Effects of Dielectric Saturation upon the Diffuse Double Layer and the Free Energy of Hydration of Ions

David C. Grahame

Additional information on J. Chem. Phys.

Effects of Dielectric Saturation upon the Diffuse Double Layer and the Free Energy of Hydration of Ions*

DAVID C. GRAHAME

Department of Chemistry, Amherst College, Amherst, Massachusetts

(Received March 13, 1950)

The theory of the diffuse double layer is developed for the case of a dielectric of variable dielectric constant. Using experimental data by Malsch, calculations have been made of the properties of the diffuse double layer. It is found that those properties which are experimentally significant are almost unaffected by the onset of dielectric saturation. The Born equation for the free energy of hydration of ions is elaborated to include the effects of dielectric saturation, and it is found that these effects are negligible in the case of the alkali halide ions.

IN connection with our studies of the properties of the electrical double layer it has become necessary to ascertain what effects, if any, are to be attributed to the onset of dielectric saturation in the *diffuse* double layer. At a most conservative estimate the electric intensity or field strength within the diffuse double layer reaches values of 3×10^6 volts/cm, and although data are lacking as to the magnitude of the dielectric constant at such field strengths, the results of measurements made at much lower field strengths[1] leave little room for doubt that the dielectric constant falls to low values within the diffuse double layer. It will be shown below that although this conclusion is almost undoubtedly correct, the effects of dielectric saturation on the properties of the double layer are not such as to alter materially the results of calculations made on the assumption of a constant dielectric constant. In particular, the qualitative significance of results which depend upon those calculations[2] is not altered.

Previous treatments of the kinetic theory of the diffuse double layer have been carried through on the assumption that the dielectric constant of the solvent medium was a constant, independent of field strength. This was done chiefly because the dielectric constant was not known as a function of field strength, but also, perhaps, because the mathematical difficulties were

---

sufficiently troublesome even without this added complication. As it turns out, however, the added complication is purely arithmetical, which is to say that whereas the numerical computations are rendered more difficult, the mathematical problem is unaltered except for changes in the functions to be integrated. Since any function can be integrated by numerical means if not otherwise, it will be assumed in the next section that all necessary integrations are possible. In the same way it will be assumed that the elimination of a given constant between two not inconsistent equations is always possible, at least in the types of equations with which we shall have to deal.

I. THE MATHEMATICAL PROBLEM

This section deals with the general problem of solving the basic differential equation of the diffuse double layer where the dielectric constant is regarded as an unspecified function of the field strength. A discussion of the analogous problem where the dielectric constant is a true constant has already been presented by the author,[2] and in order to save space, only brief explanations will be given of points treated in detail there. As much as possible, the nomenclature will also be the same.

The fundamental differential equation to be solved is the Poisson equation in one dimension,

$$d^2\psi/dx^2 = -4\pi\rho/DD_0, \tag{1}$$

where ψ is the electrical potential at a point of charge

density ρ and x is a distance measured normal to the interface, increasing as one moves from the interface into the electrolytic solution. D is the *differential dielectric constant*, to be called the dielectric *coefficient*, and represents the rate of change of the electric displacement with the electric intensity.[3] D_0 is a quantity termed by the author the diabattivity, equal to $10^9/c^2 = 1.1128\times10^{-12}$ coulomb-volt^{-1}-cm^{-1}, and introduced[2] in order to avoid the difficulties which otherwise attend efforts to express the dielectric constant in units suitable for calculation.

If D were a constant, Eq. (1) could be integrated from a definite value of x to infinity (the interior of the solution) to give

$$d\psi/dx=4\pi\eta/DD_0,\qquad(a)$$

where η is defined by the relation,

$$\eta=\int_x^\infty \rho dx,\qquad(2)$$

and is called the *surface* charge density at the plane to which $d\psi/dx$ refers. It will be seen that η is the total charge contained in a column of solution of unit cross section and extending from the plane in question into the interior of the solution, where the charge density ρ is zero.

Equation (a) obviously may not be employed over a region of variable dielectric coefficient. In that case the counterpart of Eq. (a), obtained by integrating Eq. (1), becomes

$$\int_0^{s^0} Dds=4\pi\eta^d/D_0,\qquad(3)$$

where s has been written for the field strength, $d\psi/dx$. s^0 is the value of s at the limit of integration, now taken to be the outer Helmholtz plane.[2] This latter is defined as the plane of closest approach of the centers of the cations to the surface. The anions can in general come closer, it is believed, but the equations to be developed below are valid only in those regions to which all ionic types have access without energy barriers other than Coulombic.

The superscript d in η^d refers to the diffuse double layer and indicates that η^d is the charge per unit area in the entire diffuse double layer, starting from the outer Helmholtz plane.

One interesting conclusion can be drawn from Eq. (3). For a given value of η^d the limiting value of the field strength, s^0, is independent of the concentration of the solution. Since it is found in experiments on the double layer that η^d reaches nearly the same upper limit (of about 26 μcoulomb/cm^2) at all concentrations, this means that there is also a fairly definite upper limit to the field strengths which may be encountered within the diffuse double layer. According to the tables

to be presented, this upper limit probably amounts to about 6×10^6 volts/cm, at which field strength the dielectric coefficient of water is presumed to have dropped to about 27. Both of these values are quite uncertain, but it will turn out that they are also comparatively unimportant.

Further integration of Eq. (3) requires a knowledge of η^d as a function of x, and this cannot be had without introducing a new basic assumption. For this purpose one uses the Boltzmann equation and proceeds exactly as in the classical case (i.e., where D is a constant) to find the relation[2]

$$\rho=\sum n_{0i}z_i\epsilon \exp(-z_i\epsilon\psi/kT),\qquad(4)$$

where n_{0i} is the number of ions of type i per unit of volume in the interior of the solution, z_i is their "valence," including sign, ϵ is the unit electronic charge, and k is Boltzmann's constant. The summation extends over all ionic species in the solution.

Introducing into Eq. (1) the identity

$$\frac{1}{2}\frac{d}{d\psi}\left(\frac{d\psi}{dx}\right)^2=\frac{d^2\psi}{dx^2},\qquad(5)$$

one has

$$Dds^2=-\frac{8\pi\rho}{D_0}d\psi\qquad(6)$$

or through Eq. (4) after integration

$$\int_0^{s^0} Dds^2=\frac{8\pi kT}{D_0}\sum n_{0i}[\exp(-z_i\epsilon\psi^0/kT)-1].\qquad(7)$$

Here the quantity ψ^0 is the potential of the outer Helmholtz plane measured relative to the interior of the solution.

Elimination of s^0 between Eqs. (3) and (7) gives η^d as a function of ψ^0. As explained above, this elimination can always be done numerically if not otherwise. Supposing this problem solved, let η^d be the *abc* function of ψ^0,

$$\eta^d=abc(\psi^0).\qquad(8)$$

The differential capacity of the diffuse double layer, C^d, is defined by the relation

$$C^d=d\eta^d/d\psi^0\qquad(9)$$

and can in principle be evaluated by differentiation of Eq. (8). Unless this latter is a known function, however, it will usually be easier to find the differential capacity as the product of $d\eta^d/ds$ and $ds/d\psi^0$, using Eqs. (3) and (7) as follows:

$$d\eta^d/ds=DD_0/4\pi$$

$$ds/d\psi^0=-\frac{4\pi\epsilon}{DD_0s^0}\sum n_{0i}z_i \exp(-z_i\epsilon\psi^0/kT)$$

$$C^d=d\eta^d/d\psi^0=-(\epsilon/s^0)\sum n_{0i}z_i \exp(-z_i\epsilon\psi^0/kT).\qquad(10)$$

---

[3] P. Debye, *Polar Molecules* (Chemical Catalog Company, Inc., New York, 1929). See especially p. 110 *et seq.*

Because of the appearance in this equation of the quantity s^0, the evaluation of C^d must be preceded by the solution of Eq. (7).

For symmetrical valence types Eqs. (4), (7), and (10) take on the simpler forms:

$$\rho = -2n_0 z\epsilon \sinh z\epsilon\psi^0/kT \qquad (4')$$

$$\int_0^{s^0} D ds^2 = \frac{32\pi kT n_0}{D_0} \sinh^2 \frac{z\epsilon\psi^0}{2kT} \qquad (7')$$

$$C^d = d\eta^d/d\psi^0 = \frac{2z\epsilon n_0}{s^0} \sinh \frac{z\epsilon\psi^0}{kT}. \qquad (10')$$

In order to find ψ as a function of x it is convenient to write Eq. (3) in the form

$$s = bcd(\eta) \qquad (11)$$

where the bcd function is defined by the equation itself in conjunction with Eq. (3). Strictly speaking, the s in this equation is neither s as originally defined nor s^0, the value of s at the outer Helmholtz plane. It is the limit of integration of the left-hand member of Eq. (3) when the integration extends from the interior of the solution to some arbitrarily selected plane, not closer to the interface than the outer Helmholtz plane. Then η in Eq. (11) is the corresponding value of the surface charge density.

Without the superscripts Eq. (8) could have been written

$$\eta = abc(\psi) \qquad (8')$$

in which form it can be combined with Eq. (11) to yield

$$\frac{d\psi}{s} = \frac{d\psi}{bcd(abc(\psi))} = dx. \qquad (12)$$

Equation (12) can obviously be integrated to give ψ as a function of x. The constant of integration is essentially arbitrary, but is conveniently chosen to give the same values of x as the classical theory at sufficiently small values of ψ.

Finally it is desired to find η_+^d and η_-^d, the contributions of cations and of anions separately to the charge of the diffuse double layer. These are defined by the equations

$$\eta_i^d = \int (\rho_i - n_{0i} z_i \epsilon) dx, \qquad (13)$$

where ρ_i, standing for either ρ_+ or ρ_-, is the charge density of the corresponding ion. It is given by the Boltzmann equation as

$$\rho_i = n_{0i} z_i \epsilon \exp(-z_i \epsilon \psi/kT). \qquad (14)$$

Substituting this into Eq. (13) gives

$$\eta_i^d = n_{0i} z_i \epsilon \int [\exp(-z_i \epsilon \psi/kT) - 1] dx \qquad (15)$$

or from Eq. (12)

$$\eta_i^d = n_{0i} z_i \epsilon \int [\exp(-z_i \epsilon \psi/kT) - 1] \frac{d\psi}{bcd[abc(\psi)]}. \qquad (16)$$

This completes the formal solution of the mathematical problem stated at the beginning of this section. Some of these equations are particularized and solved more explicitly in Section III.

II. THE DIELECTRIC COEFFICIENT OF WATER AS A FUNCTION OF FIELD STRENGTH

Experimental data are not yet available for the evaluation of the dielectric coefficient of water at the very high field strengths believed to be present in the diffuse double layer. The only theory so far proposed is that of Debye[3,4] and is based upon the Mosotti hypothesis, which is admittedly not applicable to so polar a liquid as water. Malsch has measured the dielectric coefficient of a number of liquids at field strengths up to a mean value of 250,000 volts/cm and has verified that the coefficient falls off as the square of the field strength, as required by the theory.[5]

At much higher field strengths than those investigated by Malsch the dielectric coefficient must approach a limiting value similar to that of non-polar liquids at zero field strength. Debye[3] and Webb[6] have used the value 3 for this purpose in a similar application, and the same will be done here. Fortunately any small value could be used with no significant change in the results to be obtained.
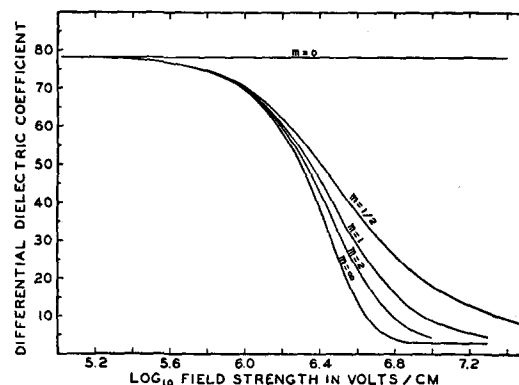

FIG. 1. Differential dielectric coefficient of water as a function of field strength where $b = 1.2 \times 10^{-13}$ cm²/volt² and m is the parameter in Eq. (17).

[4] P. Debye, Handb. d. Radiologie VI, p. 754.

[5] To be sure, the observable effects for water were so small that it was impossible to assert unequivocally that the field strength entered as the second power. But since it did so in every other case studied, and since the theoretical basis for expecting this behavior is fairly direct, it seems fair to conclude that at low field strengths, water behaves qualitatively like the other dielectrics studied. It may be mentioned in passing that the method of treating his data used by Malsch yields *differential* dielectric coefficients, or approximately so. The evaluation of the constant b depends critically upon this fact.

[6] J. Webb, J. Am. Chem. Soc. 48, 2589 (1926).

TABLE I. Potential, ψ^0, of the outer Helmholtz plane as a function of η^d, the charge of the diffuse double layer at 25°C, where $b=1.2\times10^{-13}$ cm²/volt², and $m=0$, $\frac{1}{2}$, 1, 2, or ∞.

η^d μcoulomb/ cm²	Tenth-normal aqueous solution of 1:1 electrolyte ψ^0 in millivolts				
	$m=0$	$m=\frac{1}{2}$	$m=1$	$m=2$	$m=\infty$
1	13.67	13.67	13.67	13.67	13.67
2	26.48	26.50	26.51	26.51	26.54
4	48.03	48.14	48.16	48.16	48.16
6	64.60	64.90	64.91	64.93	64.94
8	77.61	78.19	78.19	78.19	78.26
10	88.20	89.16	89.16	89.22	89.27
12	97.06	98.47	98.60	98.64	98.71
14	104.7	106.6	106.8	106.9	106.9
16	111.3	113.8	114.2	114.4	114.9
18	117.2	120.4	120.9	121.6	122.9
20	122.6	126.4	127.4	128.4	133.2
22	127.4	132.1	133.5	135.6	146.2
24	131.8	137.3	139.4	143.6	158.4
26	135.9	142.3	145.4	153.0	168.8

A family of functions having the desired characteristics is given by

$$D=\frac{a}{[1+(b/m)s^2]^m}+c, \quad (17)$$

where b is a parameter determined by experiment, $c=3$ as discussed above, and $a=\mathbf{D}-c$, where $\mathbf{D}$ is the ordinary dielectric constant at zero field strength. The coefficient of s^2 has been written as b/m because this makes it possible to evaluate b from experiment in advance of any decision concerning the best value of m. (In the series expansion of Eq. (17), m does not enter until the term in s^4, which means that it can be neglected at field strengths where the effect of the constant b can be ascertained experimentally.) From the results of Malsch, $b=1.2\times10^{-13}$ cm²/volt².

The parameter m has to do with the abruptness with which the dielectric coefficient falls off in the region where it falls most rapidly. This may be seen from Fig. 1, where the dielectric coefficient of water is plotted as a function of field strength for several assumed values of m. As m increases, the function approaches in the limit the function

$$D=ae^{-bs^2}+c, \quad (18)$$

which corresponds to the most abrupt falling off of the dielectric coefficient compatible with Eq. (17).

No really convincing argument can be given for preferring one value of m to another except that very large values $(m>2)$ can be excluded on the basis of experimental evidence to be presented below. Very small values would correspond to a very early breakdown of the square-of-the-field-strength law, which seems physically improbable. In any case, it will turn out that the particular value of m is of minor consequence as far as the main purpose of the calculation is concerned. Calculations have been made for m-values of $\frac{1}{2}$, 1, 2, and ∞. The classical calculation (constant dielectric coefficient) corresponds to $m=0$ and will be so designated in the tables.

As a sort of mean of the values of m which may be considered likely, the equations will be derived for the case where $m=\frac{1}{2}$. This may be regarded as the most probable value of m in the present state of knowledge, but fortunately the choice is not at all critical, as the results of the tables to be presented will show.

III. THEORY OF THE DIFFUSE DOUBLE LAYER

Setting $m=\frac{1}{2}$ gives for the variation of dielectric coefficient with field strength

$$D=\frac{a}{(1+2bs^2)^{\frac{1}{2}}}+c. \quad (19)$$

Introducing this into Eq. (7) and integrating gives

$$\frac{a}{b}(2bs^2+1)^{\frac{1}{2}}-\frac{a}{b}+cs^2$$

$$=\frac{8\pi kT}{D_0}\sum n_{0i}[\exp(-z_i e\psi^0/kT)-1], \quad (20)$$

For electrolytes of symmetrical valence type this reduces to the form

$$\frac{a}{b}(2bs^2+1)^{\frac{1}{2}}-\frac{a}{b}+cs^2=\frac{32\pi kTn_0}{D_0}\sinh^2\frac{ze\psi^0}{2kT}. \quad (21)$$

In these equations and in those which follow, the superscript is omitted from s^0, it being sufficiently clear what is meant without it.

Introducing Eq. (19) into Eq. (3) gives, after integration,

$$\frac{a}{(2b)^{\frac{1}{2}}}\ln(s(2b)^{\frac{1}{2}}+(2bs^2+1)^{\frac{1}{2}})+cs=4\pi\eta^d/D_0. \quad (22)$$
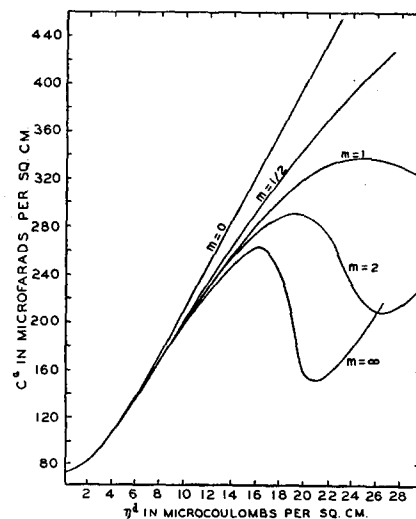

FIG. 2. Differential capacity of the diffuse double layer vs. charge on the diffuse double layer for 1:1 tenth-normal electrolytes in water at 25°C.

TABLE II. Field strength, s^0, at the outer Helmholtz plane of the diffuse double layer as a function of η^d, the charge of the diffuse double layer at 25°C, where $b=1.2\times10^{-13}$ cm^2/volt^2 and $m=0$, $\frac{1}{2}$, 1, 2, or ∞.

η^d μcoulomb/ cm^2	Tenth-normal aqueous solution of 1:1 electrolyte s^0 in megavolts/cm				
	$m=0$	$m=\frac{1}{2}$	$m=1$	$m=2$	$m=\infty$
1	0.1438	0.1440	0.1440	0.1440	0.1440
2	0.2878	0.2889	0.2889	0.2889	0.2890
4	0.575	0.583	0.583	0.583	0.583
6	0.863	0.888	0.889	0.889	0.890
8	1.151	1.210	1.212	1.213	1.217
10	1.439	1.555	1.561	1.570	1.578
12	1.726	1.929	1.955	1.970	1.992
14	2.01	2.34	2.40	2.44	2.50
16	2.30	2.79	2.91	3.02	3.23
18	2.59	3.29	3.51	3.78	4.71
20	2.88	3.85	4.28	4.93	10.92
22	3.16	4.47	5.24	6.96	18.44
24	3.45	5.16	6.49	11.11	26.0
26	3.74	5.94	8.23	17.58	33.5

TABLE III. Dielectric coefficient at the outer Helmholtz plane of the diffuse double layer as a function of η^d, the charge of the diffuse double layer at 25°C, where $b=1.2\times10^{-13}$ cm^2/volt^2 and $m=0$, $\frac{1}{2}$, 1, 2, or ∞.

η^d μcoulomb/ cm^2	Tenth-normal aqueous solution of 1:1 electrolyte dielectric coefficient				
	$m=0$	$m=\frac{1}{2}$	$m=1$	$m=2$	$m=\infty$
1	78.49	78.30	78.30	78.30	78.30
2	78.49	77.75	77.75	77.74	77.74
4	78.49	75.59	75.53	75.50	75.47
6	78.49	72.22	71.94	71.80	71.66
8	78.49	67.94	67.18	66.72	66.21
10	78.49	63.05	61.41	60.28	58.98
12	78.49	57.87	54.76	52.66	49.86
14	78.49	52.64	47.71	44.02	38.95
16	78.49	47.58	40.44	34.62	24.75
18	78.49	42.80	33.41	24.78	8.08
20	78.49	38.39	26.61	15.86	3.00
22	78.49	34.36	20.58	7.96	3.00
24	78.49	30.75	15.47	4.09	3.00
26	78.49	27.53	11.27	3.20	3.00

In conjunction with Eq. (20) or (21), this equation makes it possible to compute ψ^0 and η^d as functions, one of the other, or of s. The differential capacity may now be found from Eqs. (10) or (10').

When $m=\infty$, that is, using Eq. (18) instead of Eq. (19) the corresponding equations become

$$\frac{a}{b}(1-e^{-bs^2})+cs^2=\frac{8\pi kT}{D_0}\sum n_{0i}[\exp(-z_i e\psi^0/kT)-1], \quad (23)$$

$$\frac{a}{b}(1-e^{-bs^2})+cs^2=\frac{32\pi kTn_0}{D_0}\sinh^2\frac{ze\psi^0}{2kT}, \quad (24)$$

$$\frac{4\pi\eta^d}{D_0}=\frac{a}{2}(\pi/b)^{\frac{1}{2}}H(b^{\frac{1}{2}}s)+cs, \quad (25)$$

where $H(w)$ is the error integral defined by

$$H(w)=\frac{2}{\pi}\int_0^w e^{-y^2}dy.$$

Equation (24), like Eq. (21), is restricted to electrolytes of symmetrical valence type.

The most significant comparison which can be made of the effect of one's choice of m upon the predicted properties of the diffuse double layer is that obtained by comparing values of ψ^0 at a given value of η^d. Since η^d never goes beyond about 26 μcoulomb/cm^2, it is not necessary to consider values larger than this. For a tenth-normal solution of a 1:1 electrolyte, Table I presents the results of calculations of ψ^0 obtained by assuming values of m ranging from $m=0$ (the classical case) to $m=\infty$ (Eq. (18)). Except for the values at $m=\infty$, the extreme differences in ψ^0 amount to no more than 13 percent. Over the range of values of η^d which are of greatest interest, the differences are so small that it would not usually be worth while taking them into consideration at all, and this conclusion holds even when $m=\infty$. Experimental considerations will be

adduced to show that the value of m probably does not exceed 2, however.

A few calculations have been made at other concentrations and for other electrolyte types than those shown in Table I. The results of these calculations show no new features in these cases, and lead to the conclusion that the results deduced above are generally valid.

The values of the maximum field strength, s or s^0, are much more sensitive than is ψ^0 to one's choice of m, and the same is true of the values of the dielectric coefficient in the outer Helmholtz plane. These facts are shown in Tables II and III. The significance of these results is that the uncertainty in the value of m affects very greatly the somewhat hypothetical properties of the solvent in the outer Helmholtz plane, but is of almost negligible effect upon observable properties such as the surface charge density.

The variation of potential with distance has been calculated from Eq. (12) taking $m=\infty$. Even for this extreme case, the results are so much like the classical case that it has not seemed worth while reporting them in detail. For lesser values of m, one may presumably use the classical method of calculation without sensible error from the neglect of the variation of dielectric coefficient with field strength.

This result makes possible a simple method of calculating η_+^d and η_-^d. At elevated field strengths, where the classical calculation might be expected to differ from that obtained with another value of m, one or the other of the above-mentioned quantities will be small. Because the variation of ψ with x is almost the same as in the classical case, the calculation of this one by the classical theory will be entirely adequate for almost any purpose. Then the other can be obtained by difference from η^d, which is already known from Table I, for instance.

The differerential capacity C^d of the diffuse double layer is a sensitive function of m, and its behavior may

TABLE IV. Free energy of hydration of charged spheres of radius r_e.

r_e A	$-\Delta F^0$ Eq. (32) $m=2$ kcal.	$-\Delta F^0$ Eq. (32) $m=\frac{1}{2}$ kcal.	$-\Delta F^0$ Born Eq. $(m=0)$ kcal.	Ion of eff. rad. $=r_e$ L-P-S[8]	$-\Delta F^0$ obs. L-P-S[8] kcal.
1.45	110.2	112.5	113.0	Li$^+$	114.6
1.46	109.6	111.8	112.3	F$^-$	113.9
1.60	100.8	102.1	102.4	none	
1.80	90.4	90.9	91.1	Na$^+$	89.7
1.91	85.4	85.7	85.8	Cl$^-$	84.2
2.05	79.7	79.9	80.0	Br$^-$	78.0
2.18	75.1	75.1	75.2	K$^+$	73.5
2.26	72.4	72.5	72.5	I$^-$	70.0
2.33	70.3	70.3	70.3	Rb$^+$	67.5
2.54	64.5	64.5	64.5	Cs$^+$	60.8

be used to infer something about the value of m as follows. Values of C^d calculated as a function of η^d for various values of m are shown in Fig. 2. The important feature of this figure is the sudden falling off of C^d at values of η^d which depend upon the value of m. For $m=\infty$, the effect occurs at about 19 μcoulomb/cm^2, which is well within the range of experimentally accessible values of η^d and should produce an observable effect if m is large. Since the diffuse double layer is in series with the much smaller capacity of the non-diffuse part of the double layer,[2] the expected effect is somewhat obscured, particularly since one does not know the capacity of the non-diffuse part with any certainty. However, the true capacity of the non-diffuse part can be calculated from the over-all capacity if a correct theory of the *diffuse* double layer is available. Since dielectric saturation in the diffuse double layer is not expected to produce discontinuities or irregularities in the capacity of the non-diffuse part, any theory of the diffuse double layer which leads to such irregularities at potentials where dielectric saturation sets in is ruled out. The observed fact is that the calculated capacity of the non-diffuse part of the double layer is a smooth function of potential for any value of m up to about $m=2$. This rules out larger values of m and makes smaller values somewhat more probable. If the value of b should be somewhat larger than that indicated by Malsch's results, m would have to be correspondingly lower. In any case the qualitative conclusions reached in the foregoing paragraphs will be correct if the value of b is not too greatly different from that adopted.

IV. THE FREE ENERGY OF HYDRATION OF GASEOUS IONS

It is possible to use any member of the family of Eqs. (17) to calculate the free energy of hydration of a gaseous ion, using essentially the method of Born.[7] One supposes an ion to have an effective radius r_e, within which the gradients of the field are identical whether the ion is in a dielectric medium or in vacuum. Beyond this critical radius the field strength is given by

$$s=(\lambda\epsilon)/(r^2 D_0 I), \qquad (26)$$

where I is the *integral* dielectric coefficient of the medium, defined as the ratio of the electric displacement to the electric intensity or field strength. It is related to the differential coefficient through the equation

$$I=(1/s)\int D ds. \qquad (27)$$

When $m=\frac{1}{2}$ the integral dielectric coefficient accordingly becomes

$$I=\frac{a}{u}[\ln(u+(1+u^2)^{\frac{1}{2}})+c], \qquad (28)$$

where $u^2=2bs^2$.

λ in Eq. (26) is the charge on the ion (units of electronic charge) but differs from z, the valence, in that it is regarded as a variable parameter during the (hypothetical) charging or discharging of an ion. The free energy of hydration of a gaseous ion is then computed as the work required to discharge the ion in vacuum minus the work required to charge it in the dielectric medium. The former is given by

$$w_1=-\epsilon^2/r D_0. \qquad (29)$$

Here r is not the effective radius of the ion but the crystal radius. To introduce the effective radius, let w_e be the work required to move the ionic charge reversibly from an ion of radius r to a sphere of radius r_e. It is unnecessary to evaluate this quantity since it cancels out of the final expression. The assumption is made, however, that its value is the same in the presence or in the absence of the dielectric medium. Recalling that w_1 is the work required to discharge the ion in vacuum, one has that

$$w_1=w_e-\epsilon^2/r_e D_0. \qquad (30)$$

The work required to *charge* the ion in the dielectric medium is similarly given by

$$w_2=-w_e+\int\psi d(\lambda\epsilon) \qquad (31)$$

where ψ is the potential of the sphere of radius r_e at any instant during the charging process. For univalent ions, λ varies from 0 to 1 during this process. The free energy of hydration of an ion of radius r is the sum of w_1 and w_2 and equals the free energy of hydration of a sphere of radius r_e. Per mole, this amounts to

$$\Delta F^0=-N\epsilon^2/r_e D_0+N\int\psi d(\lambda\epsilon), \qquad (32)$$

ψ is a function of λ and is evaluated by the integration of sdr.

$$\psi=\int_{\infty}^{r_e} sdr \qquad (33)$$

---

[7] Born, Zeits. f. Physik **1**, 4 (1920). See also Webb (*loc. cit.*) and Latimer, Pitzer, and Slansky, reference 8.

s is found as a function of r through Eqs. (26) and (28) (or a corresponding equation in case m is given some value other than $\frac{1}{2}$).

This program has been carried through for $m=\frac{1}{2}$ and $m=2$, each for several values of r_e. The results are shown in Table IV along with values obtained from the Born equation ($m=0$). It is seen at once that this elaboration of the calculation to include the effect of the variation of dielectric coefficient with field strength has had almost no effect upon the results, which are practically identical with those of the simple Born equation, except possibly for Li^+ and F^- when $m=2$. Even in this case the deviation is too small to be considered significant.

Latimer, Pitzer, and Slansky[8] showed that the Born equation gave reasonably good agreement with experimental values of the free energy of hydration of the gaseous ions of the alkali halides when the effective radii of cations and anions were taken 0.85 and 0.1A, respectively, greater than their crystal radii. The results of the present calculation show that these authors were correct in assuming that the neglect of dielectric saturation effects would make no appreciable difference in their results. This was just the reverse of the assumption made by Webb,[6] who regarded dielectric saturation as a matter of such importance that it could not be neglected.

In this connection it is interesting to note that any calculation of the effect of dielectric saturation upon the free energy of hydration of the gaseous ions of the alkali halides will have the effect of reducing the absolute values of ΔF^0 for all ions, but especially of the smaller ions. This will always have the effect of worsening the fit with the experimental values, since the calculated values for the smaller ions are already too small when the adjustable parameters are chosen in such a way as to achieve a fit for the larger ions. One can therefore say with virtual certainty that the neglect of dielectric saturation effects is not the principal remaining defect of the Born equation.[9] Further improve-

[8] Latimer, Pitzer, and Slansky, J. Chem. Phys. 7, 108 (1939).

[9] *Note added in proof.*—This conclusion also increases one's confidence in the conclusions of Section III since it indicates that dielectric saturation does not set in at field strengths as low as had previously been supposed.
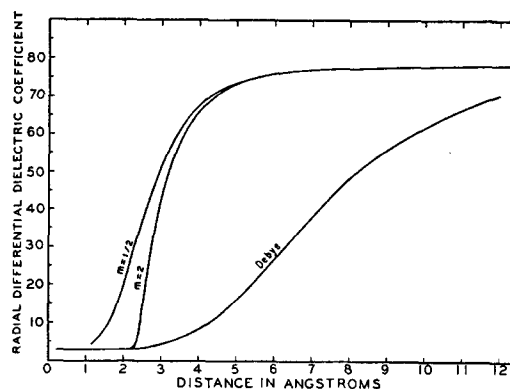

FIG. 3. Dielectric constant of water as a function of the distance from the center of a univalent ion.

ment must probably be sought in a more refined treatment of the effective radius.

In the past considerable attention has been given to the problem of calculating the dielectric constant of water in the field of an ion. Since this quantity is evaluated in the calculation discussed above, it has seemed worth while presenting the results. This is done in Fig. 3 where the radial differential dielectric coefficient of water is plotted as a function of the distance from a singly charged ion. For comparison, Debye's values (read from his curve[3] as well as possible) have been shown also. The large differences reflect the difference in the fundamental postulates upon which the calculations are based. The new curves may be said to represent an extrapolation of the experimental values of Malsch, different values of m corresponding to different methods of extrapolation.

ACKNOWLEDGMENTS