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The Solution of Some Potential Problems in the Theory of Electrolytes

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The Poisson-Boltzmann equation for the potential in an electrolyte is solved for the following cases:

(a) Electrolyte bordered by a uniformly charged plane; (b) two semi-infinite electrolytes of different composition separated by a plane boundary; (c) electrolyte confined between parallel charged planes; (d) uniformly charged cylinder immersed in an electrolyte; (e) electrolyte in a cylinder with charged walls; (f) electrolyte between two concentric charged cylinders; (g) solid charged sphere in an electrolyte; and (h) sphere of electrolyte immersed in another electrolyte extending to infinity, and of different composition.

All the problems discussed are of interest in the theory of colloids or emulsions. In each case a series solution in powers of a parameter involving the charge or charges on relevant surfaces is given. The first term of each series is the solution of the Poisson-Boltzmann equation when the so-called Debye-Hückel approximation is applied to the equation. The additional terms are built up from the first by an iterative method. No restrictions on the compositions of the electrolytes are required.

INTRODUCTION

Section 1.

IN this note we shall obtain the solutions of some potential problems which are of interest in the theory of colloidal electrolytes. According to Debye's theory,¹ the fundamental differential equation which must be satisfied by the electrostatic potential ψ in an electrolyte is

$$\nabla^2\psi = -\frac{4\pi e}{\epsilon} \sum_{i=1}^s n_i \exp(-ez_i\psi)/kT, \quad (1.1)$$

where e is the electronic charge, ϵ the dielectric constant of the solvent, k Boltzmann's constant, and T the absolute temperature. The summation extends over the s ionic species present in solution, n_i being the concentration of ions of type i when $\psi=0$, and z_i their valency. Equation (1.1) combines the Poisson and Boltzmann equations; the complete nonlinear equation has been criticized,^{2,3} but a more correct equation has not so far been obtained.

If we assume electroneutrality of the solution as a whole, then we have

$$\sum_{i=1}^s n_i z_i = 0. \quad (1.2)$$

Also, if the condition

$$e\psi/kT \ll 1 \quad (1.3)$$

holds everywhere, then Eq. (1.1) can be written

$$\nabla^2\psi = \kappa^2\psi, \quad (1.4)$$

where

$$\kappa^2 = 4\pi e^2 \sum_{i=1}^s n_i z_i^2 / \epsilon kT. \quad (1.5)$$

A considerable amount of work has been done based on the approximate equation (1.4), which is associated

with the names of Debye and Hückel. The more exact Eq. (1.1) has received much less attention, doubtless owing to its nonlinearity. The most important development using (1.1) is due to Gronwall, LaMer, and Sandved,⁴ who gave a theory for electrolytes in statistical equilibrium which is formally similar to the Debye-Hückel theory. Their work was entirely confined to a study of ordinary solutions of strong electrolytes; but it is of interest to notice that the idea underlying their method can be adapted so as to furnish solutions of a wide variety of problems which arise in another field, that of colloidal solutions. Here, instead of all the charges in the assembly being associated with free ions, some may be attached to solid boundaries or solid or liquid particles, of dimensions which may be large on the atomic scale. In most cases it is not difficult to solve Eq. (1.4) for the potential, but quite impossible to integrate (1.1) directly. Experimental work on colloidal systems indicates that the potentials may reach values as high as 200 millivolts, giving for $e\psi/kT$ a value of about 8 at room temperatures. For these cases it is obviously a very bad approximation to use Eq. (1.4) in view of condition (1.3). However, in the following paragraphs it will be shown how solutions of Eq. (1.1) can be built up from those of (1.4). The general method is to assume a series development for ψ in powers of a suitable parameter. Substitution of the series in Eq. (1.1) gives a sequence of differential equations which can be handled without difficulty. Any term in the series for ψ can be expressed in terms of preceding terms. Since the *first* term of the series turns out to be simply the solution of Eq. (1.4), the members of the series may be calculated successively, and so a complete solution of Eq. (1.1) obtained.

Although the solutions developed should be more satisfactory than those derived from Eq. (1.4) unless ψ is very small, in which case both methods give the same result, it must be pointed out that the usefulness of the method is limited by three factors. In the first

¹ P. Debye and E. Hückel, *Physik. Z.* **24**, 185 (1923).

² L. Onsager, *Chem. Revs.* **13**, 73 (1933).

³ J. G. Kirkwood, *J. Chem. Phys.* **2**, 767 (1934).

⁴ Gronwall, LaMer, and Sandved, *Physik. Z.* **28**, 358 (1928).

place, it has been shown that Eq. (1.1) is not strictly thermodynamically consistent.² It is of interest to notice however that in cases where it *has* been applied, better results have emerged than when the simpler Debye-Hückel theory was used. For example, the Gronwall-LaMer-Sandved theory gives a better account of the properties of electrolytes in equilibrium; in particular, it gives more reasonable estimates of ionic radii. In another connection, Verwey and Overbeek⁵ have shown that the Schulze-Hardy rule on the dependence of the coagulating properties of electrolytes on their valency can be explained if the analysis is based on Eq. (1.1), but not if Eq. (1.4) is used. Another difficulty arises in connection with the convergence of the solutions. Since in all cases a power series solution is derived, strictly it is necessary in each case to find the radius of convergence. This is difficult to calculate, since the method does not give the general term of the power series in a simple expression. It is easy in some cases to devise dominant series, but then it is found that these have finite radii of convergence which are less than the values sometimes indicated by experiment. A further difficulty lies in the mathematical complexity of the higher terms of the series for ψ . Although in theory it is possible to calculate any desired number of terms, in practice this becomes impracticable beyond a certain stage.

In spite of the three limitations we have mentioned, however, it seems likely that the solutions should be suitable for a useful range of potential above the upper limit for which the simple theory based on Eq. (1.4) can be legitimately employed. The next section deals with problems involving plane boundaries. First, the potential near an infinite uniformly charged plane in contact with a semi-infinite electrolyte is found. The next solution given is the potential near the plane boundary between two semi-infinite electrolytes. Then follows the general solution for an electrolyte between two infinite parallel charged planes. The next section deals with similar problems involving cylindrical boundaries; finally, questions with spherical boundaries are examined. The cases we have dealt with do not exhaust all the problems which could be solved by the method. We have confined attention to those cases which are or are likely to be of interest in the interpretation of experimental data. For example, all the solutions involving solids may be useful in refinements of the theory of the stability of colloids.

PROBLEMS INVOLVING PLANE BOUNDARIES

Section 2. The Potential near an Infinite Uniformly Charged Plane

Let σ be the surface density of the charge on the plane and ζ the potential at the surface, the potential zero being taken at infinity. If x denotes distance

measured normal to the plane, the equation to be solved is

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi e}{\epsilon} \sum_{i=1}^s n_i \exp\left(\frac{-ez_i\psi}{kT}\right), \quad (2.1)$$

with the boundary conditions

$$\psi=0, \quad x=\infty; \quad \psi=\zeta, \quad d\psi/dx=-4\pi\sigma/\epsilon, \quad x=0. \quad (2.2)$$

The solution is well known in the case $i=2$, $z_1=-z_2$ and $n_1=n_2$,⁶ Eq. (2.1) is then immediately integrable, giving

$$\log_e \tanh(z_1 e \psi / 4kT) = \log_e \tanh(z_1 e \zeta / 4kT) - \kappa x, \quad (2.3)$$

and

$$\sinh(z_1 e \zeta / 2kT) = 2\pi e z_1 \sigma / \kappa \epsilon kT, \quad (2.4)$$

where

$$\kappa^2 = 8\pi e^2 n_1 z_1^2 / \epsilon kT. \quad (2.5)$$

When n_i and z_i are not restricted in the above manner, Eq. (2.1) can be integrated once to give $d\psi/dx$. From the resulting equation, σ and ζ can be related:

$$\sigma = \left(\frac{\epsilon kT}{2\pi}\right)^{1/2} \left[\sum_{i=1}^s n_i \left\{ \exp\left(\frac{-ez_i\zeta}{kT}\right) - 1 \right\} \right]^{1/2}. \quad (2.6)$$

Unfortunately the integration cannot be carried a stage further to give ψ . For some purposes, for example, the determination of σ from measurements of the electrokinetic potential ζ , Eq. (2.6) gives all that is required. It is of interest, however, to be able to find the complete solution for ψ in the general case.

Equation (2.1) may be written in the form,

$$(d^2\psi/dx^2) - \kappa^2\psi = \kappa^2\Psi, \quad (2.7)$$

where

$$\Psi = \sum_{r=2}^{\infty} \frac{(-1)^{r-1}}{r!} \left(\frac{e}{kT}\right)^{r-1} q_r \psi^r, \quad (2.8)$$

and

$$q_r = \sum_{i=1}^s n_i z_i^{r+1} / \sum_{i=1}^s n_i z_i^2. \quad (2.9)$$

κ has been defined in Eq. (1.5); also it has been assumed that condition (1.2) is satisfied. The general solution of Eq. (2.7) is

$$\psi = C_1 e^z + C_2 e^{-z} + \frac{1}{2} \int_0^z \Psi(u) (e^{z-u} - e^{u-z}) du, \quad (2.10)$$

where we have put $z = \kappa x$.⁷ The first two terms represent the general solution of Eq. (2.7), and it is easily verified that the third term is a particular integral. Using the boundary conditions (2.2), we may write Eq. (2.10) as

$$\psi = (4\pi\sigma/\kappa\epsilon) e^{-z} + \int_0^\infty f(u, z) \Psi(u) du, \quad (2.11)$$

⁶ A. J. Rutgers and E. Verlende, Proc. Acad. Sci. Amsterdam 42, 71 (1939).

⁷ A. R. Forsyth, *A Treatise on Differential Equations* (Macmillan and Company, Ltd., London, 1888), second edition, p. 78.

⁵ E. J. W. Verwey and J. Th. G. Overbeek, Philips. Tech. Research Repts, No. I.

where

$$f(u, z) = -\frac{1}{2}(e^{u-z} + e^{-u-z}), \quad 0 < u < z, \quad (2.12)$$

$$= -\frac{1}{2}(e^{z-u} + e^{-u-z}), \quad u > z.$$

The expression on the right-hand side of Eq. (2.11) vanishes for x large, since it can easily be shown that

$$|f(u, z)| \leq e^{u-z}. \quad (2.13)$$

To solve Eq. (2.11) we write ψ as an expansion in powers of σ :

$$\psi = \sum_{m=1}^{\infty} e^{m-1} (\kappa \epsilon)^{-m} (-\mathbf{k}T)^{1-m} (4\pi\sigma)^m \theta_m(z). \quad (2.14)$$

The $\theta_m(z)$ are functions of z only, which must now be determined. From Eq. (2.8) we find that Ψ can be written in the form,

$$\Psi = \sum_{m=2}^{\infty} e^{m-1} (\kappa \epsilon)^{-m} (-\mathbf{k}T)^{1-m} (4\pi\sigma)^m \Psi_m(z), \quad (2.15)$$

where

$$\Psi_m(z) = \sum_{\substack{m_1 + \dots + m_p = m \\ p \geq 2, m_p \geq 1}} \frac{q_p}{p!} \prod_{s=1}^p \theta_{m_s}(z). \quad (2.16)$$

Substituting from Eq. (2.14) for ψ in Eq. (2.11) and using Eq. (2.15), we can then determine the functions $\theta_m(z)$ by comparing coefficients of like powers of σ :

$$\theta_1(z) = e^{-z}, \quad (2.17)$$

$$\theta_m(z) = \int_0^{\infty} f(u, z) \Psi_m(u) du, \quad m > 1. \quad (2.18)$$

From Eqs. (2.18) and (2.16), it is clear that $\theta_m(z)$ for m greater than 1, can be expressed in terms of the same functions with smaller suffixes. Hence, since $\theta_1(z)$ is known, all the $\theta_m(z)$ can be evaluated. By direct calculation we find

$$\begin{aligned} \theta_2(z) &= q_2 \left(\frac{1}{6} e^{-2z} - \frac{1}{3} e^{-z} \right), \\ \theta_3(z) &= q_2^2 \left[\frac{1}{48} e^{-3z} - \frac{1}{9} e^{-2z} + \frac{23}{144} e^{-z} \right] \\ &\quad + q_3 \left[\frac{1}{48} e^{-3z} - \frac{1}{16} e^{-z} \right], \\ \theta_4(z) &= q_2^3 \left[\frac{1}{432} e^{-4z} - \frac{1}{48} e^{-3z} + \frac{31}{432} e^{-2z} \right. \\ &\quad \left. - \frac{13}{144} e^{-z} \right] + q_2 q_3 \left[\frac{1}{144} e^{-4z} - \frac{1}{48} e^{-3z} \right. \\ &\quad \left. - \frac{1}{48} e^{-2z} + \frac{11}{144} e^{-z} \right] \\ &\quad + q_4 \left[\frac{1}{360} e^{-4z} - \frac{1}{90} e^{-z} \right], \\ \theta_5(z) &= q_2^4 \left[\frac{5}{20,736} e^{-5z} - \frac{1}{324} e^{-4z} \right. \\ &\quad \left. + \frac{13}{768} e^{-3z} - \frac{31}{648} e^{-2z} + \frac{581}{10,368} e^{-z} \right] \\ &\quad + q_2^2 q_3 \left[\frac{5}{3,456} e^{-5z} - \frac{1}{108} e^{-4z} \right. \\ &\quad \left. + \frac{5}{384} e^{-3z} + \frac{7}{216} e^{-2z} - \frac{2}{27} e^{-z} \right] \\ &\quad + q_2 q_4 \left[\frac{11}{8640} e^{-5z} - \frac{1}{270} e^{-4z} \right. \\ &\quad \left. - \frac{1}{270} e^{-3z} + \frac{137}{8640} e^{-2z} \right] \\ &\quad + q_3^2 \left[\frac{1}{2304} e^{-5z} - \frac{1}{256} e^{-3z} + \frac{11}{1152} e^{-z} \right] \\ &\quad + q_5 \left[\frac{1}{2880} e^{-5z} - \frac{1}{576} e^{-z} \right]. \end{aligned} \quad (2.19)$$

Although we have tabulated only the first five terms of Eq. (2.14), the series can, in theory at any rate, be carried through to any desired value of m , and so the potential completely determined. The terms soon become very complicated.

To complete the solution, strictly we should examine the convergence of series (2.14), and either establish its validity for all values of σ or find its radius of convergence. Unfortunately, the radius of convergence cannot be found directly, since the method does not give a general formula for any term. For the case of ions, Gronwall, LaMer, and Sandved use a dominant series to examine the convergence. The same method can be used in the present problem, but it is not very helpful. For example it can be shown that Eq. (2.14) is certainly convergent provided that

$$|4\pi e z_0 \sigma / \kappa \epsilon \mathbf{k}T| < 2 \log_e 2 - 1 = 0.386, \quad (2.20)$$

where $z_0 \geq |z_i|$. This gives a low value for σ . If we substitute $x=0$ in the right-hand side of Eq. (2.14), and then revert the resulting series, so as to give σ as a power series in ζ , then it can be shown that this series is certainly convergent provided that

$$|e\zeta/\mathbf{k}T| < 4 \log_e 2 - 1 - 2[\log_e 2(3 \log_e 2 - 1)]^{\frac{1}{2}} = 0.0426. \quad (2.21)$$

This is a very small value; with this order of magnitude the first term only of series (2.14) should be sufficient. It seems very likely, however, that the series is convergent for much larger values of $\zeta e/\mathbf{k}T$. For it is easily shown that the corresponding series derived from Eq. (2.4) is certainly convergent provided

$$e\zeta/\mathbf{k}T < 2/3. \quad (2.22)$$

The results embodied in Eqs. (2.20), (2.21), and (2.22) are significant, since they indicate that the series (2.14) cannot be used indiscriminately. The only safe procedure in any particular case would seem to be a comparison of the orders of magnitude of successive terms.

Section 3. Potential at the Plane Interface between Two Different Electrolytes

This is a simple variant of the above problem; instead of a plane solid boundary, the electrolyte is bordered by another semi-infinite electrolyte of different composition. For the case of simple electrolytes dissociating into two ions only, this problem has been solved by Verwey and Niessen.⁸ At a large distance from the interface in either direction, the potential is uniform; but, in general, the potential for x large and positive will differ from its value for x large but negative. We shall indicate all quantities to the right of the boundary by the superscript (1) to the left by the superscript (2). For complete generality it will be assumed that there is an adsorbed charge of surface density σ_s , and also a potential jump of ψ_s due to oriented dipoles,

⁸ E. J. Verwey and K. F. Niessen, *Phil. Mag* (7), 28, 435 (1939).

at the interface. The boundary conditions are

$$\psi^{(2)}=0, \quad x=-\infty; \quad \psi^{(1)}=\zeta, \quad x=\infty; \quad (3.1)$$

$$\psi^{(2)}=\psi_s+\psi^{(1)}, \quad x=0. \quad (3.2)$$

$$\epsilon^{(2)}d\psi^{(2)}/dx|_0-\epsilon^{(1)}d\psi^{(1)}/dx|_0=4\pi\sigma_s. \quad (3.3)$$

When the method of Sec. 2 is used, the series expressions for the potentials are

$$\psi^{(2)}=\sum_{m=1}^{\infty} e^{m-1}(\kappa^{(2)}\epsilon^{(2)})^{-m}(-\mathbf{k}T)^{1-m} \times (4\pi[\sigma_s-\sigma])^m \theta_m(-\kappa^{(2)}x), \quad x<0, \quad (3.4)$$

$$\psi^{(1)}=\zeta+\sum_{m=1}^{\infty} e^{m-1}(\kappa^{(1)}\epsilon^{(1)})^{-m}(-\mathbf{k}T)^{1-m} \times (4\pi\sigma)^m \theta_m(\kappa^{(1)}x), \quad x>0, \quad (3.5)$$

where σ is now effectively a parameter given by

$$\epsilon^{(1)}d\psi^{(1)}/dx|_0=-4\pi\sigma. \quad (3.6)$$

In general σ will not be specified; to find it in terms of the known quantities ζ , ψ_s , and σ_s , the solutions with x set equal to 0 must be substituted in Eq. (3.2) and the resulting series solved by reversion.

Section 4. Electrolyte between Two Parallel Charged Planes

The potential in an electrolyte confined between two parallel planes whose inner surfaces have uniform charge densities σ and σ' is required. This problem is of interest in the theory of the stability of colloids.⁹ Solutions for the particular case $s=2$, $\sigma=\sigma'$, $n_1=n_2$, and $z_1=-z_2$, have previously been given by Corkill and Rosenhead¹⁰ and Verwey.¹¹ Equation (2.7) again holds, provided the potential zero is chosen in such a manner that the n_i satisfy the electroneutrality equation (1.2). But instead of Eq. (2.2) the boundary conditions are now

$$d\psi/dx|_0=-4\pi\sigma/\epsilon, \quad d\psi/dx|_a=4\pi\sigma'/\epsilon, \quad (4.1)$$

where d is the distance between the planes. Integrating Eq. (2.7), we again get Eq. (2.10); but conditions (4.1) now give

$$\psi=\frac{4\pi e^z}{\kappa\epsilon}\left[\frac{\sigma e^{-2b}+\sigma' e^{-b}}{1-e^{-2b}}\right]+\frac{4\pi e^{-z}}{\kappa\epsilon}\left[\frac{\sigma+\sigma' e^{-b}}{1-e^{-2b}}\right] + \int_0^b g(u,z)\Psi(u)du, \quad (4.2)$$

⁹ E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier Publishing Company, Inc., New York, 1948), Part II.

¹⁰ A. J. Corkill and L. Rosenhead, *Proc. Roy. Soc. (London)* **A172**, 410 (1939).

¹¹ E. J. W. Verwey, *Trans. Faraday Soc.* **36**, 192 (1940).

where

$$\left. \begin{aligned} g(u,z) &= -[1/2(1-e^{-2b})] \\ &\times [e^{u-z}+e^{-u-z}+e^{-2b}(e^{u+z}+e^{z-u})], \quad 0<u<z \\ &= -[1/2(1-e^{-2b})] \\ &\times [e^{z-u}+e^{-u-z}+e^{-2b}(e^{u+z}+e^{u-z})], \quad z<u<b \end{aligned} \right\} \quad (4.3)$$

and

$$b=\kappa d, \quad z=\kappa x. \quad (4.4)$$

To solve Eq. (4.2), the potential ψ is expanded as a double series in powers of both σ and σ' ,

$$\psi=\sum_{m+m'>1} e^{m+m'-1}(\kappa\epsilon)^{-m-m'}(-\mathbf{k}T)^{1-m-m'} \times (4\pi\sigma)^m(4\pi\sigma')^{m'}\theta_{m,m'}(z). \quad (4.5)$$

It can now be shown as before that Ψ may be written

$$\Psi(z)=\sum_{m+m'>0} e^{m+m'-1}(\kappa\epsilon)^{-m-m'}(-\mathbf{k}T)^{1-m-m'} \times (4\pi\sigma)^m(4\pi\sigma')^{m'}\Psi_{m,m'}(z), \quad (4.6)$$

where

$$\Psi_{m,m'}(z)=\sum_{\substack{m_1+\dots+m_p=m \\ m'_1+\dots+m'_p=m' \\ p\geq 2, m_p+m_{p'}\geq 1}} \frac{q_p}{p!} \prod_{s=1}^p \theta_{m_s,m_{s'}}(z). \quad (4.7)$$

Proceeding as before, we find

$$\left. \begin{aligned} \theta_{1,0}(z) &= (e^{z-2b}+e^{-z})/(1-e^{-2b}), \\ \theta_{0,1}(z) &= (e^{z-b}+e^{-z-b})/(1-e^{-2b}), \end{aligned} \right\} \quad (4.8)$$

and the functions of higher order are derived from $\theta_{1,0}(z)$ and $\theta_{0,1}(z)$ by the formula,

$$\theta_{m,m'}(z)=\int_0^b g(u,z)\Psi_{m,m'}(u)du, \quad m+m'>1. \quad (4.9)$$

From Eqs. (4.8) and (4.9) the whole series of functions can be built up to any desired order of m and m' .

PROBLEMS INVOLVING CYLINDRICAL BOUNDARIES

Section 5. Infinite Charged Cylinder Immersed in an Electrolyte

Let the charge on the surface of the cylinder be uniformly distributed and of density σ . If r is the distance from the axis of the cylinder, the equation for the potential is

$$(d^2\psi/dr^2)+(1/r)(d\psi/dr)-\kappa^2\psi=\kappa^2\Psi, \quad (5.1)$$

and the boundary conditions,

$$d\psi/dr|_a=-4\pi\sigma/\epsilon, \quad \psi=0, \quad r=\infty, \quad (5.2)$$

where a is the radius. The general integrals of Eq. (5.1) are $I_0(\kappa r)$ and $K_0(\kappa r)$, the bessel functions with imaginary argument of the first and second kind. The

determination of the potential follows closely the method of Sec. 2, and so we shall only set down the principal results. Integration gives

$$\psi = -(4\pi\sigma/\kappa\epsilon) \cdot [K_0(z)/K_0'(b)] + \int_b^\infty f(u, z) \Psi(u) u du, \quad (5.3)$$

where

$$\left. \begin{aligned} f(u, z) &= -K_0(z) [I_0(u) - I_0'(b) K_0(u) / K_0'(b)], \\ &\quad b < u < z, \\ &= -K_0(u) [I_0(z) - I_0'(b) K_0(z) / K_0'(b)], \\ &\quad z < u < \infty. \end{aligned} \right\} \quad (5.4)$$

and

$$z = \kappa r, \quad b = \kappa a, \quad I_0'(z) = dI_0/dz, \quad K_0'(z) = dK_0/dz. \quad (5.5)$$

If ψ is again expanded as in Eq. (2.14), the solutions for the θ functions are

$$\theta_1(z) = -K_0(z)/K_0'(b),$$

$$\theta_m(z) = \int_b^\infty f(u, z) \Psi_m(u) u du, \quad m > 1, \quad (5.6)$$

where Ψ_m is given by Eq. (2.16). Hence, the problem is completely solved. The integrals of the second of Eq. (5.6) cannot be evaluated in finite terms and resort must be made to numerical integration.

Section 6. Cylinder Containing Electrolyte

This problem might be of interest in the analysis of streaming potentials and electro-osmosis through tubes sufficiently narrow for the double-layer thickness to be comparable with the radius. The equation for the

potential is again Eq. (5.1), but the boundary conditions are now

$$d\psi/dr|_0 = 0, \quad d\psi/dr|_a = 4\pi\sigma/\epsilon, \quad (6.1)$$

where a is again the radius and σ the charge density on the *inner* surface. The final solutions for the θ -functions are

$$\theta_1(z) = I_0(z)/I_0'(b);$$

$$\theta_m(z) = \int_0^b f(u, z) \Psi_m(u) u du, \quad m > 1, \quad (6.2)$$

where now

$$\left. \begin{aligned} f(u, z) &= -I_0(u) [K_0(z) - K_0'(b) I_0(z) / I_0'(b)], \\ &\quad 0 < u < z, \\ &= -I_0(z) [K_0(u) - K_0'(b) I_0(u) / I_0'(b)], \\ &\quad z < u < b, \end{aligned} \right\} \quad (6.3)$$

and $z, b, I_0'(z)$, and $K_0'(z)$ have the same meaning as in Eq. (5.5).

Section 7. Electrolyte Confined between Charged Coaxial Cylinders

This problem is formally very similar to the one solved in section 4. The boundary conditions are

$$d\psi/dr|_a = -4\pi\sigma/\epsilon, \quad d\psi/dr|_{a'} = 4\pi\sigma'/\epsilon, \quad (7.1)$$

where a is the radius, σ the charge density on the inner cylinder, and a' and σ' the corresponding quantities for the outer cylinder. Assuming an expansion for ψ of the same form as Eq. (4.5), where z is now equal to κr , the $\theta_{m,m'}(z)$ functions are given by the equations

$$\left. \begin{aligned} \theta_{1,0}(z) &= \frac{I_0(z) K_0'(b') - K_0(z) I_0'(b')}{I_0'(b') K_0'(b) - I_0'(b) K_0'(b')}, \\ \theta_{0,1}(z) &= \frac{I_0(z) K_0'(b) - K_0(z) I_0'(b)}{I_0'(b') K_0'(b) - I_0'(b) K_0'(b')}, \\ \theta_{m,m'}(z) &= \int_b^{b'} g(u, z) \Psi_{m,m'}(u) u du, \quad m+m' > 1, \end{aligned} \right\} \quad (7.2)$$

where

$$\left. \begin{aligned} g(u, z) &= [I_0(z) I_0(u) K_0'(b) K_0'(b') + K_0(z) K_0(u) I_0'(b) I_0'(b') - K_0(z) I_0(u) I_0'(b') K_0'(b) \\ &\quad - I_0(z) K_0(u) I_0'(b) K_0'(b')] / [I_0'(b') K_0'(b) - I_0'(b) K_0'(b')], \quad b < u < z, \\ &= [I_0(z) I_0(u) K_0'(b) K_0'(b') + K_0(z) K_0(u) I_0'(b) I_0'(b') - K_0(z) I_0(u) I_0'(b) K_0'(b') \\ &\quad - I_0(z) K_0(u) K_0'(b) I_0'(b')] / [I_0'(b') K_0'(b) - I_0'(b) K_0'(b')], \quad z < u < b', \end{aligned} \right\} \quad (7.3)$$

$$b = \kappa a, \quad b' = \kappa a',$$

and $\Psi_{m,m'}$ is given by Eq. (4.7).

PROBLEMS INVOLVING SPHERICAL BOUNDARIES

Section 8. Solid Sphere with Uniform Surface Charge in an Infinite Electrolyte

The solution in this case is of importance in the theory of cataphoresis.¹² If a is the radius of the sphere and Qe the total charge upon it, the potential in the electrolyte is given by

$$(d^2\psi/dr^2) + (2/r)(d\psi/dr) - \kappa^2\psi = \kappa^2\Psi, \quad (8.1)$$

$$\psi = 0, \quad r \rightarrow \infty; \quad d\psi/dr|_a = -Q/\epsilon a^2, \quad (8.2)$$

where r is the distance from the center of the sphere, and Ψ is again determined by Eq. (2.8). The solution follows the lines of the previous cases, and so we shall merely give the final results. If the ψ is expanded as a power series in Q

$$\psi = \sum_{m=1}^{\infty} e^{2m-1} (\epsilon a)^{-m} (-\mathbf{k}T)^{1-m} Q^m \theta_m(\kappa r), \quad (8.3)$$

then the θ_m functions are given by the relations

$$\theta_1(x) = be^{b-x}/(1+b)x, \quad (8.4)$$

$$\theta_m(x) = \int_b^{\infty} f(u, x) \Psi u du, \quad m > 1, \quad (8.5)$$

where

$$f(u, x) = \begin{cases} -\frac{1}{2x} \left[e^{u-x} + \frac{(b-1)}{(b+1)} e^{2b-u-x} \right], & u < x; \\ -\frac{1}{2x} \left[e^{x-u} + \frac{(b-1)}{(b+1)} e^{2b-u-x} \right], & u > x, \end{cases} \quad (8.6)$$

and $b = \kappa a$; Ψ_m is again defined by Eq. (2.16).

Section 9. Sphere of Electrolyte Immersed in Another Electrolyte of Different Composition

This may be regarded as an extension of the previous problem. It may be of interest in the study of the properties of emulsions, which consist of liquids dispersed in small droplets in a medium formed by another liquid. The solution outside the sphere will again be given by a series of the type (8.3), if Qe is the total charge contained in the sphere; for the solution inside we have to obtain the appropriate series in powers of Q . Suppose all quantities for $r < a$, where a is the radius, are distinguished by the superscript (1) and for $r > a$ by the superscript (2). The potential $\psi^{(1)}$ obeys an equation of the form of Eq. (8.1), but the boundary conditions are different,

$$(d^2\psi^{(1)}/dr^2) + (2/r)(d\psi^{(1)}/dr) + \kappa^{(1)2}\psi^{(1)} = \kappa^{(1)2}\Psi^{(1)}, \quad (9.1)$$

$$d\psi^{(1)}/dr|_0 = 0, \quad d\psi^{(1)}/dr|_a = -eQ/a^2\epsilon^{(1)}. \quad (9.2)$$

The first of Eq. (9.2) follows, since the charge density

¹² F. Booth, Proc. Roy. Soc. (London) A203, 514 (1950).

must remain finite at the origin. In the above equations, the zero of the potential $\psi^{(1)}$ is the potential which gives electroneutrality; this means that if $n_i^{(1)}$ ($i=1, \dots, s^{(1)}$) denote the concentrations when $\psi^{(1)}$ is zero, then we have

$$\sum_{i=1}^{s^{(1)}} n_i^{(1)} z_i^{(1)} = 0. \quad (9.3)$$

In general, the zero of the two potentials $\psi^{(1)}$ and $\psi^{(2)}$ will differ; but this raises no difficulties, as we shall see. The general solution of Eq. (9.1) is

$$\psi^{(1)} = \frac{C_1 e^y}{y} + \frac{C_2 e^{-y}}{y} - \frac{1}{2y} \int_0^y \Psi^{(1)} u (e^{u-y} - e^{y-u}) du, \quad (9.4)$$

where

$$y = \kappa^{(1)} r, \quad (9.5)$$

and C_1 and C_2 are constants. From the first of Eq. (9.2), it follows that

$$C_1 = -C_2, \quad (9.6)$$

and from the second we find

$$C_1 = -F(c) \left[eQc/\epsilon^{(1)} a + \frac{1}{2} \int_0^c \Psi^{(1)} u [e^{u-c}(c+1) + e^{c-u}(c-1)] du \right], \quad (9.7)$$

where

$$F(c) = [e^c(c-1) + e^{-c}(c+1)]^{-1}; \quad c = \kappa^{(1)} a. \quad (9.8)$$

If we now let

$$\psi^{(1)} = \sum_{m=1}^{\infty} e^{2m-1} (\epsilon^{(1)} a)^{-m} (-\mathbf{k}T)^{1-m} Q^m \theta_m^{(1)}(\kappa^{(1)} r), \quad (9.9)$$

then we find

$$\left. \begin{aligned} \theta_1^{(1)}(y) &= cF(c) [e^{-y} - e^y]/y, \\ \theta_m^{(1)}(y) &= \int_0^b \Psi_m^{(1)} f^{(1)}(u, y) u du, \quad m > 1, \end{aligned} \right\} \quad (9.10)$$

where

$$\left. \begin{aligned} f^{(1)}(u, y) &= \frac{1}{2} F(c) [(c+1)e^{y-c} + (c-1)e^{c-y}] \\ &\quad \times (e^{-u} - e^u), \quad 0 < u < y, \\ &= \frac{1}{2} F(c) [(c+1)e^{u-c} + (c-1)e^{c-u}] \\ &\quad \times (e^{-y} - e^y), \quad y < u < c. \end{aligned} \right\} \quad (9.11)$$

The potential is now completely determined. For any point with r greater than a , a series of the type (8.3) suffices. The potential at any point for r less than a , referred to the potential at infinity as zero, is simply

$$\psi(r) = \psi^{(2)}(a) + \psi^{(1)}(r) - \psi^{(1)}(a). \quad (9.12)$$