objections have been shown to be based on misunderstandings and his criticism to be without relevance; further, that his scale is fundamentally wrong and that the conclusions he has drawn from its application have no real bearing on the subject.

The "scale of combined influence" when applied to explain the relations between structure and configuration of organic acids and their ionization constants offers a plausible explanation for quite a number of facts, which from other points of view appear anomalous. But, when we attempt to apply it systematically to all the observed data in this field we are inevitably led to the conclusion that there are unconsidered and unknown factors entering into the determination of the values. One of these factors is, besides the chemical nature and the position of the atom,[1] its content in free *chemical* energy. The enormous increase in the constant, when we pass from maleic to acetylenedicarboxylic acid, whose value is comparable with that of the strongest mineral acids,[2] certainly cannot be due alone to the removal of two hydrogens even though they are in the sixth position to the carboxyl hydrogens; but also, in a large measure, to the great increase in the free *chemical* energy of the unsaturated carbons, which are in the fifth position. Probably for the same reason, an increase in the ionization constants takes place in passing from $\Delta^{\alpha,\beta}$- to $\Delta^{\beta,\gamma}$-acids,[3] where, in the first group, the unsaturated carbons are in the fourth and fifth, while, in the second, they are in the fifth and sixth positions, towards the carboxyl hydrogens; and, that cyan- and thiocyanacetic acids possess larger ionization constants than chloracetic acid.

SALT SOLUTIONS AND THE LAW OF MASS ACTION.

By F. H. MacDougall.

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The fact that Ostwald's dilution formula does not hold for aqueous solutions of salts, strong acids and strong bases has been a disturbing feature in our theory of solutions and an incentive to further investiga-

atom in the molecule, but any one acquainted with the literature on this subject knows that this conclusion is due to Ostwald, who also showed that in many cases there is a good agreement between the calculated and found values of ionization constants. This line of work was subsequently successfully pursued by Bethmann (*Z. physik. Chem.*, **5**, 385), Holleman and de Bruyn (*Rec. trav. chim.*, **20**, 360) and particularly by Wegscheider (*Monatsh.*, **23**, 287; **26**, 1265), whose papers Derick fails to mention. It is open to question whether the use of values representing the free energy of ionization, instead of those of ionization constants, is at present of much importance as what is now most urgent in this field is not a restatement of explanations in other terms, but a clearer insight into why so many facts elude a consistent theoretical treatment.

[1] Ostwald, *Z. physik. Chem.*, **3**, 415.

[2] Ostwald, *Ibid.*, **3**, 382.

[3] Fichter and Pfister, *Ann.*, **348**, 257 (1906).

tion. Various expressions, such as those of Rudolphi, van't Hoff and others have been put forward as empirical formulas connecting the concentrations of the non-ionized and ionized molecules. All these expressions are at best useful only for the purposes of interpolation and lack a theoretical basis.

The cause of this deviation of strong electrolytes from the behavior exhibited by weak acids and bases has been sought in many directions. The chief difference between the two classes of solutions lies evidently in the magnitude of the ionic concentration. The good results obtained by A. A. Noyes and his co-workers making use of the assumption that the degree of ionization of a salt is determined by the total ionic concentration serve to show the importance of this factor.

Any theory of solution which claims to be satisfactory must be able to take account of strong as well as weak electrolytes and must be able to include both in one general scheme. It appeared to the author that Ostwald's formula should be looked on as a limiting one and that a formula for both classes might be found which would be equivalent to Ostwald's when the total ionic concentration is small. The author accordingly proposes the following expression: $K = c\gamma^2/(1-\gamma)[1 + m(c\gamma)^n]$ where K is the dissociation constant, c the molar concentration of the solution, γ the fraction ionized and m and n constants. It is clear that this expression would approximate to the following when $c\gamma$ is small: $K = c\gamma^2/1-\gamma$ and this is Ostwald's formula for weak electrolytes.

The author does not claim to have a sure theoretical basis for the function he proposes. He was led to it by considerations of the following nature: He assumed that the activity of the ions is strictly proportional to their concentration, that therefore the abnormal results obtained are due to the fact that the activity of the non-ionized molecules does not follow this law when the ionic concentration is considerable. Since the expression $(c\gamma)^2/c(1-\gamma)$ increases rapidly with the concentration, it can be inferred that the activity of the non-ionized molecules increases with the concentration. The problem was to find a suitable expression for these relations. In the case of weak electrolytes, each undissociated molecule is surrounded mainly by uncharged molecules; the medium is not very different, we may suppose, in its effect on the molecules from pure water. On the other hand, in solutions of strong electrolytes, even when quite dilute, the undissociated molecules are surrounded by a considerable number of charged bodies. The writer's working hypothesis is that the electric field in some way increases the speed at which the molecules dissociate, so that if the activity of the non-ionized molecules in pure water be represented as proportional to $c(1-\gamma)$, the activity in a solution might be $c(1-\gamma)[1 + m(c\gamma)^n]$. On applying this formula to several salts, values of n varying between 0.56 and 0.65 were obtained. An interpretation for $n = {}^2/_3$ would be that the effect of the ionic concentration on the speed of ionization is inversely proportional to the square of the average distance between an undissociated molecule and the nearest charged particles. Thus if for the moment we let $c\gamma$ mean the number of ions in 1 cc., there would be 1 ion in the cube $1/c\gamma$ and the distance between the centers of neighboring cubes would be $(1/c\gamma)^{1/3}$. Now if we distribute the non-ionized molecule uniformly throughout the solution in the place of an equal number of ions (which in dilute solution would not appreciably affect the number of the latter) the average distance from a non-ionized molecule to the nearest ion would be $(1/c\gamma)^{1/3}$. The quantity $(c\gamma)^{2/3}$ would then be inversely proportional to the square of the said distance.

Before discussing the application of the proposed formula to particular electrolytes, the writer would like to emphasize some well known facts. The values obtained for γ from the equation $\gamma = \Lambda_c/\Lambda_0$ are subject to various errors. One is caused by the change in viscosity of the medium with the concentration. This effect can be taken into account. The possible change in the mobilities of the ions with change in concentration due to different degrees of hydration has not yet become subject to accurate measurement. From these considerations it will be evident that the value of the function $c\gamma^2/(1-\gamma)$ may be appreciably in error, especially when γ approaches unity.

Since the function I propose has three unknowns, K, m and n, assuming c and γ to be given, their values can be determined from three independent equations. In the following let c_1, c_2, c_3, and γ_1, γ_2, γ_3 be corresponding values of the concentration and of the fraction ionized. Let f stand for the expression $c\gamma^2/(1-\gamma)$.

Then we have the following equations:

$$\mathrm{K} = f_1/[1 + m(c_1\gamma_1)^n] = f_2/[1 + m(c_2\gamma_2)^n] = f_3/[1 + m(c_3\gamma_3)^n].$$

From this we deduce, for example, $m[f_3(c_1\gamma_1)^n - f_1(c_3\gamma_3)^n] = f_1 - f_3$ and

$$\frac{f_3(c_1\gamma_1)^n - f_1(c_3\gamma_3)^n}{f_3(c_2\gamma_2)^n - f_2(c_3\gamma_3)^n} = \frac{f_1 - f_3}{f_2 - f_3}$$

or simplified,

$$\frac{(c_1\gamma_1/c_3\gamma_3)^n - f_1/f_3}{(c_2\gamma_2/c_3\gamma_3)^n - f_2/f_3} = \frac{f_1 - f_3}{f_2 - f_3}.$$

From the last equation n can be found by a rather laborious process of trial.

In Table I are given the results obtained on applying my formula to potassium chloride at 0° using data presented by Washburn and MacInnes[1] in a recent number of THIS JOURNAL. These authors adopted the expression $\gamma = \Lambda_c/\Lambda_0(\eta_c/\eta_0)^{.90}$ as defining the fraction ionized. The

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[1] THIS JOURNAL, 33, 1700 (1911).

values thus obtained differ little from those calculated from the simpler expression $\gamma = \Lambda_c\eta_c/\Lambda_o\eta_o$. In these formulas η_c is the viscosity of the solution of concentration c. The value of n was determined by the writer using the data corresponding to the concentrations 0.02498, 0.04994 and 0.09975 and was found to be 0.651. The corresponding value of m is 34.17. In the same table are found the results obtained assuming n to be equal to $^2/_3$ and calculating m by the method of least squares from the data corresponding to the five concentrations from 0.02498–0.1990. The value of m thus obtained is 31.20. The bracketed values in the fifth column are identical because the data corresponding to them were used in determining the values of n and m. An examination of the values in the fifth and sixth columns shows a satisfactory constancy in the values of K within each column even up to the high concentration 0.9745. This is especially noteworthy as only the data from the five lowest concentrations were used in calculating m and n. It might be stated that there could be a considerable variation in the value adopted for m without affecting very much the constancy of the values found for K. Similar results could no doubt be obtained with all the other alkali halides. I might add here that on applying the formula to the conductivity data for potassium chloride at 18° without correcting for viscosity, the value of n is calculated to be 0.590 and that of m, 302.2. This seems to show that the calculated value of n approaches 0.667 when more nearly correct values of γ are used.

TABLE I.—APPLICATION OF FORMULA TO POTASSIUM CHLORIDE.

c.	Λ_c/Λ_o.	$\gamma = \frac{\Lambda_c}{\Lambda_o}\left(\frac{\eta_c}{\eta_o}\right)^{.90}$.	$\frac{c\gamma^2}{1-\gamma}$.	$K = \frac{c\gamma^2}{(1-\gamma)[1+34.17(c\gamma)^{0.651}]}$.	$K = \frac{c\gamma^2}{(1-\gamma)[1+31.20(c\gamma)^{2/3}]}$.
0.02498	0.9326	0.9313	0.3154	(0.07986)	0.0890
0.04994	0.9096	0.9073	0.4435	(0.07986)	0.0893
0.07486	0.8947	0.8915	0.5484	0.0799	0.0894
0.09975	0.8837	0.8793	0.6390	(0.07986)	0.0893
0.1990	0.8581	0.8477	0.9389	0.0801	0.0892
0.2977	0.8473	0.8275	1.1845	0.0816	0.0906
0.3960	0.8385	0.8119	1.3877	0.0801	0.0887
0.4936	0.8312	0.7990	1.5677	0.0798	0.0882
0.5906	0.8267	0.7905	1.7625	0.0808	0.0891
0.7837	0.8176	0.7733	2.0673	0.0806	0.0886
0.974	0.8087	0.7569	2.2965	0.0791	0.0868

TABLE II.—APPLICATION TO POTASSIUM NITRATE.

c.	$\gamma = \frac{\Lambda c}{\Lambda_0}$.	$\frac{c\gamma^2}{1-\gamma}$.	$K = \frac{c\gamma^2}{(1-\gamma)[1+155.5(c\gamma)^{0.563}]}$.
1.0	0.6363	1.015	0.0084
0.5	0.7057	0.8462	97
0.2	0.7809	0.5566	100
0.1	0.8287	0.4009	102
0.05	0.8688	0.2877	104
0.02	0.9111	0.1868	108
0.01	0.9303	0.1242	102
0.005	0.9527	0.09595	111
0.002	0.9697	0.06205	110
0.001	0.9779	0.04228	102

TABLE III.—APPLICATION TO COPPER SULFATE.

c.	$\gamma = \frac{\mu c}{\mu_0}$.	$\frac{c\gamma^2}{1-\gamma}$.	$K = \frac{c\gamma^2}{(1-\gamma)[1+68.53(c\gamma)^{0.615}]}$.	$K = \frac{c\gamma^2}{(1-\gamma)[1+64.2(c\gamma)^{2/3}]}$.
0.5	0.2287	0.03239	0.00170	0.00202
0.1	0.3266	0.01585	169	210
0.05	0.3803	0.01167	167	209
0.025	0.4437	0.008848	167	211
0.010	0.5412	0.006380	169	214
0.005	0.6222	0.005125	173	216
0.0025	0.7023	0.004143	174	214
0.0010	0.7974	0.003139	170	202

In Table II are the results obtained by applying the formula to potassium nitrate using data from LeBlanc's "Elektrochemie," 4th edition, pp. 80 and 84. Any formula holding for potassium nitrate should give good results with sodium nitrate and silver nitrate. In the case of potassium nitrate, the calculated value of n is 0.563 and that of m is 155.5. The values of m and n were calculated from the values of γ at the three concentrations 0.1, 0.01 and 0.001. The values of K are fairly constant throughout this range.

The formula was also applied to a bivalent salt, copper sulfate. The results are given in Table III. The concentration is expressed in moles per liter. The values of n and m calculated from data corresponding to the concentrations 0.1, 0.01 and 0.001 are, respectively, 0.615 and 68.53. Assuming n to be equal to $^2/_3$, the value of m is 64.2. In the last two columns of Table III are found the corresponding values of K.

Summary.

1. The abnormal behavior of strong electrolytes is supposed to be due to the effect of the electric charges of the ions in increasing the rate of ionization of the undissociated molecules.

2. This effect is supposed to be proportional to some power of the total ionic concentration. The following function is deduced taking this into account: $K = c\gamma^2/(1-\gamma)[1 + m(c\gamma)^n]$.

3. This formula has been applied to aqueous solutions of potassium chloride, potassium nitrate, and copper sulfate.
4. The value of n seems to approach $^2/_3$.

NOTE.—The manuscript of the above article was read by Dr. W. C. Bray. He has informed me that he and Dr. Kraus have obtained the same formula and that their results were presented at the Washington meeting of the Society and published in *Science*, **35**, 433 (1912). I might mention that the formula occurred to me in August, 1911, but its publication was delayed by various circumstances.

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THE DISSOCIATION OF HYDROGEN INTO ATOMS.[1]

BY IRVING LANGMUIR.

Received May 4, 1912.

In a previous paper[2] it was shown that at extremely high temperatures the power consumption necessary to maintain a tungsten wire at a given temperature in hydrogen increases abnormally rapidly with the temperature. Let us represent by n the exponent of the power with which the energy consumption varies with the temperature; or, in other words, let us define n by the equation

$$n = \frac{d(\log \mathbf{W})}{d(\log T)},$$

where $\mathbf{W}$ = watts per cm. of length necessary to maintain the wire at the temperature T (absolute).

It was found that n increased with the temperature very rapidly, thus

T.	n.
1000°	1.86
1500	2.08
2000	2.71
2500	4.03
3000	6.90
3400	10.1

An analysis of the mechanism of the convection or conduction of heat failed to suggest any reason why n should ever become greater than 2. The most probable explanation was thought to be that dissociation of the hydrogen molecules into atoms was taking place. This dissociation in the region close to the hot wire would absorb large quantities of energy. The hydrogen atoms would diffuse out into the colder gas some distance from the wire and would there recombine and give up the heat of the reaction, thus causing an abnormally high heat conductivity. Mag-

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[1] Paper read at the Washington Meeting of the Am. Chem. Soc., Dec., 1911. Abstract appeared in *Science*, **35**, 428 (1912).

[2] *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911).