ can be expressed in general by an equation of the form $\lambda_{\text{cal.}} = \lambda_0 + 625 n$, where n is the number of carbon atoms in the molecule. The quantity λ_0 has a different value for each type of substance as is shown in Table V."

TABLE V

VALUES OF λ_0 GIVEN BY LANGMUIR

Type	Formula	λ_0	Type	Formula	λ_0
Tertiary alcohol	R ₃ COH	950	Ketone	RCOR'	295
Primary amine	RCH ₂ NH ₂	600	Aldehyde	RCHO	210
Primary alcohol	RCH ₂ OH	575	Amide	RCONH ₂	-510
Ester	RCOOR'	470	Dibasic acid (or alcohol)	..	-700
Monobasic acid	RCOOH	437			

In other words, the change for each intervening CH₂ unit is a constant, namely 625 calories, or all CH₂ units are equivalent. This would be the justification for treating the intervening CH₂ units as a measure of distance, as was done in Fig. 2.

A strict interpretation of Langmuir's equation implies that if λ were obtained for a number of radicals and plotted against intervening CH₂ units, as was done in Fig. 2 for the dissociation constants of the acids, a series of parallel planes would be obtained for all polar groups. It should be pointed out that the data available to Langmuir were limited almost entirely to the aliphatic compounds or, referring to Fig. 2, to that field in which there is little change in the potential of the polar group as CH₂ units are interposed between it and the radical R. If the orientation of the molecule is a function of the polar group, as Langmuir's work indicates, $\Delta\lambda$ for any homologous series would not be a constant unless the potential of this group remained unchanged as CH₂ units were inter-

¹³ Langmuir, THIS JOURNAL, 39, 1848 (1917).

posed. In Langmuir's data, there are only two series in which this can be checked, but both of these substantiate this modification of Langmuir's equation (see Table VI).

TABLE VI

COMPARISON OF THE POLARITY OF THE CARBOXYL GROUP AS MEASURED BY THE DISSOCIATION CONSTANT, AND THE EQUIVALENCE OF ALL CH₂ UNITS AS INDICATED BY LANGMUIR'S SURFACE-TENSION STUDY

Substance	Intervening CH ₂ units	-Log K	Obs.	Δλ ^a
HCOOH	0	3.67	1078	632
HCH ₂ COOH	1	4.73	1710	
H(CH ₂) ₂ COOH	2	4.83	2290	580
H(CH ₂) ₃ COOH	3	4.80	2910	
HOCCOOH	0	1.00	516	764
HOOC(CH ₂)COOH	1	2.78	1280	
HOOC(CH ₂) ₂ COOH	2	4.17	1510	230

^a This should be a constant equal to 625 calories, according to Langmuir's equation.

If this limitation of Langmuir's generalization is found to hold over an extended range, it should offer an experimental means of explaining the discrepancies of the first member of each homologous series. It should be pointed out, that our present theories of valence imply that affinity is a function of potential and structure only, the quantity factor entering only as multiple units. The application of any form of electrostatics indicates that such would not be the case and offers the best explanation for these "exceptions."

Summary

It is pointed out that if the electron theory of valence holds, the properties of any polar group must be a function of the "electron-sharing ability" of the radical or element to which it is linked. The available data are collected and the mathematical relationship is pointed out between the dissociation constants and free energy of ionization of the series R.(NH₂), R.(COOH), R.(CH₂COOH), R.(CH₂CH₂COOH) and R.(OH). It is also pointed out that an exponential equation of the same general form holds for the change in the dissociation constant as intervening CH₂ units are introduced. Theories of structure have been intentionally avoided since the mathematical relationships will hold, independent of the mechanical interpretations which may be advanced in explanation of them.

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