CONTRIBUTIONS
TO THE
THEORY AND APPLICATION OF ELECTROPHORESIS

With Special Reference to Polyelectrolytes

by

Richard Andrew Mills, B.Sc.

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To my Mother and Father

SUMMARY

This thesis commences with macroscopic transport theory of electrophoresis-diffusion processes. The differential equations for multicomponent systems are formulated, an integral equation being derived which relates concentration gradients to the mobility distribution function in cases where the transport equations are linear. This integral equation is then solved and properties of the mobility distribution function discussed. Following this general theory, three-ion systems of polyelectrolyte and added salt are considered. Characteristic parameters describing perturbations from linearity (in the transport equation) and the concept of electrophoretic similarity are introduced, followed by a detailed analysis of first-order perturbation in the electrophoretic term. The solutions obtained are discussed with reference to mobility determinations and boundary spreading. Higher-order perturbations are also discussed, in particular their effects on velocities of sharp boundaries and enantiography of conjugate patterns.

The next part of this thesis deals with microscopic transport theory, commencing with a general discussion and formulation of the probelm. Reduction of the potential problem is considered, followed by methods of analysis for the surface charge density of particles undergoing transport.

The relation between electrophoretic charge and polyionic charge is discussed with reference to ion-binding. The above is then exemplified by a consideration of cylindrical macroions.

The final part contains a formulation relating electrophoretic mobilities to kinetic parameters in polyelectrolyte systems. Mobility-reaction coordinate relations are analysed, mobility distribution parameters and the frequency distribution of various species in a given system being correlated and interpreted.

This thesis contains no material previously submitted for a degree or diploma in any university and, to the best of my knowledge and belief, contains no material previously written by any other person, except where due reference is made in the text.

R. A. Wills

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INTRODUCTION

Isolation of the components of complex mixtures and their characterisation by means of electrophoresis have been the objects of numerous experiments on a wide variety of materials. Studies have been particularly directed towards biologically important macromolecules, viruses and cells and a general survey of the theory and applications has been given by Abramson, Moyer and Gorin(1). A more recent assessment of work in this field may be found in the monograph by Bier(2).

In recent years, however, there has been a greater awareness of the importance of electrophoretic theory in physico-chemical studies of such phenomena as the configuration of coiled polyelectrolytes, counterion-binding to charged sites of polyions and determination of the effective charge on a polyion. The electrophoretic method has also been found useful in a number of kinetic studies and promises insight into the mechanisms of certain chemical changes.

Much progress has yet to be made in the coordination of the macroscopic approach (isolation and characterisation) with these physico-chemical studies but present indications are encouraging. Recent investigations have suggested the important role electrophoretic measurements may play in cytology(3) and neurology(4), possibly leading to a better understanding of the molecular basis of biological processes.

The development of electrophoretic theory has necessarily led to more sophisticated mathematical treatments but, as often happens, mathematical formulation of the problem has tended to outstrip available methods of solution (c.f. sedimentation analysis(5)). A major difficulty has been the appearance of nonlinear differential equations in the more realistic mathematical models and these are often beyond solution by existing methods(6). It is hoped that the present studies will be of assistance in using these models to interpret experimental results.

1. SCOPE OF THE INVESTIGATION

This work is devoted to three aspects of electrophoresis. Part I contains macroscopic transport theory associated with mobility determinations and Part II is a study of the relations between charge, zeta-potential and mobility. In Part III it is shown how charge-mobility relations may be applied to problems in reaction kinetics.

In a treatise of this size it is impossible to consider every aspect of electrophoresis in detail. The macroscopic theory given here deals only with boundary-gradient electrophoresis; certain accompanying phenomena, such as the effects of chemical reactions, strong electric fields, highly divergent electric fields (dielectrophoresis) or superimposed magnetic fields (electromagnetophoresis) have been excluded.

Ionic theory has also been restricted, the potential problem being solved only for cylindrical particles (and after neglecting certain factors, notably nonuniformity of surface charge, valence effects of supporting electrolytes, hydrodynamic and electrostatic interactions and particle conductance). The mobility-zeta-potential relationship linking the macroscopic and microscopic theory has not been investigated.

2. METHODS OF APPROACH

In each case, relevant physico-chemical concepts are synthesised in a mathematical structure, this being based wherever possible on experimental observations. While some of the parameters involved cannot as yet be determined experimentally, the general treatment given here allows for possible advances in techniques of measurement and also provides some qualitative understanding of the subject. This is important since, in view of the present state of electrophoretic theory, it is often difficult to select the dominant parameters in a given experimental situation.

The mathematical formulations are analysed to provide relations that may be used to estimate governing parameters from experimental results. In doing this, particular attention has been paid to nonlinear aspects of the theory, analytical procedures being used as far as possible before having recourse to numerical methods. The use of dimensionless monomials as another notable feature of these analyses and, in view of the multiplicity of factors to be incorporated into the mathematical framework, is particularly helpful in simplifying the algebraic detail. Parameters occurring in equations written in terms of dimensionless variables also provide a means of characterisation and comparison of systems.

PART I

MACROSCOPIC TRANSPORT THEORY

CHAPTER 1

MULTICOMPONENT SYSTEMS

1. INTRODUCTION

Because of the simultaneous influence of a number of factors in electrophoresis experiments, especially in polyelectrolyte solutions, determinations of mobilities require careful analyses of experimental patterns. For this reason a complete discussion of the macroscopic transport equations is given below, taking into consideration all the relevant factors. A general solution is not practicable and when analysing the results of particular experiments one is forced to make a judicious elimination of terms, then to endeavour to solve the simpler problem remaining. However, by first considering the phenomenological equations in general form, it is felt that more reliable interpretations of particular systems will result from due consideration of all the governing factors before deciding which of these may be neglected. Where possible, an entire boundary pattern should be utilised, not merely a single point of the boundary.

This chapter commences with a more complete formulation of electrophoresis-diffusion processes than has been available hitherto. It is then shown how, under suitable experimental conditions, the differential equations lead to an integral equation relating concentration gradients to mobility distributions. This equation has been quoted elsewhere but a new method of solution based on a knowledge of the distribution function is proposed. The general result obtained is found to agree with a number of special cases considered by earlier workers and may also be of use in calculating higher moments of the mobility distribution function.

2. FACTORS AFFECTING THE GEOMETRY OF BOUNDARY PATTERNS

Before proceeding to a mathematical formulation of the problem, the governing factors in electrophoresis-diffusion systems will be outlined, paying special attention to polyelectrolyte solutions.

(i) Diffusion

A review of diffusion in electrolytic solutions has been given recently by Wills(7). Rates of diffusion in polyelectrolyte solutions are largely dependent on molecular parameters describing shape and size(8). Thus if the polymer under consideration is polydisperse with respect to molecular weight, the problem becomes one of multicomponent diffusion and more complex phenomonological equations are required for a complete description than would be necessary in the case of monodisperse polymers. A notation based on tensor analysis has been discussed by Ljunggren(9). Charge effects also occur,(10) even in simple diffusion (i.e. in the absence of an applied electric field). A further difficulty arises in the case of polymers because rates of diffusion may be reduced by what has been termed "gel-like" behaviour, the polymer in "solution" being regarded as a single network rather than as a collection of isolated particles. Finally, it should be noted that diffusion coefficients may be markedly concentration-dependent. Nagasawa and Fujita(12) have shown how this can drastically modify Schlieren patterns.

In spite of these complications, however, a single diffusion coefficient will suffice for the type of interpretation to be considered here, namely where electrophoretic effects are much more marked than those of diffusion. When diffusion is absent, concentration profiles exhibit discontinuities and, as mentioned by Makino and Rogers,(13) the main effect of small-scale diffusion is to "smear out" such discontinuities. A single diffusion coefficient is sufficient to describe this effect.

(ii) Reactions

Reactions in solution affect the shape of boundary patterns and the number of peaks does not necessarily equal the number of components present(14).

Even when equilibrium between polyions and their counterions is achieved instantaneously at all points in the solution, a superimposed electric field will increase the apparent diffusion coefficient to some value above that obtained in simple diffusion. This is the phenomenon of electrodiffusion, the theory of which has been applied to the study of the kinetics of ionic reactions(15). Some practical considerations have recently been discussed by Ljunggren(16). Random mobility fluctuations about an equilibrium state are responsible for this effect but electrodiffusion does not proceed independently of ordinary diffusion. Thus boundary spreading due to ordinary diffusion and electrodiffusion are not simply additive. Also the total concentration profile in the limit of zero external field does not obey a simple diffusion equation unless all interacting species have identical diffusion coefficients.

(iii) Concentration-Dependence of Mobilities

The mobility of a polyion may vary markedly from point to point in an electrophoretic boundary due to variations of pH with concentration. These variations strongly influence the extent of counterion binding to polyelectrolyte chains, giving rise to changes of charge and hence of mobility. De Wael and Wegelin(17) have also shown that the concentration of supporting electrolyte is not constant throughout a moving boundary. Higher concentrations of such an electrolyte favour counterion binding and hence cause a reduction in mobility.

(iv) Field Strength Gradients

Concentration gradients of electrolytes undergoing electrophoresis will produce variation of field strength, as will the gradients of supporting electrolyte concentration mentioned above. Ion binding to polyions will reduce the contributions of both polyions and small ions to the conductivity of the solution, thus raising the field strength.

(v) Electrophoretic Heterogeneity

If a substance contains species of various electrophoretic mobilities, its boundary concentration-gradient patterns will tend to spread more rapidly than in the case of homogeneous solutes.(18)

3. GENERAL FORMULATION OF THE TRANSPORT EQUATIONS

The conservation equations for a system of N components may be written(19)

$$\frac{\partial C_i}{\partial t} = - \underline{\nabla} \cdot \underline{J}_i + R_i \qquad i = 1, 2, \ldots N \qquad (1)$$

where C_i = concentration of i^{th} component.

$\underline{J}_i$ = flux of component i (a vector whose j^{th} element gives the molar rate at which i crosses unit area normal to the j^{th} coordinate axis in the positive direction of that axis).

R_i = rate of production of component i by reaction.

In certain starch-gel electrophoresis experiments(20) and in electromagnetophoresis,(21) more than one space dimension must be considered in formulating the governing equations. These special cases will not be considered here and one space coordinate (x) will suffice. Using a single diffusion coefficient D, the flux of component i may then be described by the scaler J_i given by

$$J_i = - \left\{ D \frac{\partial C_i}{\partial x} - u_i(\underline{C}) . E(\underline{C}) . C_i \right\} \qquad i = 1, 2, \ldots N \qquad (2)$$

where u_i is the mobility of the i^{th} component and $\underline{C} = (C_1, C_2, \ldots C_N)$ is the composition vector for the system. The mobilities (u_i) and field strength (E) in equation (2) are written in terms of the composition vector because the concentrations of <u>all</u> species in solution are liable to influence the flux of any one component (c.f. the Johnston-Ogston effect in sedimentation$^{(5)}$). One example of the differential equations (for transport by diffusion and electrophoresis, accompanied by first order reversible reaction) has been given by Bak and Kauman,$^{(22)}$ for a two-component system. In the analysis to follow, such kinetic effects will not be considered. In addition, to keep the problem in tractable form, equations (2) will be written in terms of the total solute concentration (C) given by

$$C = \sum_{i=1}^{N} C_i \qquad (3)$$

Thus the relations (2) become, to this degree of approximation,

$$J_i = -\left\{D\frac{\partial C_i}{\partial x} - u_i(C).E(C).C_i\right\} \qquad i = 1,2, \ldots .N \qquad (4)$$

Combination of (1) and (4) then yields the system of quasi-linear equations

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x}\left[D(C).\frac{\partial C_i}{\partial x} - u_i(C).E(C).C_i\right] \qquad i = 1,2, \ldots .N \qquad (5)$$

4. MOBILITY DISTRIBUTIONS

Analysis in the case of heterogeneous systems is much more difficult than for electrophoretically homogeneous substances and care must be taken not to introduce too many parameters. Alexander and Johnson(23) have mentioned similar difficulties in connection with polydisperse substances undergoing simple diffusion and warn against attempts to give detailed analyses of experiments carried out on unfractionated materials. In view of the more complex situation to be considered here, attention will be focused on very dilute solutions, where the field strength and mobilities are essentially constant for any particular experiment.

(i) Relation between Total Concentration Gradient and the Mobility Distribution Function

Under the conditions just given, the relations (5) are linear and solutions are readily found. Typically, the concentrations of the various species will be given by the solution to the Cauchy problem,

$$\frac{\partial C_i(x,t)}{\partial t} = D \frac{\partial^2 C_i(x,t)}{\partial x^2} - u_i E \frac{\partial C_i(x,t)}{\partial x} \qquad t \geq t_o > 0, \; -\infty < x < \infty, \quad i = 1,2, \ldots N \tag{6}$$

$$C_i(x,t_o) = C_i^{\,o}\, \phi(x) \tag{7}$$

where diffusion has been allowed to proceed for a time t_o before electrophoresis, i.e.

$$\phi(x) = \frac{1}{2}\,\mathrm{erf}_c\,\frac{-x}{2\sqrt{Dt_o}} \tag{8}$$

This problem may be solved (see Appendix 1) and in analysing Schlieren patterns it will be convenient to use the intermediate integrals

$$\frac{\partial C_i}{\partial x} = \frac{C_i^{\,o}}{\sqrt{4\pi Dt}}\,.\,e^{-(x-u_iEt_E)^2/4Dt} \qquad i = 1, 2, \ldots.N \tag{9}$$

where t_E is the time for which electrophoresis has been in progress. The gradient of total concentration is then given by

$$\frac{\partial C}{\partial x} = \frac{1}{\sqrt{4\pi Dt}} \sum_{i=1}^{N} C_i^{\,o}\; e^{-(x-u_iEt_E)^2/4Dt} \tag{10}$$

If, in the initially uniform region $x > 0$, $g(u_i)$ is the mole-fraction of particles with mobility u_i and the total concentration is C^o, then

$$g(u_i) = \frac{C_i^{\,o}}{C^o} \tag{11}$$

and (10) may be rewritten

$$\frac{\partial c}{\partial x} = \frac{c^{0}}{\sqrt{4\pi Dt}} \sum_{i=1}^{N} g(u_i)\, e^{-(x-u_i E t_E)^2/4Dt} \qquad (12)$$

Heterogeneity arising from (for example) a chain of first-order reactions may be described in terms of a discrete distribution of mobilities (see Chapter 5) and equation (12) relates concentration gradients to such mobility distributions. It will be seen that (12) involves a superposition of functions of Gaussian form. In practice[(24)] the resolution of such functions into their components is only practicable for small N and another method for finding the mobility distribution must be sought. With this in mind, equation (12) will be recast in an alternative form.

Due to the large number (N) of charged sites on a macromolecular chain, it is permissible to approximate $g(u_i)$ by means of a suitable continuous distribution function $q(u)$, i.e. a function such that the fraction of polyions (denoted by $Q(u_i,u_j)$) with mobility u in the range (u_i,u_j) is given by

$$Q(u_i,u_j) = \int_{u_i}^{u_j} q(u)\,du \qquad (13)$$

Equation (12) is then replaced by the integral equation

$$\frac{\partial C}{\partial x} = \frac{C^0}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} e^{-(x-uEt_E)^2/4Dt}\, q(u)du \qquad (14)$$

(ii) Solution for the Mobility Distribution Function

Since equation (14) is an integral equation of the first kind, explicit solution for $q(u)$ is difficult on both theoretical and practical grounds. Every object function ($q(u)$) which is merely integrable produces a differentiable result function ($\partial C/\partial x$), i.e. the manifold of $q(u)$ is transformed into a much more restrictive manifold by the transformation (14)$^{(25)}$. Thus unless the function $\partial C/\partial x$ satisfies very stringent conditions, solution for $q(u)$ is not possible. Equations of the type (14) have been formally solved by Morse and Feshbach$^{(26)}$ but their method leads to a function $q(u)$ expressed in terms of the space differential coefficients of $\partial C/\partial x$ at $x = 0$, i.e. $\partial C/\partial x$ must be analytic in x at $x = 0$. In practice, even if $\partial C/\partial x$ does meet these requirements, successive numerical differentiation of data from experimental patterns (of limited accuracy) is unsatisfactory. Brown and Cann$^{(27)}$ were able to find another form of the explicit solution for mobility distributions by using an empirical expression to describe observed concentration-gradient patterns. This method (see discussion by Baldwin et al)(28) is restricted by the fact that the final expression must be truncated before numerical computation can be carried out, yet the point of truncation may only be assessed from estimates of the higher terms in the series solution. Such estimates are extremely prone to error. The method to be described here is less arbitrary than the use of empirical formulae, provided the form of q(u) is known (e.g. from kinetic considerations). In addition, one is able to compute an upper bound to the error involved in truncating after a given number of terms.

An implicit method of solution will be used in which a suitable expression is substituted for q(u) in equation (14). The mobility distribution arising from chemical reaction in polyelectrolyte systems is almost Gaussian so that a Gram-Charlier series(29,30) is adequate and one may write

$$q(u) = \frac{1}{h\sqrt{2\pi}}\, e^{-(u-\bar{u})^2/2h^2} \left\{ 1 + \sum_{j=3}^{\infty} \frac{\alpha_j}{j!} H_j \left(\frac{u - \bar{u}}{h} \right) \right\} \qquad (15)$$

where $\bar{u}$ and h are the mean and standard deviation, respectively, of the mobility distribution. The α_j may be expressed in terms of the higher moments of the distribution and H_j is the Hermite polynomial of order j. It will be noted that (15) is more general than earlier treatments in that the polymer need not be at its average iso-electric point ($\bar{u} = 0$). If (15) is substituted in (14) and the necessary integration performed (see Appendix II), one obtains the result

$$\frac{\partial C}{\partial x} = \frac{C^0}{\Sigma\cdot\sqrt{2\pi}}\, e^{-(x-\bar{u}Et_E)^2/2\Sigma^2} \left\{ 1 + \sum_{j=3}^{\infty} \frac{\alpha_j \omega^j}{j!} H_j \left(\frac{x - \bar{u}Et_E}{\Sigma} \right) \right\} \qquad (16)$$

where ω and Σ are defined by

$$\omega = \frac{hEt_E}{\Sigma} \qquad (17)$$

$$\Sigma^2 = h^2E^2t_E^2 + 2Dt \qquad (18)$$

Equations (16) - (18) relate the mobility distribution parameters ($\bar{u}$, h and the α_j) to the measured quantities $\partial C/\partial x$, x, t_E, and E by means of a Gram-Charlier series, i.e. the concentration gradient curve is of the same form as the mobility distribution function (cf. the explicit solution for $g(u)$ found by Brown and Cann$^{(27)}$).

(iii) Evaluation of Results

(a) When diffusion is negligible, (18) shows that the standard deviation of the concentration-gradient curve is proportional to the time of electrophoresis (in agreement with the result of Sharp et al$^{(18)}$).

(b) For homogeneous polymers ($h = 0$), Σ^2 varies directly as the total time t. Thus, curvature of a plot of Σ^2 as a function of t will serve as a diagnostic for heterogeneity. It is important to remember, however, that solutions must be sufficiently dilute to prevent any appreciable influence of concentration-dependence of diffusion coefficients, field strengths or mobilities.

(c) In general, if one rewrites (18) in the form

$$\frac{\Sigma^2}{2t} = D + \frac{h^2 E^2}{2} \cdot \frac{t_E^{\;2}}{t} , \qquad (19)$$

a plot of $\Sigma^2/2t$ as a function of $t_E^{\;2}/t$ is seen to be a straight line. This agrees with the calculations carried out by Alberty(31) who has used an equation of this type to determine some values of the heterogeneity constant (h) for a number of proteins(32). Also, if $\bar{x}$ denotes the position of the centroid of the $\partial C/\partial x$ curve, equation (16) immediately gives

$$\bar{x} = \bar{u}Et_E \tag{20}$$

Longsworth(33) has shown that in homogeneous systems the centroids of $\partial C/\partial x$ patterns should be used in calculating mobilities. Equation (20) extends this result to mobility distributions of the type (15) and shows that the centroid will now yield the average mobility.

In practice one can only measure about four moments of a curve about a given point (to any satisfactory degree of precision). In addition there are difficulties in correlating observed refractive index gradients and concentration gradients(34), simple proportionality between these quantities often being assumed. Experimental limitations of this type are discussed by Fujita(5) in his study of sedimentation in chemically reacting systems. Nevertheless this theory has been developed because electrophoresis, as a tool in studying reaction kinetics, is most valuable in the investigation of slow reactions on account of its ability to register small changes of charge and it is in the case of very slow reactions that mobility distributions are most likely to deviate from normality (see Chapter 5). Such mobility distributions have been found (35) and it should be possible to determine at least one of the a_j. (Similarly, non-normal distributions of sedimentation coefficients have been reported for calf thymus DNA (36).)

CHAPTER 2

THREE-ION SYSTEMS

1. INTRODUCTION

Electrophoretic velocities have usually been equated to the velocities of maxima in Schlieren refractive-index gradient curves. These, in conjunction with conductivity measurements (referring in most cases to the bulk of the electrolyte under study), have been used to calculate mobilities. In general, however, the values obtained from ascending and descending boundaries do not coincide and the discrepancy becomes worse at higher concentrations of the substance undergoing electrophoresis. A typical set of values obtained by Nagasawa et al(37) is as shown in Figure 1.

In view of these difficulties, it has been customary to minimise the influence of factors with which one is not directly concerned (e.g. field strength gradients through boundaries may be reduced by including a sufficiently large quantity of supporting electrolyte) but this may also tend to restrict the influence of an important effect being studied, e.g. variation of mobility with concentration. Thus a more detailed analysis is required so that one may allow certain secondary factors to be operative. When a polyelectrolyte yields only a single electrophoretic species (apart from small

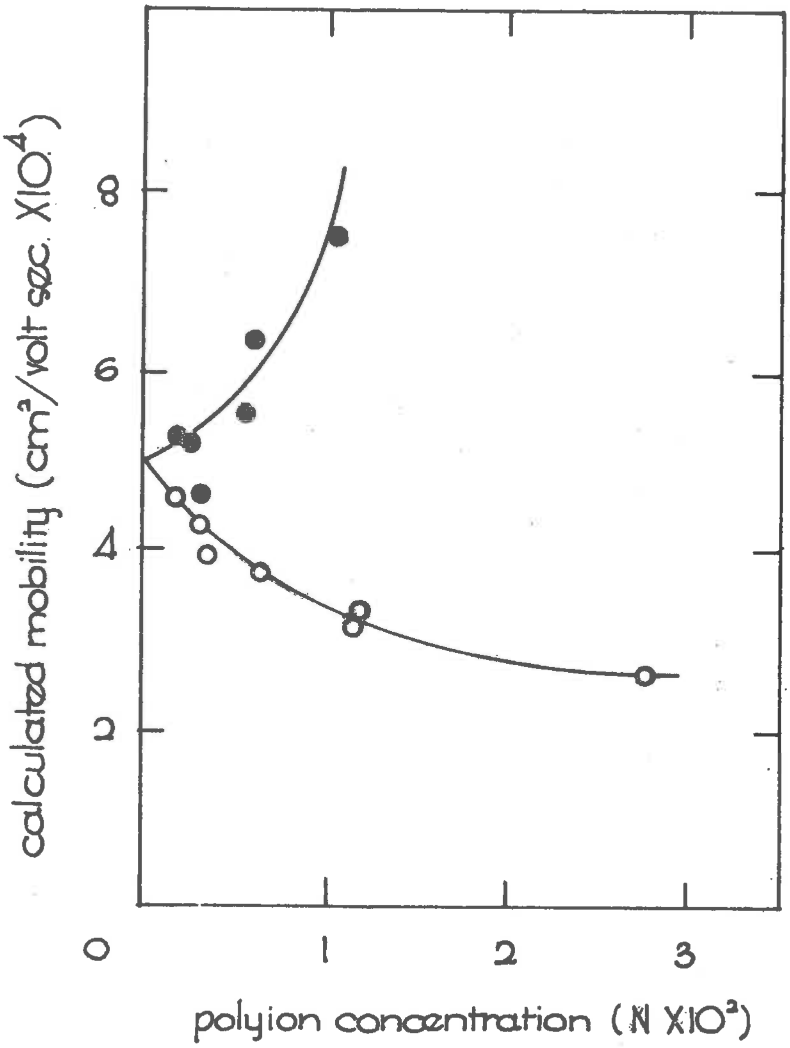

Fig. I. Variation of calculated mobility with polyion concentration for sodium polyvinyl alcohol sulphate in 0·005 N NaCl (after Nagasawa et al.)

- ● calculated from ascending boundary.
- ○ calculated from descending boundary.

ions), it is possible to study more concentrated solutions, with associated secondary effects, than considered in Chapter 1 because the set (5) governing the concentration of polyions reduces to a single equation. This may be solved without assuming a constant value for the field strength or mobility. The other conditions involved in the formulation of equations (5) are still assumed to hold.

This chapter deals with the formulation and analysis of the transport equation for the concentration of polyions in a solution containing polyelectrolyte and simple electrolyte (for simplicity, it will be assumed that the latter contributes ions identical to the counterions of the polyelectrolyte). Characteristic parameters and the concept of electrophoretic similarity are introduced, followed by a consideration of perturbation in the electrophoretic term by concentration-dependent field strengths or mobilities. The solution in the case of first-order perturbation is obtained, this being shown to agree with a number of results obtained by other workers. This solution is then used in calculating mobilities from the velocities of both moving boundaries. It is also shown how first-order perturbation leads to symmetric spreading or sharpening of boundaries and a method is suggested for the calculation of diffusion coefficients in these cases. Higher-order perturbations are then considered, a general expression for the velocity of a sharp boundary being derived. In the special case of constant mobility, this shows how boundary velocity combined with the field strength in the supporting electrolyte or bulk of the polymer solution yields a "zeroth-order" or "first-order" approximation, respectively. The conditions for enantiography of conjugate patterns are derived and confirm some apparently intuitive suggestions made by others. The final section deals with the iterative solution of the transport equation for perturbations of second or higher orders (associated with asymmetric boundaries).

2. CHARACTERISTIC PARAMETERS AND ELECTROPHORETIC SIMILARITY

(i) Characteristic Parameters

If C is the concentration of polyelectrolyte at position x and time t, equations (5) reduce to a single parabolic equation of the Fokker-Planck type[(38)], viz.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D(C) \cdot \frac{\partial C}{\partial x} - u(C) \cdot E(C) \cdot C\right] \qquad (21)$$

The set $\underline{U} = (D, u, E)$ is characteristic of the particular compound being investigated and serves as a basis for comparison with other substances. Thus, as mentioned in Chapter 1, the diffusion coefficient is closely related to molecular parameters describing shape and size (e.g. the axial ratio of the equivalent hydrodynamic ellipsoid), while the electrophoretic mobility is strongly dependent upon the surface charge density of the suspended particles$^{(2)}$. The field strength is largely an external factor in the sense that it depends on the applied potential, but its divergence is also bound up with the properties of the charged particles themselves.

As mentioned in the introduction, non-linearities occur in the differential equations of electrophoresis, these being due here to the concentration-dependence of the elements of $\underset{\sim}{U}$. Nagasawa and Fujita$^{(12)}$ have intimated that this aspect of the diffusion coefficient may be as important as activity or osmotic coefficients in the characterisation of polyelectrolyte solutions. It thus appears that a set of parameters describing the concentration dependence of $\underset{\sim}{U}$ would provide a concise method of characterisation under a much wider variety of conditions.

Before deriving these parameters, it will be convenient to introduce the dimensionless variable θ defined by

$$\theta(x,t) = \frac{C(x,t)}{C^o} \qquad (0 \leq \theta \leq 1), \tag{22}$$

where C° is a suitable reference value. Thus a typical set of initial conditions defining C° would be

$$C(x,o) = C^{\circ} \cdot H(x) \tag{23}$$

in which H(x) is the Heaviside unit step function defined by(39)

$$H(x) = \begin{cases} 1 \text{ if } x > o \\ 0 \text{ if } x < o \end{cases} \tag{24}$$

A set of equations analogous to the virial expansion may then be written

$$D = D_o\left\{1 + \sum_{i=1}^{\infty} k_i \theta^i\right\} \tag{25}$$

$$u = u_o\left\{1 + \sum_{i=1}^{\infty} r_i \theta^i\right\} \tag{26}$$

$$E = E_o\left\{1 + \sum_{i=1}^{\infty} \lambda_i \theta^i\right\} \tag{27}$$

Alternative expressions, such as the one proposed by Gosting and Fujita(40) for the diffusion coefficient, may be preferable under certain circumstances but for present purposes equations (25) to (27) are adequate. In practice, only a limited number of the coefficients in these equations can be determined and the argument here will be restricted to a discussion of D_o, u_o, E_o, k_1, r_1 and λ_1, although immediate extension to a greater number of characteristic constants (used in Section 4 of this chapter) will be obvious. For convenience u_o has been used rather than the customary zeta-potential but the latter might equally well have been included in the discussion. Actually, the limiting mobility at zero concentration and the zeta-potential are quite simply related (see, for example, Levich$^{(41)}$).

(ii) Reduction of the Transport Equation

Since there is now only one dependent variable, it is possible to use dimensionless quantities$^{(42)}$ to simplify the analysis. Thus, if (25) to (27) are truncated after the first power of θ, (21) becomes

$$\frac{\partial\theta}{\partial T} = k_1\theta\,\frac{\partial^2\theta}{\partial X^2} + \frac{\partial^2\theta}{\partial X^2} + h\left(\frac{\partial\theta}{\partial X}\right)^2$$

$$- 3\lambda_1 r_1\theta^2\,\frac{\partial\theta}{\partial X} - 2(\lambda_1 + r_1)\theta\,\frac{\partial\theta}{\partial X} - \frac{\partial\theta}{\partial X} \qquad (28)$$

(see appendix III)

(iii) Electrophoretic Similarity

Although dimensional analysis alone will not give the complete solution to the transport equation, the π-theorem does indicate the general form of the latter and one is able to write

$$\theta = \theta(X, T, k_1, \tau_1, \lambda_1). \tag{29}$$

It is immediately obvious from equation (29) that regardless of the limiting diffusivity (D_o) or mobility (u_o) of the electrophoresing species, or even of the applied field strength (E_o), all substances having the same values for the coefficients k_1, τ_1 and λ_1 have the same $\theta - X - T$ behaviour. Such substances may be said to be electrophoretically similar and it follows from the definitions of the above coefficients that interionic interactions during electrophoresis will be identical for all electrophoretically similar compounds.[*]

[*] It may be noted that if the characteristic constants k_1, τ_1 and λ_1 are not considered (as in the work of Sharp et al(18)), the form of solution obtained by dimensional analysis becomes

$$\theta = \theta(X, T). \tag{30}$$

Now equation (21) may be solved subject to the initial condition (23), the result (in terms of the new variables) being

$$\theta = \frac{1}{2} \operatorname{erf}_c \left(\frac{T - X}{2\sqrt{T}} \right) \tag{31}$$

This is seen to be in accordance with the general form of solution indicated by equation (30).

To test for electrophoretic similarity of systems, the constants D_o, u_o and E_o are evaluated first. The work of Sharp and co-workers$^{(18)}$ enables one to calculate D_o, u_o and E_o from experimental curves, the degree of accuracy of this method improving as more dilute solutions are investigated (it will be remembered that their treatment is equivalent to assuming $k' = f' = \lambda' = 0$). Thus, extrapolation to infinite dilution will yield the required values which are then used in the diagonal transformation of variables defined by

$$\begin{pmatrix} \theta \\ X \\ T \end{pmatrix} = \begin{pmatrix} 1/C_o & 0 & 0 \\ 0 & u_oE_o/D_o & 0 \\ 0 & 0 & (u_oE_o)^2/D_o \end{pmatrix} \begin{pmatrix} C \\ x \\ t \end{pmatrix} \qquad (32)$$

Experimental observations of $C(x,t)$ may then be converted to values of $\theta(X,T)$ via equations (32) and it then follows from equation (29) that solution surfaces defined by $\theta(X,T)$ in (θ,X,T) space will be identical for electrophoretically similar systems.

3. THE LIMITING CASE

Before passing to more general considerations, the reduced concentration-gradient curve for the case $k_i = r_i = \lambda_i = 0$ $(i=1,2, \ldots)$ may be written

$$\frac{\partial\theta}{\partial X} = \frac{1}{\sqrt{4\pi T}} e^{-(X - (T-T_o))^2/4T} \qquad (33)$$

This result follows directly from Appendix I (for an initial condition of the form (8)). Systems for which this is true are examples of the simplest type of electrophoretic similarity and are approximately realised when the concentration of the substance undergoing electrophoresis is low or when there is a high concentration of supporting electrolyte.

4. FIRST-ORDER PERTURBATIONS IN THE ELECTROPHORETIC TERM

As discussed in Section 2 (iv) of Chapter 1, the field strength will vary across an electrophoretic boundary, such variations being minimal under the conditions mentioned in the limiting case above. In certain systems, however, the introduction of sufficient supporting electrolyte to effectively eliminate field strength gradients will considerably reduce mobilities, perhaps bringing them close to zero (the isoelectric point). In fact, ion-binding to polyelectrolytes may be so strong that as supporting electrolyte is added, a reversal of charge occurs. Finally, the use of higher concentrations of electrophoretic species (tending to increase field strength gradients) will make boundaries more stable with respect to convection. For these reasons certain studies require that appreciable field strength gradients be allowed to occur and it is the analysis of these systems that will now be discussed.

This type of problem was considered by Stockmayer(43) who showed that spreading of boundaries depends, in part, on the magnitude of field strength gradients. Considering only first-order varistions of field strength (and assuming a constant mobility), he found an integral form of the solution to the transport equation for a moving boundary between two solutions of the same salt.

An analogous solution for the three-ion system of polyelectrolyte and simple salt is presented in part (ii) of this Section, followed by an analysis of this in part (iii). The Section concludes with a consideration of stationary boundaries and a further analysis of boundary velocity and spreading.

(i) Variation of Field Strength with Polymer Concentration

If the expression for the field strength as a function of concentration is truncated after two terms, one obtains the approximate result

$$E = E_0(1 + \lambda_1 C) \qquad (34)$$

To justify the use of this expression, it may be noted that various authors(44,45) have found that the contribution of a polyelectrolyte to the conductance of an aqueous solution of simple salt (here used as supporting electrolyte) is relatively small and of almost the same magnitude as the ionic conductance of the polyions (if it is assumed that the conductance of the simple salt is not appreciably changed by the presence of polyions). Hence the total specific conductance (x_T) is obtained by adding a term of the form $c_1\theta$ (c_1 = const.) to the specific conductance of the simple salt solution (x_S), i.e.

$$x_T = x_S + c_1\theta \qquad (35)$$

The term $c_1\theta$ represents the ionic conductance of the polyions ($<<< x_S$ for concentrations of simple electrolyte that are not too low), higher powers of θ being negligible under these conditions. Since the concentrations of both simple salt and polyions vary across a boundary(17), x_S will not be constant. Again a linear variation of the type

$$x_S = x_S^{0} + c_2\theta \quad (c_2 < 0 \text{ for a three-ion system}) \qquad (36)$$

will be used ($|c_2\theta| <<< x_S^{0}$ if sufficient supporting electrolyte is present), giving

$$x_T = x_S^o + (\epsilon_1 + \epsilon_2)\theta \qquad (37)$$

Since the field strength at a point is inversely proportional to the specific conductance there, it follows that

$$E = \frac{A}{x_S^o + \epsilon\theta} \qquad (A = \text{const.}) \qquad (38)$$

where $\epsilon = \epsilon_1 + \epsilon_2$ (39)

For the small values of $|\epsilon\theta/x_S^o|$ envisaged here, (38) may be approximated by

$$E = \frac{A}{x_S^o}\left(1 - \frac{\epsilon}{x_S^o}\cdot\theta\right) \qquad (40)$$

which is the form (34) with $E_o = A/x_S^o$ and $\lambda_1 = -\epsilon/x_S^o$.

Usually the conductivity of a simple salt solution is lower than that of the same solution with polyelectrolyte added (i.e. $\epsilon_1 > 0$) and provided $\epsilon_1 > |\epsilon_2|$, it follows from (39) and (40) that the field strength will be lower in the polymer solution than in the supernatant electrolyte. However, when the degree of counterion binding to polyelectrolytes is large, ϵ_1 is small and the field strength may be higher in the polymer solution than in the simple electrolyte. The conductivity of certain electrolytes may even be lowered by the addition of polyelectrolyte (i.e. ϵ_1 may be negative$^{(45,46)}$). The sign of ϵ (and hence of λ_1) is thus dependent upon the interionic forces operating in the solution and, as in the case of the second virial coefficient of an imperfect gas, will depend on whether there is mutual repulsion (or attraction) between particles.

(ii) Solution of the Transport Equation for the Descending Boundary

Under the conditions considered in this section, the transport equation may be written in the dimensionless form

$$\frac{\partial\theta}{\partial T} = \frac{\partial^2\theta}{\partial X^2} - (1 + 2\lambda_1\theta)\frac{\partial\theta}{\partial X} \qquad T \geq T_o, \ -\infty < X < \infty \qquad (41)$$

with the initial condition

$$\theta(X,T_o) = \frac{1}{2}\,\mathrm{erf}_c\,\frac{-X}{2\sqrt{T_o}} \qquad (42)$$

If one then introduces the moving coordinate (Y) defined by

$$Y = X - (T - T_o)\,(1 + \lambda_1) \qquad (43)$$

and a new reduced time variable $(\tilde{T})$, viz.

$$T = T - T_o \qquad (44)$$

it follows (see Appendix IV) that the solution corresponding to (33) is

$$\frac{\partial\theta}{\partial Y} = \frac{\left\{\begin{aligned}&\left[\int_{-\infty}^{\infty} e^{-y^2} f(y)dy\right]\left[\int_{-\infty}^{\infty} e^{-y^2} \cdot \frac{Y}{\sqrt{\tilde{T}}} \operatorname{erf}\left(y\sqrt{\frac{\tilde{T}}{T_o}}\right) \cdot f(y)dy\right] \\ &- \left[\int_{-\infty}^{\infty} e^{-y^2} \operatorname{erf}\left(y\sqrt{\frac{\tilde{T}}{T_o}}\right) \cdot f(y)dy\right]\left[\int_{-\infty}^{\infty} e^{-y^2} \frac{Y}{\sqrt{\tilde{T}}} \cdot f(y)dy\right]\end{aligned}\right\}}{2\left[\int_{-\infty}^{\infty} e^{-y^2} f(y)dy\right]^2} \qquad (45)$$

where

$$f(y) = \exp\left[\frac{Y}{\sqrt{\tilde{T}}} \cdot y - \frac{\lambda_1}{2}\left(2\sqrt{\tilde{T}} \cdot y \operatorname{erf}\left(y\sqrt{\frac{\tilde{T}}{T_o}}\right)\right.\right.$$

$$\left.\left.+ 2 \cdot \sqrt{\frac{\tilde{T}_o}{\pi}} \left(\exp\frac{-y^2\tilde{T}}{T_o} - 1\right)\right)\right] \qquad (46)$$

(iii) Analysis of the Solution

(a) When $\lambda_1 = 0$, $f(y) = \exp Yy/\sqrt{\tilde{T}}$ and (see Appendix IV)

$$\frac{\partial\theta}{\partial Y} = \frac{e^{-y^2/4T}}{\sqrt{4\pi T}} \qquad (47)$$

which is equivalent to (33).

(b) When $T_0 = 0$ (i.e. when there is no diffusion prior to electrophoresis) it is shown in Appendix IV that

$$\frac{\partial\theta}{\partial Y} = \frac{\dfrac{e^{-Y^2/4T}}{\sqrt{4\pi T}} \cdot e^{-\lambda_1^2 T/4} \cdot \left\{ e^{\lambda_1 Y/2} \operatorname{erf}_c \dfrac{Y + \lambda_1 T}{2\sqrt{T}} + e^{-\lambda_1 Y/2} \operatorname{erf}_c \dfrac{-Y + \lambda_1 T}{2\sqrt{T}} - \lambda_1 \sqrt{\pi T}\, e^{Y^2/4T + \lambda_1^2 T/4} \operatorname{erf}_c \dfrac{Y + \lambda_1 T}{2\sqrt{T}} \cdot \operatorname{erf}_c \dfrac{-Y + \lambda_1 T}{2\sqrt{T}} \right\}}{\frac{1}{2} \left\{ e^{\lambda_1 Y/2} \operatorname{erf}_c \dfrac{Y + \lambda_1 T}{2\sqrt{T}} + e^{-\lambda_1 Y/2} \operatorname{erf}_c \dfrac{-Y + \lambda_1 T}{2\sqrt{T}} \right\}^2} \qquad (48)$$

It is readily checked that this agrees with (33) or (47) when $\lambda_1 = 0$. Equation (48) also shows that as $T \to \infty$, a steady-state solution is obtained when $\lambda_1 < 0$, viz.

$$\lim_{T \to \infty} \frac{\partial\theta}{\partial Y} = \frac{-\lambda_1}{4} \operatorname{sech}^2 \frac{\lambda_1 Y}{2} \qquad (49)$$

This type of solution was also considered by Stockmayer(43) and (Longsworth(33)) for moving concentration boundaries of the type observed experimentally by Longsworth(33). It is shown in Part (vi) of this Section that when $\lambda_1 < 0$, the electrophoretic term describes an effect tending to sharpen a boundary and as $T \to \infty$, the spreading effect of diffusion is balanced by this sharpening effect. When $\lambda_1 \geqslant 0$, boundary spreading continues indefinitely.

(c) The expressions in (47) and (48) are clearly even functions of the coordinate Y and it is shown in Appendix IV that the same is true of the expression in (45). This proves Stockmayer's assertion that concentration gradient patterns will remain symmetric under these conditions.

(d) The centre of the concentration gradient curve is located at $Y = 0$ or, in terms of the original variables at $x = \bar{x}$ where

$$\bar{x} = ut_E \, E_o \, (1 + \lambda_1) \qquad (50)$$

i.e. where

$$v = u \, E_o \, (1 + \lambda_1) \qquad (51)$$

(v is the velocity of the centre of the peak).

This justifies, to the degree of approximation considered so far, the use of the field strength in the bulk of the solution being studied, viz. $E_o(1 + \lambda_1)$, in calculating mobilities from velocities of peaks. However, it is known that field strengths across moving boundaries are influenced by the presence of certain "boundary anomalies" or stationary boundaries(47) which have not yet been considered. It may be possible to eliminate these by adjustment of concentrations before an experiment is performed(48) but a slight error in making these adjustments may give rise to density inversion and cause convection. In back-compensated electrophoresis, such as that used in certain charge determinations(49), the δ-boundary (the stationary boundary at the initial position of the ascending boundary) is removed. However, this requires a series of experiments to determine the ionic strength at which the δ-boundary will disappear and it may happen that at the required ionic strength the mobility is low. Hence it is desirable in many cases to be able to calculate mobilities from experiments in which stationary boundaries are allowed to occur and the necessary modifications of the analysis will now be discussed.

(iv) Dilution across Stationary Boundaries and Variation of Field Strength

It has been shown(47) that the Kohlrausch regulating function for a phase α defined by

$$\omega^{\alpha} = \sum_{j} c_j^{\alpha}/r_j \qquad (52)$$

has the same value in every phase on one side of a stationary boundary. (The summation in (52) is over all ionic species j, C_j^α being their respective concentrations in coulomb/cc. The r_j are their mobilities relative to that of a reference ion and are here treated as constants.) On crossing a stationary boundary between two phases (α and β), the regulating function changes according to the equation

$$\frac{\omega^\alpha}{\omega^\beta} = \rho, \qquad (53)$$

the solution on one side of such a boundary being derivable from that on the other side by dilution with solvent (by a factor ρ). These boundaries are partly responsible for field strength variations and should be considered before applying equation (45) to the calculation of mobilities.

The parameters E_0 and λ_1 in equation (34) were introduced to describe the variation of field strength across a moving boundary. If the reduced concentration of polyelectrolyte (θ) falls from 1 to 0 across a boundary and E_0 is the field strength at that part of the boundary where $\theta = 0$, then the field strength will change from E_0 to $E_0(1 + \lambda_1)$. In the absence of stationary boundaries, E_0 may be identified as the value of the field strength in the bulk of the supporting electrolyte. In general, however, this will not be true and the field strength will vary as indicated in Figures II and III. In Figure II the field strength in the bulk of the supporting electrolyte (E^*) is reduced by a factor ρ on crossing the ϵ-boundary (due to an increase in salt concentration). $E_{0D} = E^*/\rho$ is therefore the E_o value for the descending boundary. If $\lambda_{\phi D}$ is the value of λ_ϕ appropriate to the descending boundary, the field strength will change to $E_{0D}(1 + \lambda_{\phi D})$ on crossing this boundary. On reaching the δ-boundary (Figure III), the field strength increases by the factor ρ, then (across the ascending boundary) changes to E^* since this boundary ends in supporting electrolyte. Thus $E_{0A} = E^*$ is the E_o value for the ascending boundary. The field strength in the solution between the δ- and ascending boundaries may therefore be written $E_{0A}(1 + \lambda_{\phi A})$. It will be noted that the same factor ρ has been used at the δ- and ϵ-boundaries. This follows since the regulating function only changes twice (once across each stationary boundary) and must have the same value in each of the end solutions (since these are

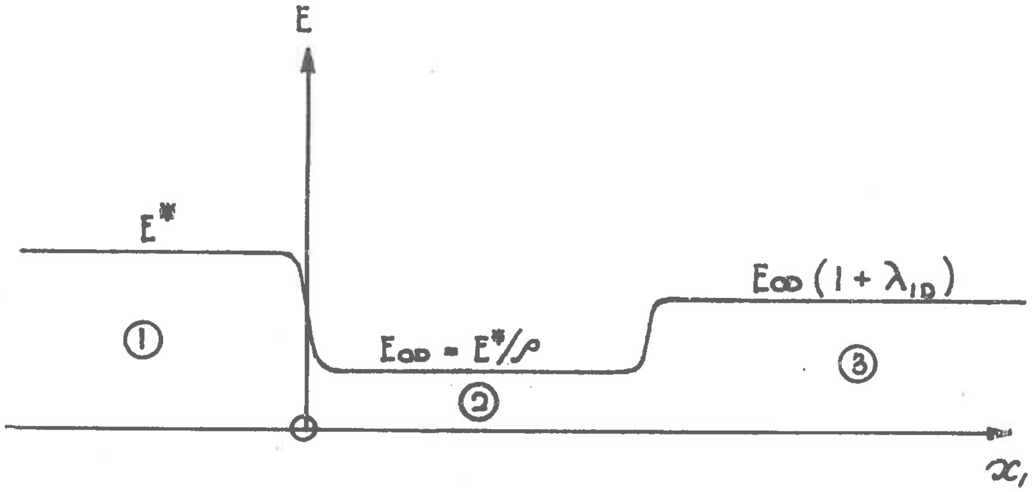

Fig. II. Field strength near the descending boundary.

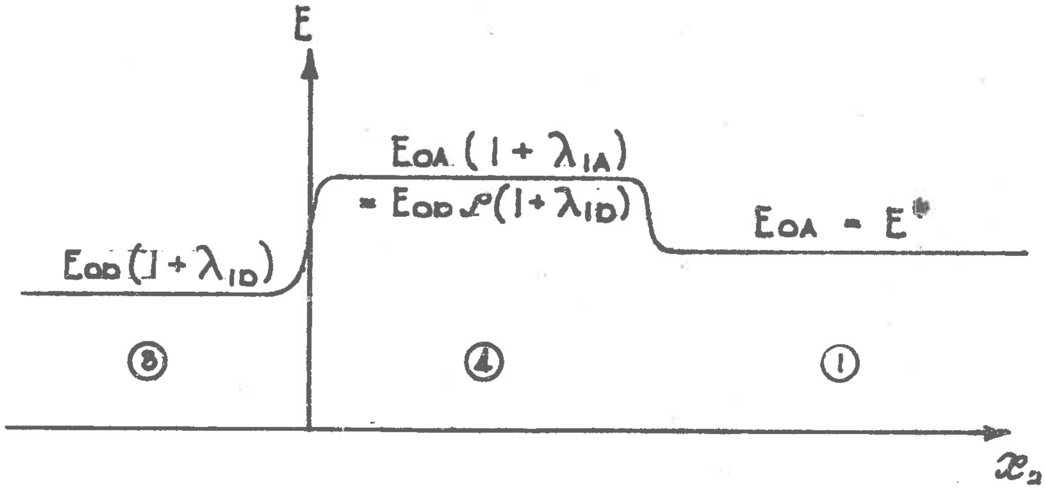

Fig. III. Field strength near the ascending boundary.

x_1 - distance from ξ - boundary in the direction of motion.
x_2 - distance from δ - boundary in the direction of motion.
① - bulk supporting electrolyte.
② - concentrated supporting electrolyte.
③ - bulk polyelectrolyte solution.
④ - diluted polyelectrolyte. solution.

identical).

From this, one may write (for the ascending and descending boundaries respectively)

$$E_A = E^{\circ}(1 + \lambda_{1A}\theta_A) \tag{54}$$

$$E_D = \frac{E^{\circ}}{\rho}(1 + \lambda_{1D}\theta_D) \tag{55}$$

Also,

$$\lim_{\theta_A \to 1} E_A = \rho \cdot \lim_{\theta_D \to 1} E_D \tag{56}$$

Thus,

$$\lambda_{1A} = \lambda_{1D} \tag{57}$$

In what follows, the parameters in (57) will be denoted by λ_1.

It should be noted that although a single value λ_1 suffices for each of the two moving boundary regions, the latter are not electrophoretically similar. Inclusion of initial conditions (see part (vi)) shows that their $\theta - X - T$ behaviour is influenced by <u>effective</u> λ_1 values of opposite sign. Also, dilution across stationary boundaries gives rise to differences in C° (the polymer concentration where $\theta = 1$) and in the concentration of supporting electrolyte, i.e. interionic interactions in the two regions will differ.

*It will be recalled that electrophoretic similarity is based upon invariance of the $\theta(X,T)$ function under a group of transformations which, for constant u and D, has elements (T) of the form

$$T: \quad X = \frac{uE_o}{D} \cdot x \qquad (58)$$

$$T = \frac{(uE_o)^2}{D} \cdot t \qquad (59)$$

while other factors (such as bulk concentrations of the various species) are held constant.

(v) Calculation of Mobilities

Boundary velocities are readily obtained from (51) using E_o and λ_1 values from (iv). Thus the velocity of the descending boundary (v_D) is given by

$$v_D = u \frac{E^*}{\rho} (1 + \lambda_1) \qquad (60)$$

and that of the ascending boundary (v_A) by

$$v_A = u E^* (1 - \lambda_1) \qquad (61)$$

(remembering that the effective λ_1 values for these boundaries have opposite signs). This leads to the relation

$$\frac{v_A}{v_D} = \rho \frac{(1 - \lambda_1)}{(1 + \lambda_1)} \qquad (62)$$

which, for $\lambda_1 = 0$, reduces to a result derived by Longsworth$^{(47)}$. Conductivity measurements yield the field strength in the bulk of the supporting electrolyte (E^*) and in the bulk of the polymer solution ($E^*(1 + \lambda_1)/\phi$), thus enabling one to calculate $(1 + \lambda_1)/\phi$. Substituting this and the ratio of boundary velocities (v_A/v_D) in (62), λ_1 may then be determined (and hence the dilution factor ϕ) without recourse to sampling techniques which tend to disturb boundaries. The mobility then follows directly from (60) or (61).

(vi) Spreading of Boundaries

Equation (45) provides a means for estimating the diffusion coefficient (D) from the spreading of a boundary and must be used whenever appreciable spreading occurs prior to electrophoresis. By means of (43), (44), (58), (59) and the defining relation for Θ (equation (22)), one may relate the experimentally determined function $\frac{\partial C(x,t)}{\partial x}$ to $\frac{\partial \Theta(Y,\tilde{T})}{\partial Y}$ by means of the equation

$$\frac{\partial \Theta}{\partial Y} = \frac{D}{C^o u E_o} \cdot \frac{\partial C}{\partial x} \qquad (63)$$

The determination of the diffusion coefficient then proceeds as follows:

A first estimate of D (e.g. one based on simple boundary spreading due to diffusion alone) is used in (63) and the resulting estimate of $\frac{\partial\theta(Y,\tilde{T})}{\partial Y}$ compared with the right hand member of (45) (evaluated numerically by the method given in Appendix V). At this stage, comparison need only be made of the maximum ordinates of the $\partial\theta/\partial Y$ curves obtained from (45) and (63) in turn. Stockmayer(43) used the central ordinate of the concentration-gradient curve in determining a parameter (λ/D) of his system, fitting empirical expressions to the integrands in an equation corresponding to (45) at $Y = 0$. However, no details were given in his paper and the method outlined in Appendix V is recommended here since tables are available for carrying out the integrations. In addition, this method is shown to be very accurate provided a sufficiently large number of values of the integrands is used. The procedure is repeated for different values of D until the maximum ordinates from (45) and (63) coincide. Let this occur when $D = \bar{D}$.

If greater accuracy is desired, the values of $\partial\theta/\partial Y$ at a number of points Y_i $(i = 1, 2, \ldots n)$ may be calculated for values of D near to $\bar{D}$ by means of (45) and (63). If the corresponding ordinates found from (45) and (63) are denoted by $y_{i,1}$ and $y_{i,2}$ respectively, the value of D for which the sum

$$S^2 = \sum_{i=1}^{n} (y_{i,1} - y_{i,2})^2 \qquad (64)$$

is a minimum is then selected as the final estimate of the diffusion coefficient. In this way a number of ordinates is used and the effect of error in the measurement of any one is greatly reduced.

When electrophoresis commences with a sharp boundary, numerical integration is no longer necessary and an explicit solution (equation (48)) is available in place of (45). A number of estimates of D is still required and this would be a lengthy procedure for hand computation. However, the right hand member of (48) is readily found (for given values of λ_1, Y and T) by using high speed computers. In addition, computer calculations based on (48) have indicated the significance of the parameter λ_1 in describing boundary spreading (Figure IV), positive values of this parameter being associated with more rapid boundary spreading than in free diffusion and,

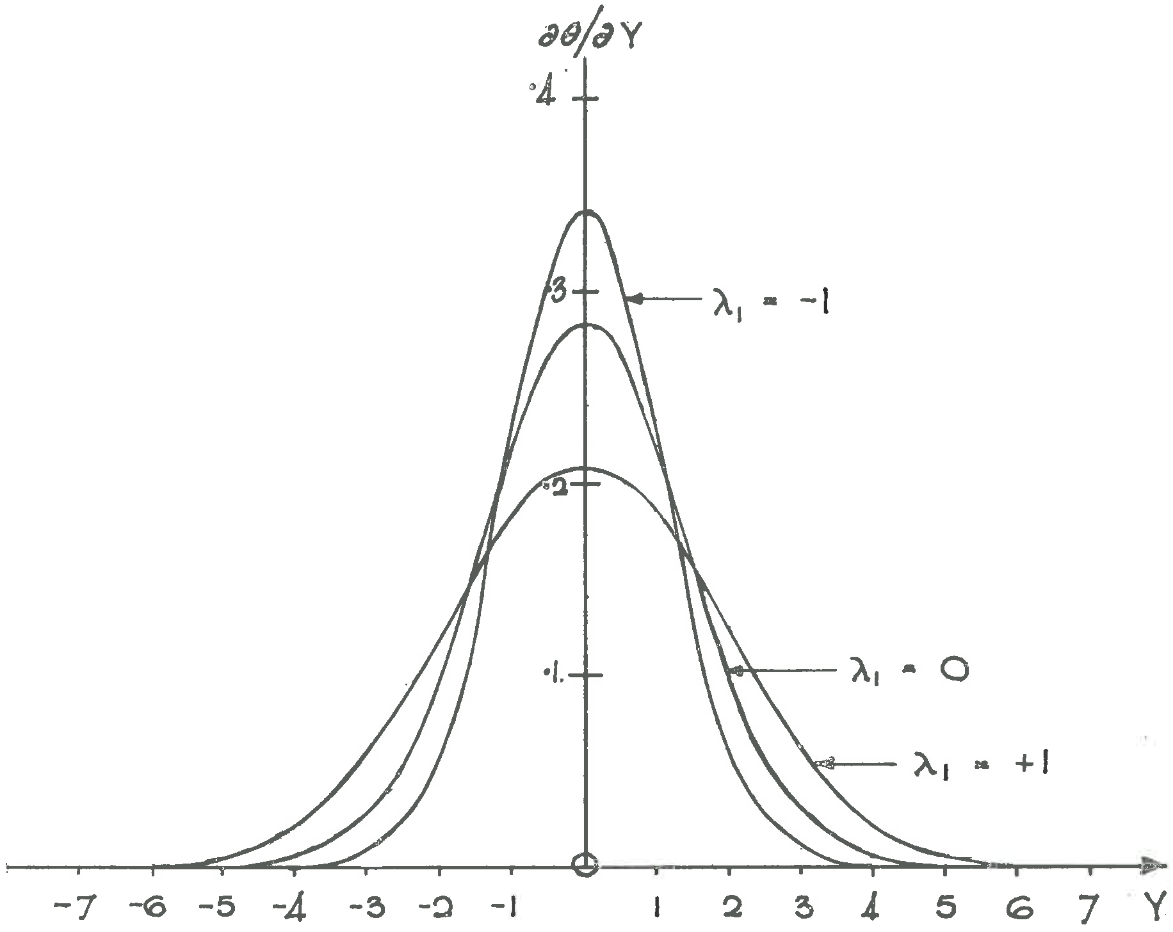

Fig. IV. Boundary spreading at $T = 1$ for different values of λ_1 $(T_0 = 0)$

DATA.

Curve $\lambda_1 = +1$:

ordinates	·208	·185	·127	·061	·019	·004	·0004
abscissae	0	1	2	3	4	5	6

Curve $\lambda_1 = 0$:

ordinates	·282	·220	·104	·030	·005	·0005
abscissae	0	1	2	3	4	5

Curve $\lambda_1 = -1$:

ordinates	·394	·233	·060	·009	·0009
abscissae	1	1	2	3	4

conversely, when λ_1 is negative, boundaries that are sharper than those obtained in free diffusion.

Apart from having an explicit solution (48) when boundaries are initially sharp, this type of boundary is also to be preferred in view of the limitations on the field strength representation described in Figures II and III. For example, if a diffuse descending boundary and the ε-boundary overlap, changes in field strength due to both the higher concentration of supporting electrolyte below the ε-boundary and the variation in polymer concentration across the moving boundary will be combined (Figure V).

However, as mentioned in Section 2 (i) of Chapter 1, only cases in which electrophoretic effects are much more marked than those of diffusion are being considered and adequate separation of boundaries will be achieved under these circumstances.

The general shape of concentration gradient curves may be described as a distorted Gaussian function. Introducing the variable

$$Z = \frac{Y}{\sqrt{2\tilde{T}}} \left(= \frac{X - \bar{\tilde{T}}}{\sqrt{2\tilde{T}}} \right) \tag{65}$$

the limiting case $\lambda_1 = 0$ (equation 33) may be written

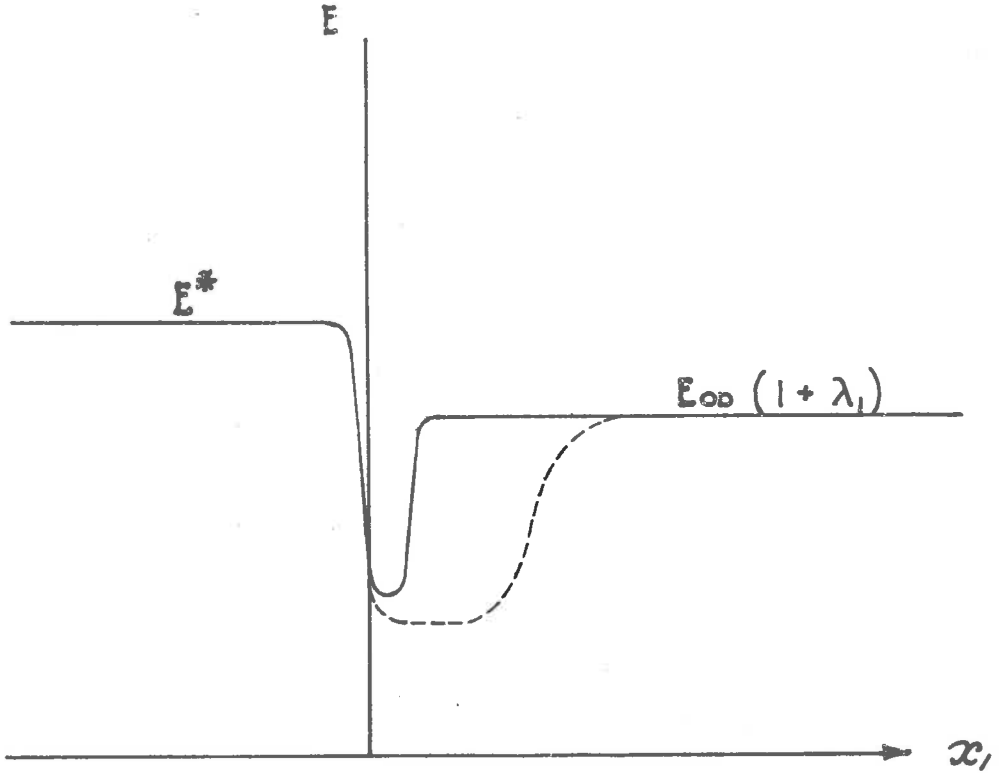

Fig. V. Field strength near ξ - and descending boundaries.

x_1 = distance from ξ - boundary in the direction of motion.

Firm line : overlapping ξ - and descending boundaries.

Dotted line : distinct ξ - and descending boundaries.

$$\frac{d\theta(Z)}{dZ} = \frac{e^{-Z^2/2}}{\sqrt{2\pi}} \qquad (66)$$

i.e. each value of Z is a standard normal deviate. The boundary spreading observed in this case is the same as for simple diffusion but, more generally,

$$\theta = \theta(Z,\tilde{T},T_0,\lambda_1) \qquad (67)$$

This reflects the fact that spreading of a boundary will, in general, depend on a number of factors, viz. (i) diffusion, (ii) the relative magnitude of electrophoretic and diffusion terms (see equation 59), (iii) the ratio of times of diffusion without electrophoresis to diffusion with electrophoresis and (iv) field strength variations.

Although the dimensionless parameter λ_1 has the same vale for the ascending as for the descending boundary the geometries of these boundaries differ. The reason for this is that λ_1 has been defined only in terms of the variation of field strength with concentration of polymer, and although the governing equation (41) holds for both moving boundaries, the initial condition (42) does not. This brings out a point discussed by Kline$^{(50)}$, viz. that it is important to examine the governing equations of a problem together with all the necessary boundary or initial conditions. Thus for the ascending boundary

$$\frac{\partial\theta}{\partial T} = \frac{\partial^2\theta}{\partial X^2} - (1 + 2\lambda_1\theta)\frac{\partial\theta}{\partial X} \qquad T \geq T_o, \; -\infty < X < \infty \tag{41}$$

as before, but

$$\theta(X,T_o) = \frac{1}{2}\,\mathrm{erf}_c\,\frac{X}{2\sqrt{T_o}} \tag{68}$$

which differs from (42). By using a moving coordinate $Y' = -Y$ and the time variable $\tilde{T}$, however, one obtains

$$\frac{\partial\theta}{\partial\tilde{T}} = \frac{\partial^2\theta}{\partial Y'^2} + \lambda_1(2\theta - 1)\frac{\partial\theta}{\partial Y'} \tag{69}$$

with

$$\theta(Y',0) = \frac{1}{2}\,\mathrm{erf}_c\,\frac{-Y}{2\sqrt{T_o}} \tag{70}$$

(69) and (70) are of the same form as the corresponding equations for the descending boundary (see Appendix IV), equations (4.8), (4.9) and (4.11) except that λ_1 has been replaced by $-\lambda_1$. Thus, when field strength gradients tend to make a descending boundary spread more rapidly than under the action of diffusion alone, the opposite effect

is observed at the ascending boundary and vice versa.

5. HIGHER-ORDER PERTURBATIONS IN THE ELECTROPHORETIC TERM

There has been no quantitative treatment of this problem to date but the above solutions are clearly inadequate for the interpretation of asymmetric boundary patterns. Lagercrantz(51) made corrections to "apparent" mobility values (i.e. values based on the field strength in the bulk of the solution under study) but gave no details about the type of correction he used. In addition, he was unable to obtain complete agreement between mobilities estimated from ascending and descending boundaries.

(i) Formulation of the Problem

The relevant factors have been discussed in Chapter 1 (Sections 2 (iii) and 2 (iv)) and the transport equation may be written in the dimensionless form

$$\frac{\partial\theta}{\partial T} = \frac{\partial^2\theta}{\partial X^2} - \frac{\partial}{\partial X}\left[\left(\sum_{i=0}^{\infty} r_i\theta^i\right)\left(\sum_{i=0}^{\infty} \lambda_i\theta^i\right)\theta\right] \qquad (71)$$

where $r_0 = \lambda_0 = 1$. If the infinite series in (71) are to represent adequately the mobility and field strength as functions of the reduced concentration (θ), they must be convergent. In addition, for small perturbations of u and E from their reference values u_0 and E_0, it is reasonable to expect that at least one of these series will be absolutely convergent so that one may write

$$\frac{\partial\theta}{\partial T} = \frac{\partial^2\theta}{\partial X^2} - \left(\sum_{i=0}^{\infty}(i+1)\gamma_i\theta^i\right)\frac{\partial\theta}{\partial X} \qquad (72)$$

in which the γ_i are the Cauchy products

$$\gamma_i = \sum_{j=0}^{i} r_j\lambda_{i-j} \qquad (73)$$

When applying (72) and (73), it should be borne in mind that great care is needed in truncating these because the orders of magnitude of the phenomenological coefficients r_i and λ_i are difficult to assess. Thus, if r_1 is considered as well as λ_1, it may happen that $|r_1| \lll |\lambda_1|$ but $|r_1| \doteq |\lambda_2|$, i.e. first-order mobility variations may be no more important than second-order field strength variations and allowance should therefore be made for the latter. Some ancillary information on the variation of pH and buffer concentration across a boundary is useful in choosing the necessary coefficients.

Finally, equation (57) is no longer valid because (54) and (55) are replaced by expressions of the form

$$E_A = E^* \left(1 + \sum_{i=1}^{\infty} \lambda_{iA} \theta_A^i\right) \qquad (74)$$

$$E_D = \frac{E^*}{\rho} \left(1 + \sum_{i=1}^{\infty} \lambda_{iD} \theta_D^i\right) \qquad (75)$$

Thus, although (56) is applicable to solutions of strong electrolytes (where conductivity and concentration may be considered proportional), (57) is replaced by

$$\sum_{i=1}^{\infty} \lambda_{iA} = \sum_{i=1}^{\infty} \lambda_{iD} \qquad (76)$$

and the λ_{iA} are not necessarily equal to the corresponding λ_{iD}. A similar statement is true of the r_{iA} and r_{iD}.

Some general results on the speed and geometry of boundaries will now be derived.

(ii) Velocity of Sharp Boundaries

When the diffusion coefficient is very small, boundary spreading is no longer appreciable but the velocity of a boundary remains dependent on the electrophoretic parameters y_i. To determine the form of this dependence, it will be convenient to introduce a slight artifice at first, viz. to suppose that a small amount of diffusion is allowed to occur before electrophoresis starts, then to neglect diffusion during the subsequent electrophoresis. In this way one is able to use a continuous initial condition (a solution of the diffusion equation) for the electrophoresis process, thereby obtaining a continuous solution of the conservation equation. (If diffusion is neglected entierely, one is forced to deal with discontinuous solutions. Apart from the difficulty of handling these, the fundamental theorems on homogeneous functions used in the present system of dimensional analysis(42) presuppose continuity conditions.) The relation between the boundary velocity (v) and the y_i is then obtained by letting the time of diffusion tend to zero (see Appendix VI), giving

$$v = u_o E_o \sum_{i=0}^{\infty} \frac{(i + 1)y_i}{2^i} \qquad (77)$$

Thus, the mobility (u_o) is equal to the velocity of the boundary divided by a field strength equal to E_o corrected by the factor shown. It is interesting to note that when the mobility is constant (i.e. the v_i are all zero for $i > 0$), the corrected field strength (E_c) has the form

$$E_c = E_o \left\{ 1 + \lambda_1 + \frac{3\lambda_2}{4} + \frac{\lambda_3}{2} + \dots \right\} \qquad (78)$$

since (by 73) $y_i = \lambda_i (i = 0,1,2 \dots)$. This is seen to be a generalisation of equation (51) and justifies the use of the latter as a first approximation.

(iii) <u>Enantiography of Conjugate Patterns</u>

From equation (72) (for the descending boundary), it follows that a reflection $X' = - X$ will only give the same form of the governing equation for the ascending boundary if

$$y_{iA} = - y_{iD} \qquad (i = 1,2, \dots) \qquad (79)$$

This is trivially satisfied if all the y_i are zero. When considerable perturbation from the values u_o and E_o occurs, it is unlikely that these relations will be satisfied. Longsworth(35) stated (without proof) that a constant electric field will generally be necessary for enantiography. The above substantiates this and, in addition, indicates the need for constancy of mobility as well. Longsworth(47) also suggested that conductivity and mobility variations may tend to mask each other. This may be seen by considering the case where τ_1 and λ_1 are small and $\tau_2, \tau_3, \ldots \lambda_2, \lambda_3, \ldots$ negligible.

Then,

$$y_1 = \tau_1 + \lambda_1 \tag{80}$$

$$y_2 = \tau_1 \lambda_1 \tag{81}$$

and

$$y_3 = y_4 = \ldots = 0 \tag{82}$$

Then if $\tau_1 = -\lambda_1$, (80) gives $y_1 = 0$ and (81) shows $y_2 \doteqdot 0$ so that conjugate patterns may appear to be enantiographic.

(iv) Solution of the Transport Equation

No closed-form solutions of (72), beyond the first-order treatment given, have been found to date. In addition, any values obtained for the y_i would require careful interpretation since they contain information related to <u>both</u> conductivity and mobility changes across boundaries.

The existence of solutions is assured by the work of Blagoveshchenskii$^{(52)}$, from whose analysis it follows that a convergent sequence of approximations $\theta_0, \theta_1, \theta_2, \ldots$ exists, where θ_0 is the initial condition and successive θ_n satisfy

$$\frac{\partial \theta_n}{\partial T} = \frac{\partial^2 \theta_n}{\partial X^2} - \left(\sum_{i=0}^{\infty} (i + 1) \gamma_i \theta_{n-1}^i \right) \frac{\partial \theta_n}{\partial X} \quad n = 1, 2, \ldots \qquad (83)$$

In applying this result to the solution of (72), one is restricted because in spite of the fact that the iteration for θ_n involves a linear differential equation (θ_{n-1} having been found), the coefficient of $\partial\theta_n/\partial X$ will not be simple at any stage. John$^{(53)}$ has given a method for replacing such linear equations by equivalent integral equations but the latter may be equally difficult to solve.

Thus, although the existence of higher-order solutions to equation (72) is assured, further information on the coefficients γ_i and suitable methods of solution based on these are necessary before asymmetric boundaries can be satisfactorily interpreted.

PART II

MICROSCOPIC TRANSPORT THEORY

CHAPTER 3

GENERAL CONSIDERATIONS

1. INTRODUCTION

The electrophoretic mobility of a particle moving through a viscous fluid is the outcome of an electrostatic-hydrodynamic force balance. These forces must be considered in the derivation of mobility-zeta-potential relations and if one wishes to calculate the charge on a particle from its mobility, the relationship between zeta-potential and charge must also be determined. Current solutions to these problems involve gross simplifications and it would appear worthwhile to analyse more exact formulations. Even if more accurate relations are obtained, however, it will still be necessary to determine the nature of the electrophoretic charge. For polyelectrolyte solutions, in particular, it is recognised that the kinetic unit undergoing transport is not merely a polyion but includes a number of counterions as well. Ion binding studies to date have failed to indicate the extent of counterion-binding during transport and polyionic charges must, at present, be found by other methods (e.g. titration). The "particles" referred to below are statistical entities, indicating time-average properties of the kinetic units.

The mobility-zeta-potential relationship for a particle forms a link between a macroscopic observable and a microscopic parameter. Relationships of this kind have been considered elsewhere$^{(1,2,46,54)}$ and, in keeping with the subject of Part II of this thesis, attention will be focused on the relation between two microscopic parameters, charge and zeta-potential.

This chapter commences with a survey of the factors governing electrophoretic motion. A physical model is described, this being followed by a mathematical formulation of the potential problem. Two methods for reducing this are then outlined, one converting the differential equations to a single equation, the other reducing that to dimensionless form. The rest of the chapter is largely concerned with the derivation of expressions for the charge density at the surface of shear. One of the methods used has already been described by Gorin$^{(1)}$ and is briefly mentioned for purposes of comparison. The second method involves approximation of the Poisson-Boltzmann equation in the manner indicated by Alexandrowicz and Katchalsky$^{(56)}$. While this method may yield a satisfactory estimate of the electrostatic potential near a polyion, it is unlikely to be generally satisfactory in charge determinations (see Chapter 4) and a third approach to the problem is discussed. The chapter ends with a consideration of ion-binding and the relation between polyionic charge and electrophoretic charge.

2. FACTORS GOVERNING ELECTROPHORETIC MOTION

As in the macroscopic theory (see Chapter 1), governing factors will be outlined before formulating the problem in mathematical terms, emphasis being placed on the special characteristics of polyelectrolytes.

(i) Properties of the Particles

(a) Surface Charge Density

This is the primary factor determining the electrostatic force acting on a particle in a given electric field. In polyelectrolyte solutions it is largely determined by the polyionic charge but the magnitude of the latter is reduced by the screening effect of counterions. The influence of these small ions will partly depend on the temperature, thermal agitation tending to reduce their concentration near each polyion. Polyion-counterion interactions will also depend on the dimensions of the various ions in solution, as well as the ionic strength. The last quantity reflects the increased screening obtained by using supporting electrolytes of higher concentrations and/or valence types. Specific adsorption of counterions(57) tends to override the effects of by-ions, the latter having a relatively minor influence on electrophoretic mobility.

(b) Charge Distribution

This will influence the electric field in the vicinity of a particle. Considerable simplification of the analysis is possible if the surface charge density (arising from charged sites) is considered to be "smeared out" uniformly, remembering that the true charge density will vary from point to point on the surface of the particle. In the case of polyions, screening by counterions will tend to eliminate such charge density variations on the surface of shear. Although the smeared-charge model is more accurate at the surface of shear than at the polyion itself, the effect of this approximation on expressions for the charge density has not yet been determined. In view of the work of Karasz and Hill(58), it would seem to warrant further investigation.

(c) Conductivity

Conduction of electricity (through a particle and/or along its surface) will modify the electric field around the particle, reducing the mobility to below the corresponding value for an insulator. However, the passage of current through a particle will be opposed by surface polarisation. Since, in addition, it is difficult to assess the magnitude of surface conductance, analyses to date have largely been confined to insulating particles.

(d) Geometry

Particle shape and size influence both the hydrodynamic resistance to motion and distortion of the electric field in the double layer, the latter being particularly important when the dimensions of the particle are large compared to the "thickness" (Debye-Hückel radius) of the double layer. In polyelectrolyte solutions, the polyion concentration will partly determine inter-ionic interactions (gel effects(11) being noticeable in more concentrated solutions) and thus influences the geometry of the moving units. The state of aggregation of polyions will also depend on the temperature. Changes in the electrokinetic properties of platelets during their aggregation have recently been studied by Seaman and Vassar(59).

The electrophoresis of rigid and partially free-draining spheres(60,61), discs(1) and long rods(1) have been considered by various authors. It has been suggested that a cylindrical model be adopted for polyions$^{(62)}$ and, although such a model may prove of doubtful utility in the case of flexible polyions, it is suited to the study of rigid macroions, e.g. in certain DNA solutions. This model is analysed in Chapter 4.

(ii) Environmental Factors

(a) Average (Macroscopic) Field Strength

Distortion of lines of force in the double layer around a particle will vary with the strength of the electric field, thus influencing the mobility.

The electric field also tends to align multipoles parallel to itself, this effect being more marked at higher field strengths. The resultant "streamlining" of the particles with respect to the electrical and hydrodynamic force fields increases their mobility to beyond the value for randomly-oriented particles. However, thermal agitation will oppose this effect and, to date, random orientation of particles has been assumed. The error involved in making this assumption would be difficult to estimate but it is less serious at lower field strengths.

(b) Microscopic Variations of Field Strength

These will be most marked in the vicinity of a polyion.

(c) Variations of Dielectric Constant

The dielectric constant of a solution has been shown to vary with the ionic strength(63). Hence the bulk dielectric constant of the supporting solution will not be strictly applicable near a moving particle (where there is a local excess of counterions and deficiency of by-ions). This discrepancy can be reduced by increasing the ionic strength and so far has not been included in mobility theory.

(d) Streaming of Counterions

Counterions contribute to drag forces by streaming in the opposite direction to that of the particles undergoing electrophoresis.

(e) Relaxation

Motion of particles relative to their ionic atmospheres also gives rise to electrostatic retardation(64). Thus, at equilibrium the ionic atmosphere of a given particle is, on a time-average, symmetrically distributed. Under these conditions the ions surrounding the particle exert no resultant force on the latter but during electrophoresis the central particle moves to an off-centre position with respect to its ionic atmosphere. This causes a restoring force to act until thermal motion rearranges the ionic atmosphere. There will be a corresponding reduction in mobility but the magnitude of this effect will be small provided the thickness of the ionic atmosphere is much less than the dimensions of the particle. It has been shown that this effect may be safely ignored when analysing the electrophoretic behaviour of linear polyelectrolytes(46).

(f) Hydrodynamic Factors

The viscosity, compressibility and Reynold's number of flow past the particles will partly determine the drag forces (see also (d)). A complete analysis of their action would be very complex, especially in view of their interaction with the other factors considered here. Under the usual conditions of atmospheric pressure and low velocity, the fluid motion may be considered incompressible and laminar. It is also customary to treat the motion as one of creeping flow (for which the inertia terms in the hydrodynamic equations of motion are negligible and equations such as Stokes' equation for spheres are applicable).

(iii) Fluid-Particle Interactions

A layer of solvent may associate with a polyion-counterion unit, thus increasing its effective size. Unfortunately no reliable estimate of the thickness of this layer has been available to date.

Wetting of particles by the solvent is normally considered to occur, thus allowing the use of a no-slip boundary condition in solving the Navier-Stokes equations (this condition is more likely to hold for macroions than for small ions).

3. THE PHYSICAL MODEL

A kinetic unit (possibly solvated) will be represented by a rigid solid of dielectric constant ϵ_1 and surface charge density σ, this being immersed in a solvent of dielectric constant ϵ_2. Counterions (of radius r_1*) are clustered about the central macroion, as are ions of the supporting electrolyte (bulk concentration $C_1^{\circledast}$), giving rise to an uncharged region of thickness r_1 about each particle. In the solution

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*Those counterions nearest a polyion will have a smaller effective radius than that determined from conductivity measurements in simple salt solutions since the strong electrostatic attraction between polyions and their counterions tends to remove water of hydration, at least from the outer co-ordination spheres of the small ions. At present, however, there is no way of allowing for this effect.

beyond this region, the charge density will be taken as continuous, i.e. the discrete structure of the double layer will not be considered. For simplicity, only three-ion systems will be considered (as in Chapter 2) and all small ions will be taken as univalent.

4. FORMULATION OF THE PROBLEM

The potential problem reduces to solving the Poisson-Boltzmann equation over the electrical double layer surrounding a particle. It has been objected(46,113) that this equation is incorrect since the ensemble average work (appearing in the Boltzmann distribution law) required to place an ion in a given configuration with respect to a charged particle is not linearly related to the potential function. This is true since the introduction of an ion will disturb the ionic atmosphere of the particle under consideration. However, Katchalsky et al (62) have pointed out that the distribution of small ions around a macroion is dominated by the powerful central field of the latter, other interaction effects being relatively small. In addition, Bolt(65) (see also van Olphen(66)) has carried out a semi-quantitative analysis of the problem, showing that after correcting space coordinates (measured from a suitable origin within the particle) by several Angstrom units, the Gouy-Chapman theory will give essentially correct results. For these reasons, the Poisson-Boltzmann equation will still be used but it should be remembered that any particle dimensions employed should allow for the factors discussed by Bolt.

(i) The Differential Equations

The potential function will be considered over three regions.

(a) Within the surface of shear (S_o).

Since there is no volume charge density within this region, the Poisson equation for the potential ($\Psi_1(\underline{r})$) at a point $\underline{r}$ reduces to Laplace's equation, viz.

$$\nabla^2 \Psi_1(\underline{r}) = 0 \tag{84}$$

(b) Between S_o and the surface of closest approach (S_1) of counterion centres to S_o.

Again, the potential ($\Psi_2(\underline{r})$) must satisfy

$$\nabla^2 \Psi_2(\underline{r}) = 0 \tag{85}$$

(c) From S_1 to infinity.

The Poisson equation for the potential ($\Psi_3(\underline{r})$) over this region will be approximated by the Poisson-Boltzmann equation which, for the three-ion system considered, reduces to

$$\nabla^2 \Psi_3(\underline{r}) = \frac{8\pi N C_1{}^{o} q}{\epsilon_2} \sinh \frac{q\Psi_3(\underline{r})}{kT} \tag{86}$$

where q = magnitude of the electronic charge k = Boltzmann's constant

T = absolute temperature

N = Avogadro's number* and the remaining symbols have been defined above**.

(ii) <u>Boundary Conditions</u>

Since each of the three potential equations is of second order, six boundary conditions are needed for their complete solution. These are derived as follows:

(a) The potential at $\underline{r} = \underline{o}$ is finite, i.e. there exists a constant A such that

$$\lim_{|\underline{r}| \to o} \Psi_1(\underline{r}) = A \tag{87}$$

(b) The potential is continuous across the surface of shear, i.e.

$$\left(\Psi_1(\underline{r})\right)_{S_o} = \left(\Psi_2(\underline{r})\right)_{S_o} \tag{88}$$

(This potential is, by definition, the zeta-potential, ζ).

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* Included in (86) since $C_1^{\,o}$ is usually given the dimensional formula $M\ L^{-3}$, not L^{-3} as required by the corresponding formula of Rice and Nagasawa$^{(46)}$.

**For convenience, the potential function in (86) has been taken as positive. When the surface of shear includes a net negative charge, this function will be negative near the particle (note the electrostatic potential curves given by Morawetz(46), for example, strictly apply only to positively charged particles.

(c) The electric displacement changes across the charged surface in such a way that(67)

$$-\epsilon_1\left(\underline{\nabla}\Psi_1(\underline{r})\right)_{S_0} + \epsilon_2\left(\underline{\nabla}\Psi_2(\underline{r})\right)_{S_0} = -4\pi\sigma \qquad (89)$$

(d) The potential is continuous at S_1, i.e.

$$\left(\Psi_2(\underline{r})\right)_{S_1} = \left(\Psi_3(\underline{r})\right)_{S_1} \qquad (90)$$

(e) The electric displacement is continuous across S_1 (since there is no <u>surface</u> charge density there). In addition, it has been assumed that there is no change in dielectric constant on crossing this boundary, i.e.

$$\left(\underline{\nabla}\Psi_2(\underline{r})\right)_{S_1} = \left(\underline{\nabla}\Psi_3(\underline{r})\right)_{S_1} \qquad (91)$$

(f) The position of zero-potential may be arbitrarily selected. It is customary to choose this position at infinity, i.e. away from the influence of the electrostatic field of the polyion, giving

$$\lim_{|\underline{r}| \to \infty} \Psi_3(\underline{r}) = 0 \qquad (92)$$

5. USE OF BOUNDARY CONDITIONS

In solving the linearised potential equation for a sphere, Abramson et al[1] used the boundary condition at infinity and the potential gradient at the surface of the particle, i.e. conditions analogous to (91) and (92). The derivation of Gorin's formula[1] for cylinders has never been published but his result appears to have been derived in a manner analogous to that of Dube[68], who also used boundary conditions corresponding to (91) and (92). An alternative choice would be equations of the type (90) and (91), i.e. conditions at the surface of the particle. Both of these approaches are, in general, inadequate as the following will show.

Firstly, Gronwall et al[69] have found that in cases of spherical symmetry and negligible counterion radius, conditions of the type (91) and (92) yield a solution of the form

$$\phi, = \frac{1}{\zeta} \sum_{n=0}^{\infty} a_n \, (r,p). \, Q^n \qquad (93)$$

i.e. the double layer potential may be expressed as a power series in the charge at the surface of shear (Q) with coefficients that are functions of the radial coordinate (r) and various parameters of the system (p). The remaining condition (of the type (90)) then leads to the result

$$\zeta = \sum_{n=0}^{\infty} b_n (r_o, p) \cdot Q^n \qquad (94)$$

where r_o is the radius of the surface of shear. It is found that the series (94) diverges for large Q, although Levine(70) has shown that inversion of this series leads to one of the type

$$Q = \sum_{n=0}^{\infty} c_n (r_o, p) \cdot \zeta^n \qquad (95)$$

which converges for <u>all</u> finite values of ζ. The b_n, however, are not simple and this inversion will, in general, be difficult to achieve. Similar difficulties may be expected for other particle shapes. Wall and Berkowitz(71) have used boundary conditions analogous to (91) and (92) for coiled polyions, a similar approach being adopted by Kotin and Nagasawa(72) for cylindrical particles. In view of the difficulties just mentioned, their solutions must be treated with caution at higher zeta-potentials.

Secondly, one might attempt to solve (86) subject to the conditions (90) and (91), i.e. as an initial value problem. However (see Garabedian(73)) boundary data rather than initial data are required to determine the solution of an elliptic equation, i.e. it is necessary to find a solution in the large. This is harder to achieve than a local solution and the need for global constructions makes it especially difficult to master non-linear elliptic equations, as in the present case. Kotin and Nagasawa(72) have observed that integrating outward from the surface of a particle may lead to instability. If a poor estimate is made of the initial value of the potential, the solution will become unbounded at large distances from the particle.

One is therefore left with the third alternative, viz. solution of (86) subject to the Dirichlet conditions (90) and (92). This is exemplified in the next chapter.

6. REDUCTION OF THE POTENTIAL PROBLEM

(i) Reduction to a Single Boundary-Value Problem

Equations (84) and (85) are solved first, boundary conditions (87), (88) and (89) being introduced to eliminate three constants of integration. The fourth constant may be expressed in terms of the potential in (88), viz. ζ. The differential equation (86) and boundary conditions (90), (91) and (92) remain. Two of these conditions would suffice for purposes of integration but a third is required to determine the unknown parameter σ.

It will be noted that the above equations imply a relation between σ and ζ. This is consistent with Rice and Nagasawa's demonstration that particle charge and surface potential are not independent$^{(46)}$, each being determined by the other parameters of the system.

(ii) Use of Dimensionless Monomials

Dimensionless π-monomials may be constructed to facilitate both the solution of (86) and the comparison of solutions obtained for different values of the parameters. Since each member of (88) is equal to the zeta-potential there are effectively seven boundary conditions and one of the quantities appearing in the above formulation is superfluous (e.g. as mentioned, σ and ζ are not independent). The multiplicity of the dimensional basis is thus one unit too large and in forming π-monomials, σ or ζ (for example) should be omitted. It will be found convenient to omit σ at this stage rather than ζ since the latter is useful in normalising the potential and σ (the main object of this analysis) is left as a free parameter (i.e. not absorbed into any monomial).

7. SOLUTION FOR THE CHARGE DENSITY (σ)

(i) Gorin's Approximation

Cases for small surface potential may be treated by means of the approximate Debye-Huckel equation. It is commonly believed that this is only suitable when the reduced potential ($q\Psi_3/kT$) is much smaller than unity but Levine$^{(70)}$ has shown that for spherical particles (whose radii are not too large) this treatment remains satisfactory at higher potentials.

If the charge density term on the right hand side of (86) is expanded as an infinite series and truncated after the first power in Ψ_3, one obtains the linear approximation

$$\nabla^2 \Psi_3(\underline{r}) = \frac{8\pi N C_1^{\,0} q^2}{\varepsilon_2 kT} \cdot \Psi_3(\underline{r}) \qquad (96)$$

Gorin's method of solving equations of this form will be discussed in Chapter 4 with reference to the case of cylindrical symmetry.

(ii) A Boundary-Layer Solution

When the surface potential is large, Ψ_3 changes rapidly near the surface of shear but only slowly in the more diffuse part of the double layer. Thus one has to deal with non-uniform behaviour over a semi-infinite region$^{(50)}$ and mathematical difficulties are to be expected. In particular, the usual finite-difference approximations cannot be applied. Loeb et al$^{(74)}$ have used a method involving variable mesh-size (with respect to their radial coordinate) but it is probably better to consider increments in

Ψ_3 rather than $\underline{r}$ in any discretisation process. The underlying theory of such problems is still largely unknown but a body of useful ideas is being developed. The approach to boundary-layer problems introduced by Prandtl(75), viz. the utilisation of different estimates in different regions of the system, will be used here.

Alexandrowicz(55) and Alexandrowicz and Katchalsky(56) have solved the Poisson-Boltzmann equation by this method for cases of cylindrical symmetry and their type of solution will be applied to the charge problem in Chapter 4. In general, one replaces (86) by the approximate equations

$$\nabla^2 \Psi_{3,1}(\underline{r}) = \frac{8\pi N C_1{}^{\circ} q}{2\varepsilon_2} \, e^{q\Psi_{3,1}(\underline{r})/kT} \qquad \underline{r} \in D_1 \qquad (97a)$$

$$\nabla^2 \Psi_{3,2}(\underline{r}) = \frac{8\pi N C_1{}^{\circ} q^2}{\varepsilon_2 kT} \cdot \Psi_{3,2}(\underline{r}) \qquad \underline{r} \in D_2 \qquad (97b)$$

where

D_1 is a domain lying between S_1 and a surface S_2 (the potential at the latter being small enough to make the linear approximation (96) useful beyond this domain

and

D_2 lies between S_2 and infinity.

Over D_1, the contribution of co-ions to the charge density is neglected* (these ions being repelled from the polyion) while the linear (low-potential) approximation is used over D_2.

Four boundary conditions are required, two of these following directly from (90) and (92). In addition, $\Psi_{3,1}$ and $\Psi_{3,2}$ are matched so that the potential and field are continuous across S_2, i.e.

$$\left(\Psi_{3,1}(\underline{r})\right)_{S_2} = \left(\Psi_{3,2}(\underline{r})\right)_{S_2} \qquad (98a)$$

$$\left(\underline{\nabla}\Psi_{3,1}(\underline{r})\right)_{S_2} = \left(\underline{\nabla}\Psi_{3,2}(\underline{r})\right)_{S_2} \qquad (98b)$$

It now remains to choose the surface S_2. This is done in such a way that the errors in the approximate charge density terms of (97a) and(97b) respectively are of equal magnitude at S_2, i.e.

$$\left(\frac{1}{2}\, e^{q\Psi_{3,1}(\underline{r})/kT} - \sinh\frac{q\Psi_{3,1}(\underline{r})}{kT}\right)_{S_2} = \left(\sinh\frac{q\Psi_{3,2}(\underline{r})}{kT} - \frac{q\Psi_{3,2}(\underline{r})}{kT}\right)_{S_2} \qquad (99)$$

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*The surface S_2 found below has been found to approximately coincide with the position of the minimum in the counterion probability density function (c.f. the division introduced by Bjerrum to describe pairwise association of ions in simple electrolytes)(72).

In the method described below, the charge density term (right hand side) of (86) is replaced by a continuous approximation rather than the discontinuous one described by equations (97).

(iii) General Solution

The only exact first integral of the Poisson-Boltzmann equation that has been found to date refers to flat surfaces(46). Several approximate methods have been proposed for integrating this equation in cases of spherical symmetry. Hoskin(76) obtained a numerical solution but Loeb et al(74) have found his method of integration leads to inaccuracies at higher surface potentials, probably as a result of the greater potential gradient near each particle in such cases. The numerical analysis of Loeb et al takes this factor into account and also covers a wider range of the parameters. Pierce(77) has also integrated the potential equation (by a perturbation technique) and has presented his result as a series of functions, thus making manipulation easier than with tabular solutions. However, his Taylor expansion of the charge density term, while extending the linearisation of Gorin to a wider range of surface potentials, may not be satisfactory at high charge densities since the additional terms in his series lead to a great amount of computation. Further, he has used asymptotic expansions (valid only at large distances from a particle) to evaluate certain integrals.

The method proposed here involves piecewise linearisation of the charge-density function. A sequence of n domains D_i bounded by equipotential surfaces S_i and S_{i+1} $(i = 1,2, \ldots n)$ is established in such a way that the increment in the potential $\Psi_{3,i}$ over D_i is constant, i.e.

$$\left(\Psi_{3,i}(\underline{r})\right)_{S_i} = \frac{n - i+1}{n} \cdot \left(\Psi_3(\underline{r})\right)_{S_1} \quad (i = 1,2, \ldots n) \qquad (100)$$

and the $\Psi_{3,i}(\underline{r})$ also satisfy linear equations of the form

$$\nabla^2\Psi_{3,i}(\underline{r}) = \frac{8\pi N C_1{}^{o} q}{\epsilon_2} \cdot \left(a_i\Psi_{3,i}(\underline{r}) + b_i\right) \quad (i = 1,2, \ldots, n) \qquad (101)$$

where constants a_i and b_i are chosen so that

$$\left(a_i\Psi_{3,i}(\underline{r}) + b_i\right)_{S_i} = \left(\sinh \Psi_{3,i}(\underline{r})\right)_{S_i} \quad (i = 1,2, \ldots n) \qquad (102a)$$

$$\left(a_{i-1}\Psi_{3,i-1}(\underline{r}) + b_{i-1}\right)_{S_i} = \left(\sinh \Psi_{3,i}(\underline{r})\right)_{S_i} \quad (i = 2,3, \ldots, n + 1) \qquad (102b)$$

Solution proceeds by integrating equations (101), the constants of integration and surfaces S_{i+1} being found from the boundary conditions (90) and (92), equations (100) and the following continuity relations for the potential and field:

$$\left(\psi_{3,i-1}(\underline{r})\right)_{S_i} = \left(\psi_{3,i}(\underline{r})\right)_{S_i} \qquad (i = 2,3, \ldots, n) \quad (103a)$$

$$\left(\underline{\nabla}\psi_{3,i-1}(\underline{r})\right)_{S_i} = \left(\underline{\nabla}\psi_{3,i}(\underline{r})\right)_{S_i} \qquad (i = 2,3, \ldots, n) \quad (103b)$$

The solution is completed by solving over D_n (evaluating as many constants as possible), then successively solving over D_{n-1}, D_{n-2}, ... D_1. On reaching D_1, any undetermined constants that have been carried through are found from the last boundary condition (equation (90)).

8. POLYIONIC CHARGE AND ELECTROPHORETIC CHARGE

Serious difficulties are encountered in the calculation of polyionic charges from electrophoretic measurements on account of binding of small ions to each macroion. Charges calculated as above utilise the zeta-potential (referring to the surface of shear), not the Nernst potential of the polyion. Hence it is desirable to estimate that fraction of counterions transported with the polyions.

The division of counterions into "bound" and "free" categories is arbitrary since a polyion exerts long-range electrostatic forces on *all* counterions in solution. Hence none of the latter will behave as if the polyions were absent. Kotin and Nagasawa$^{(72)}$ have introduced a definition of the degree of ion binding which is independent of the added salt concentration but dependent on the polyion charge density. It follows from this definition and the potential equation that "bound" ions will be present in diffuse layers surrounding the polyions, i.e. one cannot, in general, consider "bound" ions to be held close to polyions. However, by working with high concentrations of supporting electrolyte, the extent of these diffuse regions can be reduced. This will minimise the liberation of bound ions by hydrodynamic shear forces during electrophoresis and also enable one to satisfactorily approximate the radius of each kinetic unit by that of a polyion.

CHAPTER 4

CYLINDRICAL MACROIONS

1. INTRODUCTION

The cylindrical model for polyions mentioned in Part 2 of Chapter 3 will be analysed with a view to obtaining a more accurate solution than Gorin's.(1) As before, microscopic parameters will be the main object of study, the mobility-zeta-potential relationship used by Gorin being retained.*

This chapter contains a formulation and analysis of the problem according to the methods outlined in Chapter 3.

2. FORMULATION OF THE PROBLEM

Consider a cylindrical particle of radius r_o surrounded by a symmetric ionic atmosphere. Let r be the radial distance of a point from the axis of the cylinder. Then the surface of shear (S_o) is the surface $r = r_o$ and S_1 is the surface

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*In deriving this, Gorin used Henry's relations(78) for cylinders oriented parallel to and normal to the applied electric field, averaging the two cases to obtain a formula for randomly oriented cylinders. His method of averaging has been criticised by Overbeek(79) but the latter did not suggest any alternative procedure.

$r = r_0 + r_1$ (where, as before, r_1 is the effective radius of a counterion), the differential equations being

$$\frac{1}{r}\frac{d}{dr}\left(r\,\frac{d\Psi_1(r)}{dr}\right) = 0 \qquad 0 \leq r < r_0 \tag{104}$$

$$\frac{1}{r}\frac{d}{dr}\left(r\,\frac{d\Psi_2(r)}{dr}\right) = 0 \qquad r_0 < r < r_0 + r_1 \tag{105}$$

$$\frac{1}{r}\frac{d}{dr}\left(r\,\frac{d\Psi_3(r)}{dr}\right) = \frac{8\pi N C_1{}^{0} q}{\epsilon_2}\sinh\frac{q\Psi_3(r)}{kT};\; r_0 + r_1 \leq r \leq \infty \tag{106}$$

The boundary conditions on these are as follows:

$$\lim_{r \to 0} \Psi_1(r) = A \tag{107}$$

$$\Psi_1(r_0) = \Psi_2(r_0) \tag{108}$$

$$-\epsilon_1\Psi_1'(r_0) + \epsilon_2\Psi_2'(r_0) = -4\pi\sigma \tag{109}$$

$$\Psi_2(r_0 + r_1) = \Psi_3(r_0 + r_1) \tag{110}$$

$$\Psi_2'(r_0 + r_1) = \Psi_3'(r_0 + r_1) \tag{111}$$

$$\lim_{r \to \infty} \Psi_3(r) = 0 \tag{112}$$

A zeta-potential-mobility relation follows directly from the work of Gorin(1) and may be written

$$u = \frac{e_2}{F'(Kr_0) \cdot \pi\eta} \cdot \zeta \qquad (113)$$

where η is the viscosity of the supporting electrolyte, κ is the reciprocal of the Debye-Hückel radius and the function $F'(\kappa r_0)$ allows for distortion of the electric field in the double layer (for different values of the ratio of particle radius to double layer thickness). Once the potential problem (104) - (112) has been solved, ζ may be found from (108) (in terms of σ) and substitution in (113) then yields σ in terms of the mobility (u).

3. REDUCTION OF THE POTENTIAL PROBLEM

(i) Reduction to a Single Boundary-Value Problem

Equation (104) is readily integrated, yielding the general solution

$$\Psi_1(r) = A_1 l_n r + A_2 \qquad (114)$$

where A_1 and A_2 are constants. From the boundary conditions (107) and (108) it then follows that

$$\Psi_1(r) = \zeta \qquad (115)$$

A similar integration of (105), followed by substitution of the conditions (108) and (109) gives (on using the previous result),

$$\Psi_2(r) = \zeta - \frac{4\pi\sigma r_0}{e_2} l_n\left(\frac{r}{r_0}\right) \qquad (116)$$

Equations (106), (110), (111), (112) and (116) then enable one to formulate the potential problem in the following manner:

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\psi_3(r)}{dr}\right) = \frac{8\pi N C_1{}^{\circ} q}{\varepsilon_2} \cdot \sinh\frac{q\psi_3(r)}{kT} ; r_o + r_1 \leq r \leq \infty \qquad (106)$$

$$\psi_3(r_o + r_1) = \zeta - \frac{4\pi\sigma r_o}{\varepsilon_2} \ln\left(\frac{r_o + r_1}{r_o}\right) \qquad (117)$$

$$\psi_3'(r_o + r_1) = -\frac{4\pi\sigma r_o}{\varepsilon_2(r_o + r_1)} \qquad (118)$$

$$\lim_{r \to \infty} \psi_3(r) = 0 \qquad (112)$$

Thus, provided (106) can be integrated (subject to the above boundary conditions), a solution of the form

$$\psi_3 = \psi_3(r, \sigma, \zeta, \varepsilon_2, C_1{}^{\circ}, q, k, T, r_o, r_1) \qquad (119)$$

will be obtained. If values for the last seven parameters are substituted and ζ replaced by using the expression (113), a relation of the form

$$\psi_3 = \psi_3(r, \sigma, u, \eta) \qquad (120)$$

is obtained (u and η being known parameters). As mentioned in Chapter 3, two of the above boundary conditions ((117) and (112)) are used to integrate (106), the remaining condition (118) providing a relation between σ and ζ (or u).

The charge (Q) or charge per unit length of cylinder (Q/l) is then found from

$$Q = 2\pi r_o l\sigma \qquad (121)$$

(ii) Reduction to Dimensionless Form

This is done in Appendix VII and the final form of the problem reads:

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{dW}{dR}\right) = \frac{1}{Z_o}\sinh Z_o W \qquad R_o + R_1 \leq R \leq \infty \qquad (122)$$

$$W(R_o + R_1) = 1 - \frac{4\pi\sigma r_o}{\epsilon_2\zeta} l_n\left(\frac{r_o + r_1}{r_o}\right) \qquad (123)$$

$$\lim_{R \to \infty} W(R) = 0 \qquad (124)$$

$$W'(R_o + R_1) = -\frac{4\pi\sigma r_o}{\epsilon_2(r_o + r_1)} \cdot \frac{1}{\zeta\kappa} \qquad (125)$$

where
$$W = \frac{\Psi_3}{\zeta} \qquad (126)$$

$$R = \kappa r \qquad (127)$$

$$R_o = \kappa r_o \qquad (128)$$

$$R_1 = \kappa r_1 \qquad (129)$$

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_1 kT}{8\pi q^2 NC_1^{\circ}}} \qquad (130)$$

and the remaining symbols have been defined above.

b. SOLUTION FOR THE CHARGE DENSITY (σ)

(i) Gorin's Approximation

Equation (96) becomes (in dimensionless form)

$$\frac{d^2W}{dR^2} + \frac{1}{R}\frac{dW}{dR} - W = 0 \qquad (131)$$

which has the general solution

$$W = A_1 \cdot I_o(R) + A_2 \cdot K_o(R) \qquad (132)$$

where A_1 and A_2 are constants and I_o, K_o are modified Bessel functions of the first and second kinds respectively, each of order zero. Since $I_o(R)$ is unbounded as $R \to \infty$, $A_1 = 0$ (by (124)) i.e.

$$W = \frac{W(R_o + R_1)}{K_o(R_o + R_1)} \cdot K_o(R) \qquad (133)$$

Differentiating (133) (see Appendix VIII), substituting in (125), replacing $W(R_o + R_1)$ by the expression (123) and rearranging, one finally obtains

$$\sigma = \frac{F'(\kappa r_o) \quad \eta\kappa \cdot \left(\frac{r_o + r_1}{4r_o}\right) \frac{K_1(R_o + R_1)}{K_o(R_o + R_1)}}{\left[1 + \frac{K_1(R_o + R_1)}{K_o(R_o + R_1)} \cdot \kappa(r_o + r_1)\, l_n\left(\frac{r_o + r_1}{r_o}\right)\right]} \cdot u \qquad (134)$$

which approximately agrees with Gorin's equation*.

Gorin appears to have used the method which he developed for spheres. In this, the electrical potential at any point is resolved into two components, one due to the charges of the ionic atmosphere and the other due to the charged cylinder. The above shows that this is unnecessary.

(ii) Boundary Layer Solution**

Following the method outlined in Chapter 3, a system of equations may be written thus:

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{dW_1}{dR}\right) = \frac{1}{2Z_0}e^{Z_2 W_1} \qquad R_0 + R_1 \leq R \leq R_2 \tag{135a}$$

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{dW_2}{dR}\right) = W_2 \qquad R_2 \leq R \leq \infty \tag{135b}$$

together with the boundary conditions

$$W_1(R_0 + R_1) = 1 - \frac{4\pi\sigma r_0}{\varepsilon_2 \zeta_0} l_n\left(\frac{r_0 + r_1}{r_0}\right) \tag{136a}$$

$$W_1(R_2) = W_2(R_2) \tag{136b}$$

---

*A term (1 + 2a) in his equation has been replaced by 1. The difference will be negligible for a <<< 1 ("a" in his notation is equivalent to r_0 above).

**Since this section was written, a paper has appeared$^{(114)}$ on this method. The authors do not mention the earlier work of

Alexandrowicz(55) and Alexandrowicz and Katchalsky(56) and have not calculated the surface charge density. Further, they have shown that their method cannot be applied to certain substances such as DNA and the method of piecewise linearisation (see below) is suggested as a more general method for dealing with such cases.

$$W_1'(R_2) = W_2'(R_2) \qquad (136c)$$

$$W_2(\infty) = 0 \qquad (136d)$$

and the equation defining R_2, viz.

$$\frac{1}{2Z_0} e^{Z_0 W_1(R_2)} - \frac{1}{Z_0} \sinh Z_0 W_1(R_2) = \frac{1}{Z_0} \sinh Z_0 W_2(R_2)$$
$$- W_2(R_2) \qquad (137)$$

To solve this potential problem near each polyion, use will be made of a transformation (due to Shifer) employed by Fuoss et al(80) in their study of rod-like polyelectrolytes in the absence of added salt (see Appendix IX). The solution may be written

$$W_1(R) = \frac{1}{Z_0} \ln \left\{ \frac{4\beta_1^2}{R^2 \sinh^2[\beta_1 \ln(\beta_2 R)]} \right\} \qquad (138)$$

where β_1^2 and β_2 are real numbers, β_1^2 passing from positive values through zero to negative values with increasing charge density. Since high charge densities (where Gorin's equation is inadequate) are being considered here, let β_3 be the modulus of β_1, i.e.

$$\beta_1 = i\,\beta_3 \tag{139}$$

so that

$$W_1(R) = \frac{1}{Z_0} \ln \left\{ \frac{4\beta_3^2}{R^2 \sin^2[\beta_3 \ln(\beta_2 R)]} \right\} \tag{140}$$

The solution for $W_2(R)$ is of the same form as (132), viz.

$$W_2(R) = \beta_4 I_0(R) + \beta_5 K_0(R) \tag{141}$$

To determine the constants, equations (136) and (137) are applied to (140) and (141), the charge density following by (125). The following algorithm for calculating σ is developed in Appendix X.

(a) Find the real root of

$$2e^A \left\{ \sinh A - A \right\} = 1 \tag{142a}$$

(The Newton-Raphson procedure gives $A = 1.011922$ to six decimal places after two iterations, using $A = 1$ as the initial approximation.)

(b) Assuming a value for R_2, estimate β_3 from

$$\beta_3 = \sqrt{\frac{R_2^2}{4} e^A - \left[\frac{R_2}{2} \frac{A K_1(R_2)}{K_0(R_2)} - 1 \right]^2} \tag{142b}$$

(c) Estimate β_4 by means of

$$\cot \beta_6 = \left(\frac{R_2 A}{2}\,\frac{K_1(R_2)}{K_0(R_2)} - 1\right)\Big/\beta_3 \qquad (142c)$$

(It suffices to select the positive root in (142c). Clearly equation (140) is unaltered by reversing the sign of β_3.)

(d) Estimate β_2 from

$$\beta_2 = \frac{1}{R_2}\, e^{\beta_6/\beta_3} \qquad (142d)$$

(e) Estimate σ from (10.5), i.e.

$$\sigma = \frac{\epsilon_2 kT}{2\pi r_0 q}\left\{1 + \beta_3 \cot\left[\beta_3 \ln(\beta_2(R_0 + R_1))\right]\right\} \qquad (142e)$$

(f) Substitute this value into (10.1), viz.

$$1 - \frac{4\pi\sigma r_0}{\epsilon_2 \zeta} \ln\left(\frac{r_0 + r_1}{r_0}\right)$$

$$= \frac{1}{Z_0} \ln\left\{\frac{4\beta_3^2}{(R_0 + R_1)^2 \sin^2\left[\beta_3 \ln(\beta_2(R_0 + R_1))\right]}\right\} \qquad (142f)$$

If this latter equation is not satisfied, a second value is assumed for R_2 and the procedure repeated until (142f) is satisfied as closely as desired.

(iii) Piecewise Linearisation

The surfaces S_i (see Chapter 3) are concentric cylinders, S_0 being the surface of shear ($R = R_0$) and

S_1 the surface $R = R_o + R_1$. The remaining S_i are the surfaces $R = R_i$ ($i = 2, 3, \ldots, n+1$), the R_i being defined by the relations given in Chapter 3 (note, R_{n+1} is at infinity). The formulation of Section 3 (ii) of this chapter will be used, W_i being the reduced potential over D_i.

Considering D_n first, one may write

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{dW_n}{dR}\right) = a_n W_n + b_n \tag{143}$$

which has the general solution

$$W_n = \alpha_n K_o(R\sqrt{a_n}) + \beta_n I_o(R\sqrt{a_n}) - \frac{b_n}{a_n} \tag{144}$$

Since $W_n(R) \to 0$ as $R \to \infty$, $\beta_n = b_n = 0$ and (144) simplifies to

$$W_n = \alpha_n K_o(R\sqrt{a_n}) \tag{145}$$

In general, over D_i

$$W_i = \alpha_i K_o(R\sqrt{a_i}) + \beta_i I_o(R\sqrt{a_i}) - \frac{b_i}{a_i} \quad (i = 1, 2, \ldots n) \tag{146}$$

where a_i and b_i are found by combining equations analogous to (100) and (102). Thus,

$$a_i \frac{(n - i + 1)}{n} \cdot W(R_o + R_1)$$

$$+ b_i = \frac{1}{Z_o} \sinh \left[Z_o \frac{(n - i + 1)}{n} \cdot W(R_o + R_1) \right] \quad (i = 1, 2, \dots n) \tag{147a}$$

$$a_{i-1} \frac{(n - i + 1)}{n} \cdot W(R_o + R_1) + b_{i-1}$$

$$= \frac{1}{Z_o} \sinh \left[Z_o \frac{(n - i + 1)}{n} \cdot W(R_o + R_1) \right] \quad (i = 2, 3, \dots n + 1) \tag{147b}$$

$W(R_o + R_1)$ being given (in terms of σ) by (123).

The α_1 and β_1 must satisfy continuity relations of the type (103), i.e.

$$\alpha_{i-1} K_o(R_i \sqrt{a_{i-1}}) + \beta_{i-1} I_o(R_i \sqrt{a_{i-1}}) - \frac{b_{i-1}}{a_{i-1}}$$

$$= \alpha_i K_o(R_i \sqrt{a_i}) + \beta_i I_o(R_i \sqrt{a_i}) - \frac{b_i}{a_i} \quad (i = 2, 3, \dots.n) \tag{148a}$$

$$\alpha_{i-1} K_1(R_i \sqrt{a_{i-1}}) - \beta_{i-1} I_1(R_i \sqrt{a_{i-1}})$$

$$= \alpha_i K_1(R_i \sqrt{a_i}) - \beta_i I_1(R_i \sqrt{a_i}) \quad (i = 2, 3, \dots.n) \tag{148b}$$

The R_i in equations (148) must satisfy relations of the type (100), viz

$$W_i(R_i) = \frac{n - i + 1}{n} \cdot W(R_o + R_1) \quad (i = 2, 3, \dots.n) \tag{149}$$

In general, the following procedure applies:

(a) Assign a value to n.

(b) Select a first approximation to σ.

(c) Calculate the a_i and b_i.

(d) Calculate the α_i and β_i.

(e) Estimate σ from (125). If this value does not equal that used in (b), use the estimate from (e) in place of the previous one and repeat the calculations until the values obtained from (b) and (e) are as close as desired.

(f) Increase n stepwise until a constant value of σ is obtained.

5. SOME NUMERICAL RESULTS

The data of Watanabe and Ui(81) (on Tobacco Mosaic Virus) and Ross(82) (on DNA) have been analysed by each of the three methods given above, estimates of the charge parameter* being set out below.

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*Charges are expressed in electronic units per Å of polyion. Some useful conversion factors employed in these calculations are given in Appendix XII.

	Gorin's Approximation	Boundary-Layer Solution	Piecewise Linearisation**
TMV	0.529	0.586	0.581
DNA (I*=0.005)	0.154	0.175	0.168
DNA (I*=0.01)	0.170	0.192	0.188
DNA (I*=0.02)	0.188	0.210	0.207
DNA (I*=0.05)	0.206	0.222	0.220

*I = ionic strength.

**These results refer to n = 2. It is doubtful whether the present formulation is accurate enough to warrant the use of larger n. The method of Section 4 (iii) can, however, be modified to achieve greater accuracy for n = 2 (see Appendix XI).

6. ION BINDING

(i) Electrophoretic-POLYIONIC Charge Relation

The difference between electrophoretic charge and polyion charge was discussed in Section 8 of Chapter 3. An expression for the polyion charge density will now be derived using the formula for the degree of counterion binding given by Kotin and Nagasawa(72).

If f^* is the degree of counterion binding and S_p the polyionic charge per unit length*,

$$f^* = 1 - \frac{\epsilon_s kT}{2q} \cdot \frac{1}{S_p} \qquad (149)$$

Also from the definition of f^*, the magnitude of the counterion charge bound per polyion (per unit length), S_B, is obtained by multiplying f^* by the magnitude of the total counterionic charge and dividing by the number of polyions and the length of a polyion, i.e.

$$S_B = f^* \frac{(S_p l C_p VN/M + qC_s VN)}{(C_p VN/M) \cdot l} \qquad (150)$$

where C_p = concentration of polymer (mass per unit volume of solution)

C_s = concentration of 1 - 1 electrolyte (moles per unit volume of solution)

V = volume of solution

N = Avogadro's number

M = molecular weight of polymer.

---

*For simplicity, S_p will be taken to be positive in this Section. An analogous treatment holds for polyanions.

Hence by (149) and (150),

$$S_B = \left(1 - \frac{\epsilon_s kT}{2qS_p}\right)\left(S_p \frac{C_p}{M} + \frac{qC_s}{1}\right) / \frac{C_p}{M} \qquad (151)$$

If one now introduces the electrophoretic charge per unit length of polyion (S_E), viz.

$$S_E = S_p - S_B \qquad (152)$$

and substitutes (151) in (152), a rearrangement of terms yields the result

$$S_p = \frac{S_o}{1 + \frac{C_p l}{C_s qM}\left(S_E - S_o\right)} \qquad (153)$$

where

$$S_o = \frac{\epsilon_s kT}{2q} \qquad (154)$$

Equation (153) then enables one to estimate the polyionic charge density (S_p) from the electrophoretic charge density (S_E).

(ii) Analysis of the Above

A number of interesting conclusions may be derived as follows:

(a) Since (by definition) $0 \leq f^* \leq 1$, equation (149) indicates that (153) only applies when $S_p \geq S_o$. This

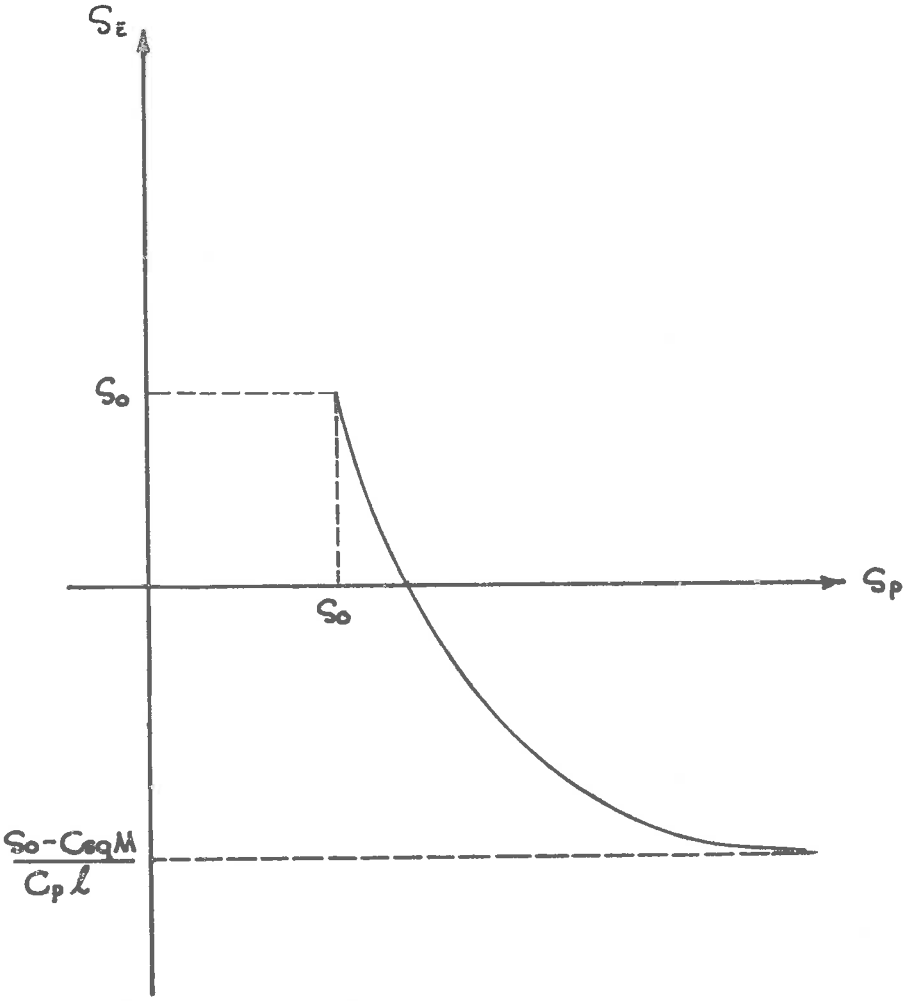

Fig. VI. Variation of electrophoretic charge (ς_z) with polyionic charge (ς_p). Other quantities are as defined in the text.

is seen to be qualitatively correct since, at low polyionic charge, weak electrolyte behaviour (and hence covalent bonding between counterions and polyions) must be considered. Kotin and Nagasawa explicitly excluded this type of interaction from the derivation of (149).

(b) Equation (153) is only valid for $S_E < S_o$, otherwise one would obtain $S_p < S_o$, the case excluded by (a).

(c) As $S_p \to \infty$, $S_E \to \frac{C_s}{C_p}\frac{qM}{l}$. In this limit of very high polyionic charge, $f^* = 1$, i.e. all counterions are bound.

(d) The relation between S_p and S_E is shown in Figure VI. Differentiating (153) and substituting from that equation,

$$\frac{dS_E}{dS_p} = -\frac{\frac{C_s qM}{C_p l} + (S_E - S_o)}{S_p} = -\frac{S_o}{S_p{}^2} \Big/ \frac{C_p l}{C_s qM} \qquad (155)$$

Thus, on increasing the salt concentration and/or decreasing the polymer concentration, the lower limit for S_E in (c) is reduced and, by (155), the curve in Figure VI becomes steeper. Hence a sufficiently high value of the ratio C_s/C_p, in addition to giving a more compact double layer, also prevents small errors in S_E from causing large errors in the determination of S_p.

(e) At the isoelectric point ($S_E = 0$),

$$S_p = \frac{\epsilon_s kT}{2q\left[1 - \dfrac{C_p l}{C_s qM} \cdot \dfrac{\epsilon_s kT}{2q}\right]} \qquad (156)$$

This suggests that for given values of the polyelectrolyte parameters (S_p and M/l), as well as ϵ_s and T, there is a unique value of C_s/C_p at which the electrophoretic mobility is zero.

(f) In all cases, M/l must be known before the ion-binding correction can be applied to the electrophoretic charge.

No ion binding correction has been applied to the previous table since the accuracy of (153) is somewhat uncertain (even when the condition $S_p \geq S_c$ is satisfied). The results of this section are only intended to provide qualitative information and a more exact analysis would have to include weak electrolyte behaviour.

PART III

APPLICATION TO KINETIC STUDIES

CHAPTER 5

ELECTROPHORETIC DETERMINATION OF KINETIC PARAMETERS IN POLYELECTROLYTE SYSTEMS

1. INTRODUCTION

This chapter commences with a discussion of the correlation between electrophoretic mobility and the extent of reaction, the formal treatment being shown to be consistent with experimental data and physico-chemical theory (to a first order approximation). The inadequacy of a linear mobility-reaction coordinate relationship is demonstrated, followed by a discussion of the binomial distribution (derived by Pressman and Sternberger(83)) of species produced by a chain of first order reactions. Relations between mobility distribution parameters and rate constants are derived, initially where only one mobility is observable. The linear approximation to this relation is shown to agree with experiment. General relations between parameters of the mobility distribution and the distribution of species are then determined, followed by interpretations of these. The chapter closes with some possible alternative methods for determining rate constants by means of other transport processes.

2. GENERAL PRINCIPLES

It has been shown(46) that, for a polyelectrolyte system, electrophoretic mobility under fixed conditions of temperature, pH and ionic strength is related to the charge per unit length of polyion. The importance of this lies in the fact that a correlation is possible between observed mobilities and certain properties of polyelectrolytes. Thus it has been verified experimentally(37) that a change of 17% in the degree of sulphonation of poly(sodium vinyl sulphonate) gives rise to a change of mobility also equal to 17% (within the limits of experimental error). One would therefore expect that the course of a reaction may be followed by measuring electrophoretic mobilities, provided the valency of each macroion changes as reaction proceeds.

Certain reactions involving biological materials have been studied in this way by separating reactants, intermediates and products and Brinton and Lauffer(84) have summarised the convenient properties of the electrophoretic method as follows: (i) The concentrations of the various components can be measured in the Tiselius apparatus. (ii) The passage of an electric current large enough to separate components does not affect their activity or structure. (iii) Electrophoresis is capable of detecting small charge differences. However, only those systems in which the various components can be separated in this manner are described by the above authors and, after isolation of these, they consider independent methods of identification to be necessary. It will be seen in what follows that for certain systems these restrictions may be removed and that the method is of much greater utility. By repeating the reaction at different temperatures, the Arrhenius parameters (frequency factor and energy of activation) may then be determined in the usual way.

In many cases other methods are available (e.g. chemical analysis) but the electrophoretic technique is often preferable. Thus, as mentioned in (i) above, concentrations of several components may be found in this way, whereas chemical analysis may only yield an average composition for the whole sample. It will also be seen from (ii) that electrophoresis succeeds in some instances where analysis is made difficult by the breakdown of molecular structure. Finally, mobility determinations will often yield more accurate results than other methods due to the charge-sensitive property (iii). Thus the action of formaldehyde on tobacco mosaic virus may be studied by an alternative method(85), viz. by determining the infectivity of the virus after different reaction times. Such a technique, however, apart from its inconvenience, does not yield results of very high precision.

For some chain mechanisms (such as the sulphonation of polystyrenes), consecutive reactions may proceed very rapidly until a certain species is formed, then cease. In such instances, mobility measurements are unable to follow the kinetics of the chain, i.e. electrophoresis cannot be used to study fast reactions. It may also be argued that even where reaction is slower and electrophoretic heterogeneity exists, the range of mobilities in a given mixture is often too small to be detected (with sufficient accuracy) from observed concentration-gradient profiles. Peaks of electrophoresis patterns may spread quite noticeably for several other reasons (diffusion, field strength gradients or concentration-dependence of mobilities) and estimation of boundary spreading due to electrophoretic heterogeneity may become very difficult. Fischer and Lauffer(86), for example, noted that boundary spreading with a treated virus would only be about 2% greater than that obtained with untreated virus. However, they did discover that the mean mobility was sensitive to the extent of reaction prior to electrophoresis and it will be shown below that the method is still useful in these cases. Where electrophoretic heterogeneity is marked, one may use the distribution function mentioned by Baldwin, Laughton and Alberty(28) as discussed below.

In all cases it must be ensured that the reaction can be stopped before electrophoresis is begun. Fischer and Lauffer(86) were able to do this by adding specially prepared buffer to lower the pH to the isoelectric point of their virus, thus causing precipitation. Other workers(e.g. Gilbert and Jenkins(87), Bak and Kauman(22)) have studied systems in which reaction and transport occur simultaneously, but such a technique tends to make interpretation of results difficult. Also, transport processes are temperature-sensitive so that heats of reaction could become troublesome. It will be seen that the present method avoids these disadvantages.

3. RELATION BETWEEN MOBILITY AND THE EXTENT OF REACTION

(i) The General Equation

Consider the class of chain reaction which may be described by

$$
\begin{aligned}
&A_0 + X \rightarrow A_1 \\
&A_1 + X \rightarrow A_2 \qquad\qquad (157) \\
&\cdots\cdots\cdots\cdots \\
&A_{N-1} + X \rightarrow A_N
\end{aligned}
$$

where A_i represents a polyelectrolyte which, in solution, liberates macroions bearing $(i + a)$ charged groups (a being the number of these groups initially present on each polyion). In general, after a given time has elapsed, all the species A_0, A_1, ... A_N of a particular system are liable to be present in the reaction mixture and electrophoresis may be used to determine their relative concentrations. Each polyion will be treated as a sequence of N^* units linked together to form a single long chain.

Denoting the mobility of A_i by u_i, the following relation will be postulated:

$$u_i = K \cdot \phi\ (\alpha_i) \tag{158}$$

where

$$\alpha_i = \frac{i + a}{N^*} \quad (i = 0,\ 1,\ 2,\ \ldots.\ N) \tag{159}$$

the constant K having the same dimensions as the mobility. It will be noted that each α_i is proportional to the charge per unit length of polyion. Rewriting equations (159) in the form

$$\alpha_i = \frac{i/N + a/N}{N^*/N} \quad (i = 0,\ 1,\ 2,\ \ldots.\ N) \tag{160}$$

the mobilities, u_i, on the basis of (158), are seen to depend upon form factors: (i) the solute-solvent system (characterised by the constant K and function ϕ); (ii) the initial valence of the polyions relative to their maximum possible change of valence (i.e. a/N); (iii) the extent of reaction prior to electrophoresis (i.e. the reaction coordinate i/N); and (iv) the total number of units in a polyion relative to the number of these which may acquire a charge by reaction (i.e. N^*/N).

An important point to note here is that, unlike diffusion coefficients, electrophoretic mobilities are essentially independent of molecular weight (in a given homologous series). This follows from the work of Hermans and Fujita$^{(61)}$ and is confirmed by a number of experimental studies.$^{(57,88-92)}$ For this reason, only the relative quantities i/N, a/N and N^*/N appear in equations (160), not N itself.

(ii) First-Order Approximation

Since the density of the set $[\alpha_0, \alpha_1 \ldots\ldots \alpha_N]$ is very great for large N, α may be treated as a continuous variable. Then provided $\phi(\alpha)$ is analytic over the interval $\alpha_0 \leqslant \alpha \leqslant \alpha_N$, (158) may be expanded in a Taylor series about α_0, i.e.

$$u_i = K\left[\phi(\alpha_0) + (\alpha_i - \alpha_0)\phi'(\alpha_0) + \frac{(\alpha_i - \alpha_0)^2}{2!}\phi''(\alpha_0) + \ldots\right] \qquad (161)$$

and, for sufficiently small values of $(\alpha_i - \alpha_0)$, a good approximation is furnished by truncating after the first derivative, giving

$$u_i - u_0 = (u_N - u_0) \cdot \frac{\alpha_i - \alpha_0}{\alpha_N - \alpha_0} \qquad (162)$$

From the definition (159), it immediately follows that

$$u_i - u_0 = (u_N - u_0) \cdot \frac{i}{N} \qquad (163)$$

i.e. for small changes in α, the mobility increments $(u_i - u_o)$ are proportional to the corresponding reaction coordinates (i/N).

The constant of proportionality $(u_N - u_0)$ could be evaluated by measuring the mobilities (u_i) for known values of i/N (determined by chemical analysis). Equation (163) would then enable one to determine the extent of reaction (i/N) for any other homologue (obtained from a polymer A_0 of different molecular weight) by measuring its mobility under the same conditions of temperature, pH and ionic strength. However, as mentioned earlier, auxiliary analyses are unnecessary in rate constant determinations and a more direct method is given in Section 5.

(iii) <u>Justification of the Linear Law</u>

Equation (163) has only been formally derived from the postulated relation (158) and must therefore be tested by other means. It will be shown (see Section 5) that when (163) is combined with the kinetic treatment of Section 4, an expression is obtained which agrees with experimental observations of mean mobilities after different reaction times.

Apart from this empirical justification, it is also possible to show that (163) is consistent with current physico-chemical theory. This will first be done for rigid (non-draining) macroions.

The viscous retarding force (F_1) acting on a particle moving through a fluid at low Reynolds number is very nearly proportional to the velocity (v) of the particle relative to the fluid$^{(93)}$, i.e.

$$F_1 = fv \qquad (164)$$

where f is the frictional coefficient. If the particle has a charge Q, an electric field of strength E will exert an accelerating force (F_2) given by

$$F_2 = QE \qquad (165)$$

In steady electrophoretic motion, these two forces will be equal in magnitude and, introducing the definition of the mobility (u), viz.

$$u = \frac{v}{E} \qquad (166)$$

it readily follows from (164) and (165) that

$$u = \frac{Q}{f} \qquad (167)$$

If the frictional coefficient is essentially constant throughout the reaction, the mobility-charge relationship (167) will be linear. Introducing the expression for the total charge, viz.

$$Q = m(a + i) \tag{168}$$

(167) assumes the form

$$u_i = \frac{ma}{f} + \frac{m}{f} \cdot i \tag{169}$$

which may be written

$$u_i - u_e = (u_N - u_e) \cdot \frac{i}{N} \tag{163}$$

The factor m is introduced into (168) since the friction factor f and charge Q in (164) and (165) respectively refer to a "particle" as described in Part II of this thesis, viz. one bounded by the average surface of shear (inner Helmholtz surface$^{(94)}$), whereas (a + i) is the charge that would obtain in the absence of counterions. Provided m (which expresses the degree of counterion binding) does not change appreciably during reaction, equation (163) will be valid.

The electrophoresis of flexible macroions with partial free drainage has been treated by Hermans and Fujita$^{(61)}$. If Q_S and f_S denote, respectively, the charge and frictional coefficient of a segment, their expression for the mobility may be written

$$u = \frac{Q_S}{f_S}\left\{1 + \frac{\sigma^2}{y^2}\left(\frac{2 + \sigma/\beta}{1 + \sigma/\beta}\right)\right\} \qquad (170)$$

in which σ is the shielding ratio of Debye and Bueche$^{(95)}$, β being the ratio of the radius of a polyion (considered as a partially-draining sphere) to the radius of its ionic atmosphere. Provided the ionic strength of the solution is sufficiently high, $\beta \ggg \sigma$ and (170) simplifies to

$$u = \frac{Q_S}{f_S} \qquad (171)$$

which is analogous to (167). Equation (163) then follows as in the case of rigid ions.

(iv) Higher-Order Approximation

The linear relation between mobility and the reaction coordinate is only valid over small ranges of x and, in general, higher-order terms in the expansion (161) will be necessary to account for the variation in charge at the surface of shear. Two charge-interaction mechanisms may be distinguished, viz. ion/induced-dipole interactions$^{(23)}$ (giving rise to van der Waals adsorption of ions on the polymer) and counterion binding$^{(46)}$. As α increases, the second process becomes relatively more important and may become so strong that the value of m in equation (168) is appreciably decreased. For these reasons, the nonlinear variation of mobility with α observed by Noda et al$^{(92)}$ is not surprising and, on the basis of the above, four regions may, in general, be expected (see Figure VII).(i) at low values of α, where ion/induced-dipole interactions are most important; (ii) at intermediate values of α, where counterion binding is more important but m is approximately constant (the linear region); (iii) at larger values of α where m becomes somewhat less than in (ii), i.e. the charge at the surface of shear varies progressively more slowly than in (ii), (iv) at largest values of α where strong polyelectrolyte behaviour is observed and an increase in α produces a *reduction* in mobility (c.f. Section 6 of Chapter 4).

In addition to variations in charge, the friction factor will also change with increasing α due to contraction of the ionic atmosphere. However, shrinkage of the *compact* part of the electrical double layer (i.e. within the surface of shear) is not likely to be great enough to have any significant

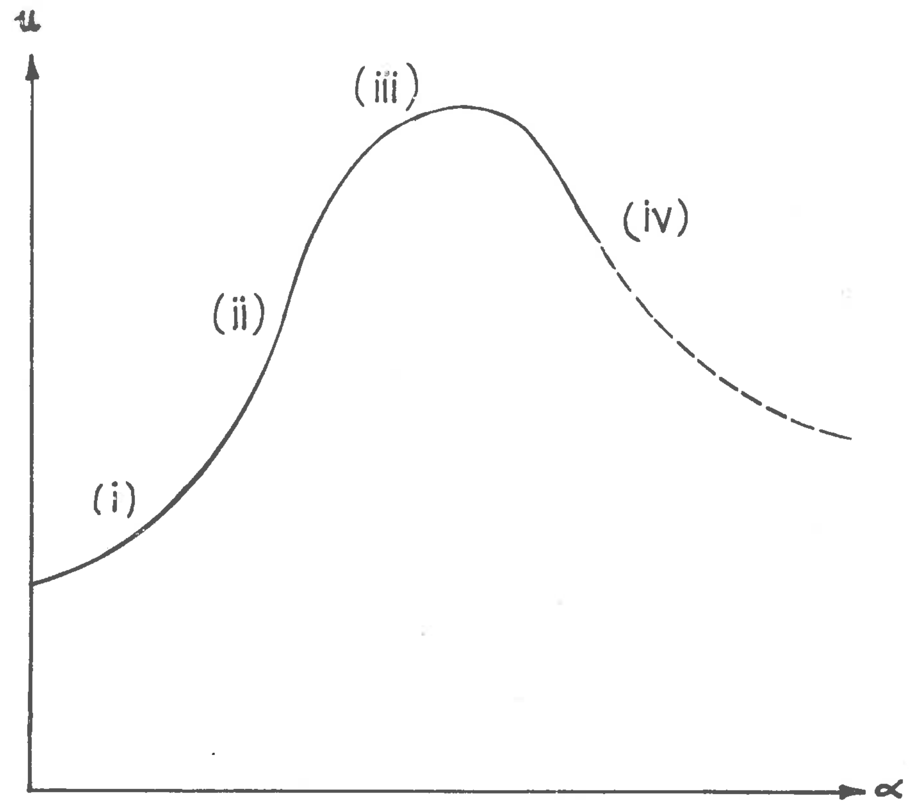

fig. VII. Mobility (u) as a function of the modified reaction coordinate (α). Numerals indicate regions defined in the text. (The last part of region iv is dotted because experimental evidence is lacking there.)

effect. Where partial free-drainage occurs, the friction factor for a polyion will depend upon the configuration of the coil but, by using sufficiently high concentrations of supporting electrolyte, this configuration will remain essentially constant, preventing any appreciable variations in friction factor.

(v) Interpretation of an Experimental Study

Noda et al(92), finding that the mobility-reaction coordinate relation for the neutralisation of polyacrylic acid was nonlinear, proposed an alternative interpretation in which the friction factor of a segment was considered to vary while the charge on a segment remained constant (a segment being defined as a sequence of spherical structural units bearing one electronic charge, q). They treated each segment as a prolate ellipsoid of resolution with axial ratio p, the latter being inversely proportional to α. Since, by definition, a segment reduces to a sphere ($p = 1$) at complete neutralisation ($\alpha = 1$), it follows that

$$p = \frac{1}{\alpha} . \qquad (172)$$

By introducing Perrin's equation(96) for the friction factor ($f(p)$) of a prolate ellipsoid, viz.

$$f(p) = 6\pi\eta\rho \cdot \frac{\sqrt{1 - p^2}}{p^{2/3}\ \ln[(1 + \sqrt{1 - p^2})/p]} \qquad (173)$$

(in which ρ is the radius of a sphere of the same volume as the ellipsoid and η the viscosity of the supporting electrolyte), their analysis leads to the result

$$u = q/f(1/\alpha) \qquad (174)$$

This treatment, however, is untenable for several reasons.

(a) Perrin's equation (173) assumes that the axial ratio has been defined so that $p < 1$, but this is clearly at variance with equation (172).

(b) Even if the axial ratio is taken as directly proportional to α, (173) predicts that in the limit $\alpha \to 0$ (i.e. at zero degree of neutralisation), $f \to \infty$, i.e. $u \to 0$ whereas, under these conditions, the polymer will most probably have a non-zero mobility due to its adsorbed charge as described above (the experimental data suggest this; see also the electrophoretic titrations of Mandel and Leyte(97)).

(c) The mobility varies almost linearly with α over the range $0.1 < \alpha < 0.5$, in agreement with the earlier interpretation, whereas the approach of Noda et al gives a poor fit to the data.

(d) Equation (172) implies that the charge-reaction coordinate relation is linear. This is not true of the charge which determines the mobility (viz. that at the surface of shear) because m decreases as α increases (see above).

It would appear that Noda et al actually used Perrin's formula for oblate ellipsoids ($p > 1$). A similar difficulty arises in the work of Abramson et al(1). Morawetz has also implied that $p > 1$ for prolate ellipsoids(98).

The correct formulae may be found in Perrin's original article(96) and also in a paper by Scheraga and Mandelkern(99).

4. COMPOSITION OF THE MIXTURE PRIOR TO ELECTROPHORESIS

The relative concentrations of the species A_i in solution (before electrophoresis) will depend upon the kinetics of the reactions (157) and only first order rate constants will be considered here. A problem of this type has been considered by Pressman and Sternberger(83) who used a protein as initial reactant (A_0), iodine being introduced in great excess to preserve first order kinetics at each stage. Successive substitution of iodine on tyrosine rests gave rise to a series of compounds A_1, A_2 .... A_N and, using $[A_i]$ to denote the concentration of species A_i after a reaction time t, their formula may be written

$$\frac{[A_i]}{A_T} = \binom{N}{i} e^{-Nkt} (e^{kt} - 1)^i \qquad (175)$$

where k is the first order rate constant for the reaction between iodine and a tyrosine rest on any of the A_i $(0 \leqslant i < N)$, A_T being the total protein concentration, i.e.

$$A_T = \sum_{i=0}^{N} [A_i] \qquad (176)$$

(A_T will also be equal to the initial concentration of A_0.) By introducing the new quantities defined by

$$\theta(t) = 1 - e^{-kt} \qquad (177)$$

and

$$f(i) = \frac{[A_i]}{A_T} \qquad (178)$$

the relation (175) assumes the form

$$f(i) = \binom{N}{i} \theta^i (1 - \theta)^{N-i} \qquad (179)$$

which is of the type discussed by Baldwin et al(28) in connection with electrophoretic heterogeneity arising from chemical reaction.

Two special cases of (179) are of particular interest:

(i) If the product kt (and hence θ) is small, it follows that for the large values of N occurring in polyelectrolyte systems, equation (179) will approximate to the Poisson form

$$f(i) = e^{-N\theta} \frac{(N\theta)^i}{i!} \qquad (180)$$

This is to be expected since the number of available reactive sites is large whereas the number of effective collisions is relatively small (since kt is small). Such distributions are more likely to occur when reaction is slow (small k) or in the early stages of a reaction (small t).

(ii) When θ is not small, a Gaussian distribution function may be used in place of (179).

5. MOBILITY DISTRIBUTION PARAMETERS IN TERMS OF RATE CONSTANTS

The distribution of mobilities in a given sample and the kinetic expression (179) for the distribution with respect to the number of reacted groups per molecule will now be combined. This is achieved by means of the correlation (158) between mobility (u) and the modified reaction coordinate (α).

(i) Cases Where Only a Single Mobility is Observed

As mentioned in Section 2, isolation of all the components in a mixture, followed by independent identification of each, is not generally necessary.

It will now be shown how rate constants may be evaluated from measurements of only the <u>mean</u> mobility of intermediates in the reaction scheme.

Starting from equation (158), one may derive the relation

$$\bar{u}(t) = K \cdot \bar{\phi}\,(\alpha(t)) \tag{181}$$

where the bars indicate averages taken over all species present. If no heterogeneity is observable, a good approximation to equation (181) is

$$\bar{u}(t) = K \cdot \phi\,(\bar{\alpha}(t)) \tag{182}$$

Returning to the binomial distribution (179),

$$\bar{I}(t) = N \cdot \theta(t) \tag{183}$$

so that, combining (159) and (183), the mean value of α is given by

$$\bar{\alpha}(t) = \frac{N \cdot \theta(t) + a}{N^*} \tag{184}$$

Hence, substituting (177) and (184) into (182), the relation between mean mobility and rate constant is obtained, viz.

$$\bar{u}(t) = K \cdot \phi \left[\frac{N(1 - e^{-kt}) + a}{N^*} \right] \tag{185}$$

Provided the function ϕ can be found (as in the experiments of Noda et al(92)), some additional information is obtainable, e.g. N/N^* and a/N^* calculated from (185) enable one to compute a quantity ν given by

$$\nu = \frac{N + a}{N^*} \tag{186}$$

i.e. the number of charged groups per structural unit (after complete reaction).

For the determination of rate constants, however, the function ϕ need not be found, provided one is working over small intervals of α. Under these conditions, equation (163) immediately gives

$$\bar{u}(t) - u_0 = (u_N - u_0)\,\frac{\bar{I}(t)}{N} \tag{187}$$

which, by (177) and (183), may be written

$$\bar{u}(t) - u_0 = (u_N - u_0)\,(1 - e^{-kt}) \tag{188}$$

This equation is of the same form as that employed by Fischer and Lauffer(86) but will only be valid over limited ranges of α. Their assumption that mobility equals K (their X) times charge cannot be justified in general.

(ii) Cases Where Heterogeneity is Observed

While mean mobilities are sufficient for the determination of rate constants, higher moments of the mobility distribution are also dependent upon the kinetics of the chain (157) and may provide further useful information.

(a) Relations between moments of the mobility and i-distributions will be derived first. The j^{th} moment (μ_j) of the mobility distribution (probability density function $q(u)$) about its mean ($\bar{u}$) is, by definition,

$$\mu_j = \int_{u_0}^{u_N} (u - \bar{u})^j \, q(u)du \qquad j = 0,1,2, \ldots \qquad (189)$$

and by (158) this may be written

$$\mu_j = K^j \int_0^N \left[\phi\left(\frac{i + a}{N^*}\right) - \phi\left(\frac{\bar{i} + a}{N^*}\right) \right]^j f(i)di \qquad j = 0,1,2, \ldots \qquad (190)$$

The approximation (182) will not, in general, be sufficiently accurate when heterogeneity is marked and the distribution function for ϕ must be considered when applying (190). In general one obtains relations of the form

$$\mu_j = K^j \int_0^N \sum_{n=0}^{\infty} a_n \, (i - \bar{i})^n \, f(i)di \qquad (191)$$

or
$$\mu_j = K^j \sum_{n=0}^{\infty} a_n \nu_n \qquad j = 0,1,2, \ldots \qquad (192)$$

where
$$\nu_n = \int_0^N (i - \bar{I})^n f(i)\,di \qquad n = 0,1,2 \ldots \qquad (193)$$

and the a_n are constants. Thus any moment of the mobility distribution is a linear combination of all moments of the i-distribution.

Under conditions where the linear relation (163) holds, however, considerable simplification of (190) is possible. Thus

$$u - \bar{u} = \frac{u_N - u_O}{N} \cdot (i - \bar{I}) \qquad (194)$$

so that (189) becomes

$$\mu_j = \left(\frac{u_N - u_O}{N}\right)^j \nu_j \qquad j = 0,1,2, \ldots \qquad (195)$$

and the two sets of moments are then proportional.

(b) The parameters in the Gram-Charlier series for the mobility distribution function, q(u) (see Chapter 1) will now be related to those of the i-distribution via (195). On substituting the expressions for moments of the binomial distribution$^{(30)}$, viz.*

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* i here denotes the complex number for which $i^2 = -1$.

$$\nu_j = \frac{1}{i^j}\left[\frac{d^j}{dt^j}(1 - \theta + \theta e^{it})^N\right]_{t=0} \tag{196}$$

one obtains

$$\bar{u} - u_0 = (u_N - u_0)\cdot\theta \tag{197}$$

(as in (186)) and

$$h^2 = \frac{(u_N - u_0)^2}{N}\ \theta(1 - \theta) \tag{198}$$

while higher moments are given by

$$\mu_3 = \left(\frac{u_N - u_0}{N}\right)^3 N\theta\ (1 - \theta)(1 - 2\theta) \tag{199}$$

$$\mu_4 = \left(\frac{u_N - u_0}{N}\right)^4 \left[3N^2\theta^2(1 - \theta)^2 + N\theta(1 - \theta)\ (1 - 6\theta + 6\theta^2)\right] \text{ etc.} \tag{200}$$

Thus q(u) assumes the form

$$q(u) = \frac{1}{h(\theta)\cdot\sqrt{2\pi}}\, e^{-(u-\bar{u}(\theta))^2/2h^2(\theta)} \left\{1 + \frac{1 - 2\theta}{3!\sqrt{N\theta(1 - \theta)}}\cdot H_3\left(\frac{u - \bar{u}(\theta)}{h(\theta)}\right) + \frac{1 - 6\theta + 6\theta^2}{4!N\theta(1 - \theta)}\cdot H_4\left(\frac{u - \bar{u}(\theta)}{h(\theta)}\right) + \cdots\cdot\right\} \tag{201}$$

where $\bar{u}(\theta)$ and $h(\theta)$ are given by (197) and (198).

Series of the type (201) are most useful when deviations from normality are small, otherwise convergence (if obtained at all) will be slow. The higher-order terms may also exhibit non-uniform behaviour* (as in the case of the Poisson distribution below). Since the error involved in (195) by using the linear approximation (163) will have an increasingly serious effect as higher-order terms are considered, moments higher than the second should be used with caution.

(c) In macromolecular systems (large N), the higher terms of (201) will be small (provided $\bar{i} = N\theta$ is not too small) and a suitable truncation is therefore possible. The two special cases mentioned in Section 4 will be considered in turn.

For small values of θ (i.e. when the product $N\theta$ is not very large), a Poisson distribution is obtained and, using the fact that all cumulants are equal for this distribution, it follows that q(u) approaches the form

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*Rather than add terms in their natural order, successive approximations are better obtained after rearrangement of a Gram-Charlier series.(100)

$$q(u) = \frac{1}{h\sqrt{2\pi}} e^{-(u-\bar{u})^2/2h^2} \left\{ 1 + \frac{1}{3!(\bar{I})^{1/2}} \cdot H_3 \left(\frac{u - \bar{u}}{h}\right) \right.$$

$$+ \frac{1}{4!(\bar{I})} \cdot H_4 \left(\frac{u - \bar{u}}{h}\right) + \frac{1}{5!(\bar{I})^{3/2}} \cdot H_5 \left(\frac{u - \bar{u}}{h}\right)$$

$$\left. + \frac{1}{6!} \left(\frac{1}{(\bar{I})^2} + 10\right) H_6 \left(\frac{u - \bar{u}}{h}\right) + \dots \right\} \qquad (202)$$

When θ is not small, the normal form

$$q(u) = \frac{1}{h\sqrt{2\pi}} e^{-(u-\bar{u})^2/2h^2} \qquad (203)$$

is obtained.

(d) It now remains to interpret the parameters of the mobility distribution. From (198) and (177), it follows that

$$h^2 = \frac{(u_N - u_0)^2}{N} e^{-kt} (1 - e^{-kt}) \qquad (204)$$

The standard deviation (h) achieves its maximum value when $t = \frac{1}{k} \cdot \ln 2$, i.e. at the half-life of the reactive sites, this value of h (denoted by h_{max}) being given by

$$h_{max} = \frac{u_N - u_0}{2\sqrt{N}} \qquad (205)$$

Correspondingly, the maximum standard deviation in the i-distribution, $(\sqrt{\nu_2})_{max}$, is

$$(\sqrt{\nu_2})_{max} = \frac{\sqrt{N}}{2} \qquad (206)$$

In general,

$$\sqrt{\nu_2} = \frac{\sqrt{N}}{2} \cdot \sqrt{4e^{-kt}\ (1 - e^{-kt})} \qquad (207)$$

Thus, once k and $(u_N - u_0)$ have been found from the mean mobilities $\bar{u}(t)$ (using (188)), (204) affords a method for calculating the number of reactive sites per molecule (N). Equation (183) will then enable one to determine the time required for reaction to proceed to a given value of $\bar{I}$, the corresponding range of products being indicated by (207). This range of products produced after a given reaction time is better expressed in terms of a coefficient of variation, viz

$$\frac{\sqrt{\nu_2}}{\bar{I}} = \sqrt{\frac{1 - \theta}{\theta}} \cdot \frac{1}{\sqrt{N}} \qquad (208)$$

(by (183) and (207)) which indicates that electrophoretic heterogeneity for given kt will, when expressed in this way, decrease in proportion to $\sqrt{N}$.

The above mechanism has been used to describe the reaction between tobacco mosaic virus and formaldehyde(86). It is also interesting to note that (188) is of a form used to describe the growth of organisms(101). The electrophoretic method may thus be useful in a number of biochemical studies as an aid to the correlation of macroscopic changes with reaction mechanisms. This is borne out by a recent investigation(3) in which mobilities have been measured at different stages of the mitotic cycle, corresponding changes in cell chemistry being suggested.

The work of Fischer and Lauffer(86), however, included the estimation of several rate constants (from the ninhydrin reaction) and Laird et al(102,103) have recently considered more general growth laws. Considerable modification of the above will therefore be necessary when investigating more complex reaction schemes and, once this is done, higher moments of mobility distributions may prove useful (e.g. in finding first approximations to the various rate constants.

6. TRANSPORT IN OTHER FIELDS

Separation of the components A_i on the basis of differing mobilities in an electric field suggests that differences in other transport coefficients may also prove useful in kinetic studies.

Resolution into components of different molecular weights has been achieved by ultracentrifugation(5) and this suggests that the kinetics of, for example, slow addition-polymerisation reactions, could be followed by measurement of sedimentation coefficients.

Differential motion has also been observed in the presence of mutually perpendicular magnetic and electric fields (electromagnetophoresis(21)). This has been found useful in the fractionation of certain cell suspensions for which ultracentrifugation is ineffective(104) (transport of this type occurs when suspended particles differ from their surrounding fluid in electrical conductivity, dielectric constant or magnetic permeability).

At present, however, no kinetic studies of these types have been reported and much experimental and theoretical work remains to be done.

CONCLUSIONS

This investigation into the theory and application of electrophoresis has led to a more complete formulation and analysis of several problems. A number of quantitative relations have been derived and these are summarised below*.

1. MULTICOMPONENT SYSTEMS

In sufficiently dilute solutions, the field strength and mobilities are almost constant. If a Gram-Charlier distribution of mobilities exists, its parameters are related to the concentration-gradient function by

$$\frac{\partial C}{\partial x} = \frac{C^0}{\Sigma \cdot \sqrt{2\pi}} e^{-(x-\bar{u}Et_E)^2/2\Sigma^2} \left\{ 1 + \sum_{j=3}^{\infty} \frac{\alpha_j \omega^j}{j!} H_j\left(\frac{x - \bar{u}Et_E}{\Sigma}\right) \right\} \quad (16)$$

where

$$\omega = \frac{hEt_E}{\Sigma} \quad (17)$$

and

$$\Sigma^2 = h^2E^2t_E^2 + 2Dt \quad (18)$$

It has been shown above that this agrees with a number of current relations, viz.

(a) When $D = 0$, Σ is proportional to t_E(18).

(b) When $h = 0$, Σ^2 is proportional to t(31) (test for homogeneity).

*For definitions of symbols, see main text.

(c) A plot of $\Sigma^2/2t$ versus $t_E^{\,2}/t$ enables one to estimate D and h.(31)

In addition, equations (16) to (18) show that,

(d) The centroid of a concentration-gradient pattern yields the average mobility since

$$\bar{X} = \bar{u}\, E t_E \tag{20}$$

and

(e) Higher moments of the $\partial C/\partial x$ function may be used to estimate the α_j (still assuming solutions are sufficiently dilute).

2. THREE-ION SYSTEMS

(a) Characteristic Parameters

A set of characteristic parameters for a polyion-simple electrolyte system has been derived by expanding the diffusion coefficient and mobility of a polyion, as well as the field strength, as power series in a normalised concentration variable, i.e.

$$D = D_o \left\{ 1 + \sum_{i=1}^{\infty} k_i \theta^i \right\} \tag{25}$$

$$u = u_o \left\{ 1 + \sum_{i=1}^{\infty} v_i \theta^i \right\} \tag{26}$$

$$E = E_o \left\{ 1 + \sum_{i=1}^{\infty} \lambda_i \theta^i \right\} \tag{27}$$

where

$$\theta = C/C^o \tag{22}$$

(b) <u>Electrophoretic Similarity</u>

By transforming independent variables according to

$$\left. \begin{aligned} X &= \frac{u_o E_o}{D_o} \cdot x \\ T &= \frac{(u_o E_o)^2}{D_o} \cdot t, \end{aligned} \right\} \tag{32'}$$

the transport equation is seen to have a solution of the form

$$\theta = \theta(X, T, k_1, \tau_1, \lambda_1) \tag{29}$$

if (25) - (27) are truncated after the first power of θ, i.e. the function $\theta(X,T)$ is invariant under the transformations (22) and (32) provided k_1, τ_1 and λ_1 are invariant. Substances which give rise to the same values for k_1, τ_1 and λ_1 are said to be electrophoretically similar. An analogous result holds if higher powers of θ are retained in (25) - (27).

(c) First-order perturbation in the electrophoretic term in the absence of stationary boundaries.

If

$$E_o = E\,(1 + \lambda_1 \theta) \tag{34}$$

and new independent variables are introduced, viz.

$$Y = X - (T - T_o)(1 + \lambda_1) \qquad (43)$$

$$\tilde{T} = T - T_o \qquad (44)$$

(i) An expression is found for the reduced concentration gradient ($\partial\theta/\partial Y$) at a descending boundary, (equations (45) and (46)). When $T_o = 0$, this may be simplified (equation (48)).

(ii) It is proved (see Appendix IV) that concentration gradient patterns are symmetric about $Y = 0$ under these conditions.

(iii) The velocity of the centre of the boundary is given by

$$v = u\,E_o\,(1 + \lambda_1) \qquad (51)$$

(iv) when $\lambda_1 < 0$, a steady-state solution is obtained, viz.

$$\lim_{T \to \infty} \frac{\partial\theta}{\partial Y} = -\frac{\lambda_1}{4}\,\mathrm{sech}^2\,\frac{\lambda_1 Y}{2} \qquad (49)$$

(d) First-order perturbation in the electrophoretic term in the presence of stationary boundaries.

If the field strengths across the ascending and descending boundaries are represented by

$$E_A = E^*(1 + \lambda_{1A}\,\theta_A) \qquad (54)$$

and

$$E_D = \underset{\rho}{\underline{E}}^*(1 + \lambda_{1D}\theta_D) \qquad (55)$$

respectively, then

(i) $\lambda_{1A} = \lambda_{1D} = \lambda_1$. (57)

(ii) The velocities of both moving boundaries may be used to estimate λ_1 and the mobility. E^* is the field strength in the bulk of the supporting electrolyte, $E^*(1 + \lambda_1)/\rho$ that is the bulk of the three-ion electrolyte, these two values yielding $(1 + \lambda_1)/\rho$. λ_1 is then found from

$$\frac{v_A}{v_D} = \rho \frac{(1 - \lambda_1)}{(1 + \lambda_1)} \qquad (62)$$

(ρ may also be found from $(1 + \lambda_1)/\rho$ if required). The mobility follows from

$$v_D = u \frac{E^*}{\rho} (1 + \lambda_1) \qquad (60)$$

or

$$v_A = uE^* (1 - \lambda_1) \qquad (61)$$

(iii) Boundary spreading may be used to estimate diffusion coefficients (Chapter 4, Section 4 (vi)). It has also been proved that a value of λ_1 associated with sharpening of a descending boundary implies spreading of the ascending boundary and vice versa.

(e) Higher-Order Perturbations in the Electrophoretic Term

This problem has been formulated and it has been found that,

(i) the velocity of a sharp boundary is given by

$$v = u_o E_o \sum_{i=0}^{\infty} \frac{(i+1)\gamma_i}{2^i} \tag{77}$$

where

$$\gamma_i = \sum_{j=0}^{i} r_j \lambda_{i-j} \tag{78}$$

(ii) if the mobility is constant, (77) reduces to

$$v = u_o E_o \left\{ 1 + \lambda_1 + \frac{3\lambda_2}{4} + \frac{\lambda_3}{2} + \dots \right\} \tag{78'}$$

which is a more general form of (51);

(iii) conjugate boundary patterns will only be enantiographic if

$$\gamma_{iA} = -\gamma_{iD} \quad (i = 1, 2, \dots) \tag{79}$$

These conditions are not likely to be satisfied unless the field strength and mobility are constant, although the effects of the r_i and λ_i may partly mask each other and give rise to apparently enantiographic patterns.

3. GENERAL MICROSCOPIC THEORY

(a) A general formulation of the potential problem is given in Chapter 3, including the correct use of boundary conditions and reduction of the equations to dimensionless form.

(b) Three methods for solving the potential equation for the charge density are discussed.

(i) Gorin's Linearisation(1)

$$\sinh \frac{q\Psi_3(\underline{r})}{kT} \doteq \frac{q\Psi_3(\underline{r})}{kT} \qquad (96')$$

(ii) A boundary-layer solution (based on Alexandrowicz and Katchalsky(56)),

$$\sinh \frac{q\Psi_3(\underline{r})}{kT} \doteq \begin{cases} \frac{1}{2}\, e^{q\Psi_3(\underline{r})/kT} & \underline{r} \in D_1 \qquad (97a') \\[2ex] \dfrac{q\Psi_3(\underline{r})}{kT} & \underline{r} \in D_2 \qquad (97b') \end{cases}$$

(iii) <u>Piecewise Linearisation</u>.

The region of solution is sub-divided into smaller domains (D_i) such that the increment in $\Psi_3(\underline{r})$ across each D_i is constant. $\sinh q\Psi_3(\underline{r})/kT$ is approximated by a linear function of $\Psi_3(\underline{r})$ in each domain such that the field and potential are continuous and satisfy the boundary conditions.

(c) Ion-binding and the nature of the electrophoretic charge are discussed in general terms.

4. TRANSPORT OF CYLINDRICAL MACROIONS

The development of Chapter 4 follows that outlined above. Formulae are derived for calculating the charge density (σ) and some numerical results are given. It is found that piecewise linearisation yields a larger value for σ than Gorin's method but a smaller value than that obtained by the boundary-layer technique.

The charge per unit length of a polyion (S_p) is related to the corresponding electrophoretic charge (S_E) by

$$S_p = \frac{S_o}{1 + \frac{C_p l}{C_s q M}\left(S_E - S_o\right)} \qquad (153)$$

where

$$S_o = \frac{e_s kT}{2q} \qquad (154)$$

These formulae are only applicable to sufficiently strong electrolytes ($S_p \gg S_o$) and low electrophoretic charges ($S_E \ll S_o$). A stronger condition than $S_p \gg S_o$ is probably required since weak electrolyte behaviour has been entirely excluded from the derivation of (153).

5. DETERMINATION OF KINETIC PARAMETERS

(a) The mobility-reaction coordinate relation.

A chain of reactions of the form

$$A_i + X \rightarrow A_{i+1} \quad (i=0,1,2, \ldots . N-1) \qquad (157')$$

(where X is in excess) has been considered, a mobility-reaction coordinate relation,

$$u_i = K \cdot \phi\ (\alpha_i) \qquad (158)$$

being postulated, where

$$\alpha_i = \frac{i + s}{N} \qquad (159)$$

A first-order approximation to (159) is derived by truncating the Taylor expansion of $\phi(\alpha_i)$, giving

$$u_i - u_o = (u_N - u_O) \cdot \frac{i}{N} \qquad (163)$$

This formal treatment is justified theoretically for both rigid and flexible macroions. Higher-order approximations are also shown to be necessary, both on theoretical grounds and for the interpretation of certain experimental results.

(b) The frequency distribution of the species A_i.

This has been derived elsewhere$^{(83)}$ and has the form

$$f(i) = \binom{M}{i} \theta^i \ (1 - \theta)^{N-i} \qquad (179)$$

where

$$\theta = 1 - e^{-kt} \qquad (177)$$

(c) General correlation of (a) and (b).

The frequency distribution $f(i)$ and the j^{th} moment of the mobility distribution are related by

$$u_j = K^j \int_0^N \left[\phi\left(\frac{i+a}{N^*}\right) - \bar{\phi}\left(\frac{i+a}{N^*}\right)\right]^j f(i)\,di \qquad j = 0,1,2,\ \ldots \tag{190}$$

(d) Correlation of (a) and (b) to a first approximation (equation (163)).

(i) The mean mobility after reaction for a time t and the first-order rate constant k are related by

$$\bar{u}(t) - u_o = (u_N - u_o) \cdot \theta(t) \tag{188}$$

This yields $(u_N - u_o)$ and k.

(ii) The variance of the mobility distribution has the form

$$h^2 = \frac{(u_N - u_o)^2}{N} \cdot \theta(1 - \theta) \tag{198}$$

(iii) If a Gram-Charlier mobility distribution exists, then

$$q(u) = \frac{1}{h(\theta)\cdot\sqrt{2\pi}}\, e^{-(u-\bar{u}(\theta))^2/2h^2(\theta)} \left\{1 + \frac{1 - 2\theta}{3!\sqrt{N\theta(1-\theta)}} \cdot H_3\, H_3\left(\frac{u - \bar{u}(\theta)}{h(\theta)}\right) + \frac{1 - 6\theta + 6\theta^2}{4!N\theta(1 - \theta)} \cdot H_4\left(\frac{u - \bar{u}(\theta)}{h(\theta)}\right) + \ldots\right\} \tag{201}$$

For large N, equation (201) may be simplified (see equations (202) and (203)).

(e) Parameters of the distribution $f(i)$.

Equation (188) yields $(u_N - u_o)$ and θ, whence N may be calculated. Also,

$$\bar{i} = N\theta \tag{183}$$

and

$$\frac{\sqrt{v_2}}{\bar{i}} = \sqrt{\frac{1 - \theta}{\theta}} \cdot \frac{1}{\sqrt{N}} \tag{208}$$

i.e. electrophoretic heterogeneity after a given reaction time, when expressed in this way, decreases with increasing N.

Some possible applications of various transport experiments are also discussed and may aid the understanding of complex reaction mechanisms, especially in biological systems.

APPENDIX I

SOLUTION OF THE LINEAR TRANSPORT EQUATION

Since equations (6) are independent, it will be sufficient to solve for a single component. The initial-value problem may be written in the dimensionless form (see Appendix III).

$$\frac{\partial\theta}{\partial T} = \frac{\partial^2\theta}{\partial X^2} - \frac{\partial\theta}{\partial X} \qquad T > T_o,\ -\infty < X < \infty \tag{1.1}$$

subject to the condition (for the descending boundary)

$$\theta(X,T_o) = \frac{1}{2}\,\mathrm{erf}_c - \frac{X}{2\sqrt{T_o}} \tag{1.2}$$

(Equation 1.2 is obtained directly from equation (8)). This type of formulation avoids explicit use of D, u and E by absorbing these parameters into the "natural coordinates"(50) X and T.

Let the Fourier transform (F) of a function f(X,T) be denoted by $\bar{f}(p,T)$, i.e.

$$F(f(X,T)) = \bar{f}(p,T) = \int_{-\infty}^{\infty} e^{-ipX} f(X,T)\,dX \tag{1.3}$$

Then it may be shown(105)

$$F\left(\frac{\partial\theta}{\partial T}\right) = \frac{\partial\bar{\theta}(p,T)}{\partial T} \tag{1.4}$$

$$F\left(\frac{\partial\theta}{\partial X}\right) = -ip\bar{\theta}(p,T) \tag{1.5}$$

$$F\left(\frac{\partial^2\theta}{\partial X^2}\right) = -p^2\bar{\theta}(p,T) \tag{1.6}$$

If p is regarded as a parameter, (1.1) is transformed to the ordinary differential equation

$$\frac{d\bar{\theta}}{dT} = -p^2\bar{\theta} + ip\bar{\theta} \tag{1.7}$$

which has the general solution

$$\bar{\theta} = \alpha(p)e^{p(i-p)T} \tag{1.8}$$

$\alpha(p)$ is determined by transforming the initial condition (1.2). Thus

$$F(\theta(X,T_o)) = \int_{-\infty}^{\infty} e^{ipX}.\ \frac{1}{2}\ \mathrm{erf}_c - \frac{X}{2\sqrt{T_o}}\ dX \tag{1.9}$$

Therefore

$$\alpha(p) = \frac{e^{-p(i-p)T_o}}{2}\int_{-\infty}^{\infty} e^{ipX}\ \mathrm{erf}_c - \frac{X}{2\sqrt{T_o}}\ dX \tag{1.10}$$

Thus by (1.8)

$$\bar{\theta}(p,T) = \frac{1}{2}\ e^{p(i-p)(T-T_o)}\int_{-\infty}^{\infty} e^{ipX}\ \mathrm{erf}_c - \frac{X}{2\sqrt{T_o}}\ dX \tag{1.11}$$

Inverting,

$$\theta(X,T) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ipX}\left[\frac{1}{2}\ e^{p(i-p)(T-T_o)}\int_{-\infty}^{\infty} e^{ipy}\ \mathrm{erf}_c - \frac{y}{2\sqrt{T_o}}\ dy\right] dp \tag{1.12}$$

and on changing the order of integration,

$$\theta(X,T) = \frac{1}{4\pi}\int_{-\infty}^{\infty} \mathrm{erf}_c \frac{-y}{2\sqrt{T_o}} \left[\int_{-\infty}^{\infty} e^{-ipX+p(i-p)(T-T_o)+ipy}\, dp\right] dy \quad (1.13)$$

The second integral in (1.13) is readily evaluated. Thus,

$$\int_{-\infty}^{\infty} e^{-ipX+p(i-p)(T-T_o)+ipy}\, dp = e^{-(T-T_o+y-X)^2/4(T-T_o)} \cdot \int_{-\infty}^{\infty} e^{-(T-T_o)P^2}\, dP \quad (1.14)$$

$$= e^{-(y-X+T-T_o)^2/4(T-T_o)} \sqrt{\frac{\pi}{T-T_o}} \quad (1.15)$$

Substituting in (1.13),

$$\theta(X,T) = \frac{1}{4\sqrt{\pi(T-T_o)}}\int_{-\infty}^{\infty} \mathrm{erf}_c - \frac{y}{2\sqrt{T_o}} \cdot e^{-(y-X+T-T_o)^2/4(T-T_o)}\, dy \quad (1.16)$$

To simplify the calculations, the following substitutions will be made:

$$K = 1/4\sqrt{\pi(T-T_o)} \quad a = 1/2\sqrt{T_o} \quad b = 1/2\sqrt{T-T_o} \quad c = (T-T_o-X)/2\sqrt{T-T_o} \quad (1.17)$$

Then,

$$\theta(X,T) = K\int_{-\infty}^{\infty} \mathrm{erf}_c\,(-ay) \cdot e^{-(by+c)^2}\, dy \quad (1.18)$$

Differentiating with respect to a under the integral sign,

$$\frac{d\theta}{da} = \frac{2K}{\sqrt{\pi}}\int_{-\infty}^{\infty} y\, e^{-[(a^2+b^2)y^2+2bcy+c^2]}\, dy \quad (1.19)$$

$$-(a^2 + b^2)\frac{d\theta}{da}$$

$$= \frac{K}{\sqrt{\pi}}\int_{-\infty}^{\infty}[-2(a^2 + b^2)y - 2bc]\, e^{-[(a^2 + b^2)y^2+2bcy+c^2]}\, dy$$

$$+ \frac{2Kbc}{\sqrt{\pi}}\int_{-\infty}^{\infty} e^{-[(a^2+b^2)y^2+2bcy+c^2]}\, dy \qquad (1.20)$$

$$= \left| \frac{K}{\sqrt{\pi}}\, e^{-[(a^2+b^2)y^2+2bcy+c^2]} \right|_{-\infty}^{\infty} + \frac{2Kbc}{\sqrt{\pi}}\int_{-\infty}^{\infty} e^{-(a^2+b^2)Y^2-a^2c^2/(a^2+b^2)}\, dY \qquad (1.21)$$

i.e.

$$\frac{d\theta}{da} = -\frac{2Kbc}{(a^2 + b^2)^{3/2}}\, e^{-a^2c^2/(a^2+b^2)} \qquad (1.22)$$

Integrating with respect to a,

$$\theta = -2Kbc\int^{a} \frac{1}{(a^2 + b^2)^{3/2}}\, e^{-a^2c^2/(a^2+b^2)}\, da + \text{const.} \qquad (1.23)$$

Making the change of variable $m = ac/\sqrt{a^2 + b^2}$,

$$\theta = -\frac{2K}{b}\int^{ac/\sqrt{a^2+b^2}} e^{-m^2}\, dm + \text{const.} \qquad (1.24)$$

Thus, by (1.17),

$$\theta(X,T) = \frac{1}{2}\,\text{erf}_c\left(\frac{T - T_0 - X}{2\sqrt{T}}\right) + \text{const.}$$

Therefore,

$$\frac{\partial\theta}{\partial X} = \frac{1}{2\sqrt{\pi T}} e^{-[X-(T-T_o)]^2/4T} \qquad (1.25)$$

or

$$\frac{\partial C}{\partial x} = \frac{C^o}{\sqrt{4\pi Dt}} e^{-(x-uEt_E)^2/4Dt} \qquad (1.26)$$

This result is to be expected since uEt_E is the displacement of the boundary after electrophoresis for a time t_E, i.e. the peak of the $\partial C/\partial x$ curve is located at $x = uEt_E$. The standard deviation of this curve is $\sqrt{2Dt}$, the same as for simple diffusion for a time t.

APPENDIX II

RELATION BETWEEN CONCENTRATION GRADIENTS AND MOBILITY DISTRIBUTIONS

Substituting (15) into (14),

$$\frac{\partial C}{\partial x} = \frac{C^{0}}{\sqrt{8\pi^{2}h^{2}Dt}} \int_{-\infty}^{\infty} e^{-(x-uEt_E)^{2}/4Dt-(u-\bar{u})^{2}/2h^{2}} \left\{1 + \sum_{j=3}^{\infty} \frac{a_j}{j!} H_j\left(\frac{u-\bar{u}}{h}\right)\right\} du \qquad (2.1)$$

which may be simplified to,

$$\frac{\partial C}{\partial x} = \frac{C^{0}}{\sqrt{8\pi^{2}h^{2}Dt}} \int_{-\infty}^{\infty} e^{-A\left(\frac{u-\bar{u}}{h}\right)^{2}+B\left(\frac{u-\bar{u}}{h}\right)+C} \left\{1 + \sum_{j=3}^{\infty} \frac{a_j}{j!} H_j\left(\frac{u-\bar{u}}{h}\right)\right\} du \qquad (2.2)$$

where

$$A = \left(\frac{h^{2}E^{2}t_E^{2}}{4Dt} + \frac{1}{2}\right) \qquad (2.3a)$$

$$B = \frac{hEt_E}{2Dt}(x - \bar{u}Et_E) \qquad (2.3b)$$

$$C = -\frac{(x-\bar{u}Et_E)^{2}}{4Dt} \qquad (2.3c)$$

Making the change of variable

$$X = \left(\frac{u - \bar{u}}{h}\right) - \frac{B}{2A} \qquad (2.4)$$

$$\frac{\partial C}{\partial x} = \frac{C^{0}}{\sqrt{8\pi^{2} D t}} \, e^{(C+B^{2}/4A)} \int_{-\infty}^{\infty} e^{-AX^{2}}$$

$$\left\{ 1 + \sum_{j=3}^{\infty} \frac{\alpha_j}{j!} H_j \left(X + \frac{B}{2A}\right) \right\} dX \qquad (2.5)$$

Let $$I_j = \int_{-\infty}^{\infty} e^{-AX^{2}} H_j \left(X + \frac{B}{2A}\right) dX \qquad (2.6)$$

At this point it is necessary to consider the properties of the Hermite polynomials. Margenau and Murphy(106) give the general form of the Gram-Charlier series of a function and a number of relations between the parameters of this series and moments of the function about the origin. However, the Hermite polynomials given by them (and also by Sneddon(39)) are not the ones appropriate to Gram-Charlier series. The correct polynomials to use here have been defined by Smart(29) (also Kendall and Stuart(30)) and the properties required here are to be found in these references.

Since

$$H_j'(\zeta) = j \, H_{j-1}(\zeta) \qquad (2.7)$$

equation (2.6) becomes

$$I_j = \int_{-\infty}^{\infty} \frac{e^{-AX^2}}{(j+1)} H'_{j+1}(X + B/2A)\, dX \tag{2.8}$$

which on integration by parts gives

$$I_j = \frac{2A}{(j+1)} \int_{-\infty}^{\infty} e^{-AX^2} X\, H_{j+1}(X + B/2A)\, dX \tag{2.9}$$

i.e.

$$I_j = \frac{2A}{(j+1)} \int_{-\infty}^{\infty} e^{-AX^2} (X + B/2A)\, H_{j+1}(X + B/2A)\, dx$$

$$- \frac{B}{(j+1)} \int_{-\infty}^{\infty} e^{-AX^2} H_{j+1}(X + B/2A)\, dX \tag{2.10}$$

or

$$I_j + \frac{B}{(j+1)} I_{j+1} = \frac{2A}{(j+1)}$$

$$\int_{-\infty}^{\infty} e^{-AX^2} (X + B/2A)\, H_{j+1}(X + B/2A)\, dX \tag{2.11}$$

Also,

$$H_{j+1}(\zeta) = \zeta H_j(\zeta) - jH_{j-1}(\zeta) \tag{2.12}$$

i.e.

$$(X + B/2A)\, H_{j+1}(X + B/2A)$$

$$= H_{j+2}(X + B/2A) + (j+1)\, H_j(X + B/2A) \tag{2.13}$$

Substituting (2.13) in (2.11),

$$I_j + \frac{B}{(j+1)} I_{j+1} = \frac{2A}{(j+1)} I_{j+2} + 2AI_j \qquad (2.14)$$

From the definition (2.6),

$$I_0 = \sqrt{\frac{\pi}{A}} \qquad (2.15a)$$

$$I_1 = \frac{B}{2A}\sqrt{\frac{\pi}{A}} \qquad (2.15b)$$

Also, from (2.3a), (2.3b), (17) and (18)

$$\frac{B}{2A} = \omega s \qquad (2.16a)$$

$$\frac{2A-1}{2A} = \omega^2 \qquad (2.16b)$$

where $$s = \frac{x - \bar{\bar{u}}Et_E}{\Sigma} \qquad (2.16c)$$

Thus if $Q_j = I_j \sqrt{\frac{A}{\pi}}$ (2.17)

equation (2.14) becomes

$$Q_{j+2}(\omega,s) - \omega s\, Q_{j+1}(\omega,s) + \omega^2 (j+1)\, Q_j(\omega,s) = 0 \quad j \geq 0 \qquad (2.18)$$

subject to the initial conditions

$$Q_0 = H_0(s) \qquad (2.19a)$$

$$Q_1 = \omega H_1(s) \qquad (2.19b)$$

The finite difference equation (2.18) has the solution (subject to (2.19a) and (2.19b))

$$Q_j = \omega^j H_j(s) \tag{2.20}$$

i.e.

$$I_j = \sqrt{\frac{\pi}{A}} \cdot \omega^j H_j(s) \tag{2.21}$$

Substituting in (2.5),

$$\frac{\partial C}{\partial x} = \frac{C^0}{\sqrt{8\pi A D t}} e^{(C+B^2/4A)} \left\{ 1 + \sum_{j=3}^{\infty} \frac{\alpha_j}{j!} \omega^j H_j(s) \right\} \tag{2.22}$$

Using the definitions (2.3) and (18), the required result is obtained, viz.

$$\frac{\partial C}{\partial x} = \frac{C^0}{\Sigma \cdot \sqrt{2\pi}} e^{-(x-\bar{u}_E t_E)^2/2\Sigma^2} \left\{ 1 + \sum_{j=3}^{\infty} \frac{\alpha_j}{j!} \omega^j H_j(s) \right\} \tag{2.23}$$

APPENDIX III

DIMENSIONAL ANALYSIS OF THE TRANSPORT EQUATION

In order to simplify the solution of the Fokker-Planck equation, dimensionless π-monomials will be used in place of the dimensional quantities in equation (21). Using the fourfold basis commonly adopted for electromagnetic phenomena (viz. mass M, length L, time T and charge Q), the dimensional table is as follows:

	C	C°	x	t	D_o	u_o	E_o
M	1	1	0	0	0	-1	1
L	-3	-3	1	0	2	0	1
T	0	0	0	1	-1	1	-2
Q	0	0	0	0	0	1	-1

In general, *all* the characteristic and universal constants belonging to the theory of a phenomenon must be taken into consideration (this is the third rule discussed by Palacios(42) in his section dealing with problem formulation). However, k_1, r_1 and λ_1 are independent and, by definition, dimensionless quantities so that three dimensionless π-monomials have already been found and need not be considered in connection with the formation of the other π-monomials from the remaining quantities. Further since C and C° have the same dimensional exponents, another of the required π-monomials (in this case a form factor) has been defined by equation (22) and only one of these quantities need be considered in the dimensional table, which therefore reads:

$$\begin{array}{c|cccccc} & C & x & t & D_s & u_o & E_o \\ \hline M & 1 & 0 & 0 & 0 & -1 & 1 \\ L & -3 & 1 & 0 & 2 & 0 & 1 \\ T & 0 & 0 & 1 & -1 & 1 & -2 \\ Q & 0 & 0 & 0 & 0 & 1 & -1 \end{array}$$

Using the first, fourth, fifth and sixth columns above, it is readily shown that the determinant (Δ_1) given by,

$$\Delta_1 = \begin{vmatrix} 1 & 0 & -1 & 1 \\ -3 & 2 & 0 & 1 \\ 0 & -1 & 1 & -2 \\ 0 & 0 & 1 & -1 \end{vmatrix} \qquad (3.1)$$

is non-zero so that the matrix of dimensional exponents is of rank four, thus confirming that a strict basis has a multiplicity of two. Hence, the exponents of x and t (denoted e_x and e_t respectively) may be arbitrarily chosen when forming π-monomials, and setting $e_x = 1$ and $e_t = 0$, one obtains the following equations for the exponents of the remaining quantities.

$$\begin{pmatrix} 1 & 0 & -1 & 1 \\ -3 & 2 & 0 & 1 \\ 0 & -1 & 1 & -2 \\ 0 & 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} e_{c} \\ e_{D_o} \\ e_{u_o} \\ e_{E_o} \end{pmatrix} = \begin{pmatrix} 0 \\ -1 \\ 0 \\ 0 \end{pmatrix} \qquad (3.2)$$

This has the solution

$$\begin{pmatrix} e_{c} \\ e_{D_o} \\ e_{u_o} \\ e_{E_o} \end{pmatrix} = \begin{pmatrix} 0 \\ -1 \\ 1 \\ 1 \end{pmatrix} \qquad (3.3)$$

i.e. the first dimensionless π-monomial (π_1) is given by,

$$\pi_1 = \frac{u_o E_o}{D_o} \cdot x, \qquad (3.4)$$

Similarly, putting $e_x = 0$ and $e_t = 1$, one obtains

$$\pi_2 = \frac{u_o^2 E_o^2}{D_o} \cdot t \qquad (3.5)$$

Hence, the complete set of π-monomials reads:

$$\frac{C}{C_o},\ \frac{u_o E_o}{D_o} \cdot x,\ \frac{u_o^2 E_o^2}{D_o} \cdot t,\ K_1,\ r_1 \text{ and } \lambda_1.$$

Having determined a suitable set of monomials, it now remains to rewrite the differential equation in terms of the new variables θ, X and T (the latter two being reduced space and time coordinates defined by w_1 and w_2 respectively), to which end the following operator relationships will be found useful:

$$\frac{\partial}{\partial x} = \frac{u_o E_o}{D_o} \frac{\partial}{\partial X} , \qquad (3.6)$$

$$\frac{\partial^2}{\partial x^2} = \left(\frac{u_o E_o}{D_o}\right)^2 \frac{\partial^2}{\partial X^2} , \qquad (3.7)$$

$$\frac{\partial}{\partial t} = \frac{u_o^2 E_o^2}{D_o} \frac{\partial}{\partial T}. \qquad (3.8)$$

If one writes the transport equation in full, the following equation is obtained:

$$\frac{\partial c}{\partial t} = \frac{D_o k_1}{C_o} c \frac{\partial^2 c}{\partial x^2} + D_o \frac{\partial^2 c}{\partial x^2} + \frac{D_o k_1}{C_o} \left(\frac{\partial c}{\partial x}\right)^2 - \frac{3\lambda_1 r_1 u_o E_o c^2}{C_o^2} \frac{\partial c}{\partial x}$$

$$- \frac{2(\lambda_1 + r_1) u_o E_o}{C_o} c \frac{\partial c}{\partial x} - u_o E_o \frac{\partial c}{\partial x} . \qquad (3.9)$$

It is then readily shown that the corresponding equation in terms of the new variables reads,

$$\frac{\partial \theta}{\partial T} = k_1 \theta \frac{\partial^2 \theta}{\partial X^2} + \frac{\partial^2 \theta}{\partial X^2} + k_1 \left(\frac{\partial \theta}{\partial X}\right)^2$$

$$- 3\lambda_1 r_1 \theta^2 \frac{\partial \theta}{\partial X} - 2(\lambda_1 + r_1)\theta \frac{\partial \theta}{\partial X} - \frac{\partial \theta}{\partial X} \qquad (3.10)$$

in which D_o, u_o, E_o and C^o no longer appear explicitly. While a general solution of (3.10) is still not possible, particular cases (e.g. by assuming $k_1 = 0$ in systems where diffusion is negligible, or $\lambda_1\tau_1 = 0$ when λ_1 and τ_1 are small) may be solved more easily than with (3.9) and solutions expressed in terms of dimensionless variables are more easily compared.

APPENDIX IV

SOLUTION OF THE TRANSPORT EQUATION WITH FIRST-ORDER PERTURBATION IN THE ELECTROPHORETIC TERM

The problem has been written (equations 41 and 42) in the form

$$\frac{\partial\theta}{\partial T} = \frac{\partial^2\theta}{\partial X^2} - (1 + 2\lambda_1\theta)\,\frac{\partial\theta}{\partial X} \qquad T \geq T_o; -\infty < X < \infty \qquad (4.1)$$

$$\theta(X,T_o) = \frac{1}{2}\,\mathrm{erf}_c - \frac{X}{2\sqrt{T_o}} \qquad (4.2)$$

(for the descending boundary).

To simplify the solution, a new space coordinate Y defined by

$$Y = X - (T - T_o)(1 + \lambda_1) \qquad (4.3)$$

has been introduced (equation 43) so that the origin $Y = 0$ moves with the boundary and the transformed equation describes only the shape of the boundary, not its speed. The reduced time variable $\tilde{T}$ (equation 44), where

$$\tilde{T} = T - T_o \qquad (4.4)$$

has also been introduced since the electrophoretic term is absent for $T < T_o$. It follows immediately that

$$\left(\frac{\partial\theta}{\partial X}\right)_T = \left(\frac{\partial\theta}{\partial Y}\right)_{\tilde{T}} \qquad (4.5)$$

$$\left(\frac{\partial^2\theta}{\partial X^2}\right)_{\tilde{T}} = \left(\frac{\partial^2\theta}{\partial Y^2}\right)_{\tilde{T}} \tag{4.6}$$

The change to a new time variable is readily carried out by means of Jacobians$^{(107)}$ thus:

$$\left(\frac{\partial\theta}{\partial T}\right)_X = \frac{\partial(\theta,X)}{\partial(T,X)}$$

$$= \frac{\partial(\theta,X)}{\partial(Y,\tilde{T})} \Big/ \frac{\partial(T,X)}{\partial(Y,\tilde{T})}$$

$$= \left(\frac{\partial\theta}{\partial\tilde{T}}\right)_Y - (1 + \lambda_1)\left(\frac{\partial\theta}{\partial Y}\right)_{\tilde{T}} \tag{4.7}$$

and (4.1) becomes

$$\frac{\partial\theta}{\partial\tilde{T}} = \frac{\partial^2\theta}{\partial Y^2} - \lambda_1(2\theta - 1)\frac{\partial\theta}{\partial Y} \tag{4.8}$$

Using the new dependent variable U given by

$$U = 2\theta - 1 \tag{4.9}$$

the problem now becomes

$$\frac{\partial U}{\partial\tilde{T}} = \frac{\partial^2 U}{\partial Y^2} - \lambda_1 U\frac{\partial U}{\partial Y} \tag{4.10}$$

$$U(Y,0) = \operatorname{erf} Y/2\sqrt{T_o} \tag{4.11}$$

Cole$^{(108)}$ has shown that (4.10) is solved by means of the Hopf transformation

$$U(Y,\tilde{T}) = -\frac{2}{\lambda_1}\frac{\partial \ln w(Y,\tilde{T})}{\partial Y} \tag{4.12}$$

where $\omega(Y,\tilde{T})$ is any solution of the simple diffusion equation

$$\frac{\partial\omega}{\partial\tilde{T}} = \frac{\partial^2\omega}{\partial Y^2} \qquad (4.13)$$

He has also proved the uniqueness of the solution (4.12). The initial condition for (4.13) corresponding to (4.11) is obtained by integration of (4.12). Thus

$$\int_b^Y \frac{\lambda_1 U(\epsilon,\tilde{T})}{-2}\, d\epsilon = \ln\left(\frac{\omega(Y,\tilde{T})}{\omega(b,T)}\right) \qquad (4.14)$$

Without loss of generality, b may be chosen to be zero, giving (for $\tilde{T} = 0$)

$$\omega(Y,0) = \omega(0,0) \cdot \exp\left[-\frac{\lambda_1}{2}\int_0^Y U(\epsilon,0)d\epsilon\right] \qquad (4.15)$$

which relates the initial values $\omega(Y,0)$ and $U(Y,0)$. The solution $\omega(Y,\tilde{T})$ of equation (4.13) may be stated in various ways, one convenient representation being

$$\omega(Y,\tilde{T}) = \frac{1}{\sqrt{4\pi\tilde{T}}}\int_{-\infty}^{\infty} \exp\left[-(Y-\epsilon)^2/4\tilde{T}\right] \cdot \omega(\epsilon,0)d\epsilon \qquad (4.16)$$

Thus by (4.15),

$$\omega(Y,\tilde{T}) = \frac{\omega(0,0)}{\sqrt{4\pi\tilde{T}}}\int_{-\infty}^{\infty} \exp\left[-(Y-\epsilon)^2/4\tilde{T} - (\lambda_1/2)\int_0^{\epsilon} U(\eta,0)d\eta\right]d\epsilon \qquad (4.17)$$

Also, from (4.12) it follows that

$$\frac{\partial \omega}{\partial Y} = \frac{-\lambda_1}{2}\, \omega U(Y,\tilde{T}) \tag{4.18}$$

Substituting (4.17) into (4.18),

$$U(Y,\tilde{T}) = \frac{-2}{\lambda_1} \frac{\displaystyle\int_{-\infty}^{\infty} \frac{\epsilon - Y}{2\tilde{T}} \exp\left[-(\epsilon - Y)^2/4\tilde{T} - (\lambda_1/2)\int_0^{\epsilon} U(\eta,0)d\eta\right]d\epsilon}{\displaystyle\int_{-\infty}^{\infty} \exp\left[-(\epsilon - Y)^2/4\tilde{T} - (\lambda_1/2)\int_0^{\epsilon} U(\eta,0)d\eta\right]d\epsilon} \tag{4.19}$$

and, on integrating by parts (in the numerator),

$$U(Y,\tilde{T}) = \frac{\displaystyle\int_{-\infty}^{\infty} \exp\left[-(\epsilon - Y)^2/4\tilde{T} - (\lambda_1/2)\int_0^{\epsilon} U(\eta,0)d\eta\right] \cdot U(\epsilon,0)d\epsilon}{\displaystyle\int_{-\infty}^{\infty} \exp\left[-(\epsilon - Y)^2/4\tilde{T} - (\lambda_1/2)\int_0^{\epsilon} U(\eta,0)d\eta\right]d\epsilon} \tag{4.20}$$

The finite integrals in (4.20) may be evaluated using the relation

$$\frac{d}{d\zeta}\left(\zeta \operatorname{erf} \zeta + \frac{e^{-\zeta^2}}{\sqrt{\pi}}\right) = \operatorname{erf} \zeta \tag{4.21}$$

Thus,

$$\int_0^{\epsilon} \operatorname{erf} \eta/2\sqrt{T_o}\, d\eta = 2\sqrt{T_o} \int_0^{\epsilon/2\sqrt{T_o}} \operatorname{erf} \zeta\, d\zeta$$

$$= \epsilon \operatorname{erf} \epsilon/2\sqrt{T_o} + 2\sqrt{\frac{T_o}{\pi}}\left(e^{-\epsilon^2/4T_o} - 1\right) \tag{4.22}$$

$$= g(\epsilon,T_o) \tag{4.23}$$

Substituting in (4.20) and dividing by $e^{-Y^2/4\tilde{T}}$ in both numerator and denominator,

$$U(Y,\tilde{T}) = \frac{\int_{-\infty}^{\infty} \exp\left[\frac{Y}{2\tilde{T}} \cdot \varepsilon - \frac{\varepsilon^2}{4\tilde{T}} - \frac{\lambda_1}{2}\, g\,(\varepsilon, T_o)\right] \operatorname{erf} \varepsilon/2\sqrt{T_o}\, d\varepsilon}{\int_{-\infty}^{\infty} \exp\left[\frac{Y}{2\tilde{T}} \cdot \varepsilon - \frac{\varepsilon^2}{4\tilde{T}} - \frac{\lambda_1}{2}\, g\,(\varepsilon, T_o)\right] d\varepsilon} \tag{4.24}$$

Substituting from (4.9), differentiating with respect to Y and changing the variable of integration to y, where

$$y = \varepsilon/2\sqrt{\tilde{T}} \tag{4.25}$$

one obtains

$$\frac{\partial U}{\partial Y} = \frac{\left\{ \left[\int_{-\infty}^{\infty} e^{-y^2} f(y)dy\right]\left[\int_{-\infty}^{\infty} e^{-y^2} \cdot \frac{Y}{\sqrt{\tilde{T}}} \operatorname{erf}\left(y\sqrt{\frac{\tilde{T}}{T_o}}\right) \cdot f(y)dy\right] - \left[\int_{-\infty}^{\infty} e^{-y^2} \operatorname{erf}\left(y\sqrt{\frac{\tilde{T}}{T_o}}\right) \cdot f(y)dy\right]\left[\int_{-\infty}^{\infty} e^{-y^2} \frac{y}{\sqrt{\tilde{T}}} \cdot f(y)dy\right] \right\}}{2\left[\int_{-\infty}^{\infty} e^{-y^2} f(y)dy\right]^2} \tag{4.26}$$

where

$$f(y) = \exp\left[\frac{Y}{\sqrt{\tilde{T}}} \cdot y - \frac{\lambda_1}{2}\left(2\sqrt{\tilde{T}} \cdot y \operatorname{erf}\left(y\sqrt{\frac{\tilde{T}}{T_o}}\right) + 2\sqrt{\frac{T_o}{\pi}}\left(\exp - \frac{y^2\tilde{T}}{T_o} - 1\right)\right)\right] \tag{4.27}$$

The Limiting Case $\lambda_1 = 0$

From (4.27) it follows that when $\lambda_1 = 0$,

$$\int_{-\infty}^{\infty} e^{-y^2} f(y)dy = \int_{-\infty}^{\infty} \exp\left[-y^2 + \frac{Y}{\sqrt{\tilde{T}}} \cdot y\right]dy$$

$$= e^{Y^2/4\tilde{T}} \int_{-\infty}^{\infty} e^{-(y-Y/2\sqrt{\tilde{T}})^2}\, dy$$

$$= \sqrt{\pi} \cdot e^{Y^2/4\tilde{T}} \tag{4.28}$$

Also, integrating by parts,

$$\int_{-\infty}^{\infty} e^{-y^2} \cdot \frac{y}{\sqrt{\tilde{T}}} f(y)dy = -\frac{1}{2\sqrt{\tilde{T}}} \int_{-\infty}^{\infty} (-2ye^{-y^2})\, e^{Yy/\sqrt{\tilde{T}}}\, dy$$

$$= \frac{Y}{2\tilde{T}} \int_{-\infty}^{\infty} \exp\left[-y^2 + \frac{Y}{\sqrt{\tilde{T}}} \cdot y\right] dy$$

$$= \frac{Y}{2\tilde{T}} \cdot \sqrt{\pi} e^{Y^2/4\tilde{T}} \tag{4.29}$$

Therefore from (4.26)

$$\frac{\partial\theta}{\partial Y} = \frac{e^{-Y^2/4\tilde{T}}}{\sqrt{4\pi\tilde{T}}} \int_{-\infty}^{\infty} e^{-y^2 + \frac{Y}{\sqrt{\tilde{T}}} \cdot y} \cdot \left(y - \frac{Y}{2\sqrt{\tilde{T}}}\right) \operatorname{erf} y \sqrt{\frac{\tilde{T}}{T_0}}\, dy \tag{4.30}$$

By perfecting the square in the exponential and integrating by parts,

$$\frac{\partial\theta}{\partial Y} = \frac{1}{\sqrt{4\pi T_0}} \cdot \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left[-\left(1 + \tilde{T}/T_0\right)y^2 + \frac{Y}{\sqrt{\tilde{T}}} \cdot y - Y^2/4\tilde{T}\right] dy$$

$$= \frac{e^{-Y^2/4T}}{\sqrt{4\pi T_0}} \cdot \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-(\tilde{T}/T_0)(y - Y T_0/2\tilde{T}\sqrt{\tilde{T}})^2} dy \qquad (4.31)$$

Hence

$$\frac{\partial\theta}{\partial Y} = \frac{e^{-Y^2/4T}}{\sqrt{4\pi T}} \qquad (4.32)$$

The Limiting Case $T_0 = 0$

When $T_0 = 0$,

$$f(y) = \exp\left\{\frac{Y}{\sqrt{T}} \cdot y - \lambda_1 y\sqrt{T}\,\left(H(y) - H(-y)\right)\right\} \qquad (4.33)$$

Then

$$\int_{-\infty}^{\infty} e^{-y^2} f(y)\,dy = \int_{-\infty}^{0} e^{-y^2 + \frac{Y}{\sqrt{T}} \cdot y + \lambda_1 y\sqrt{T}}\,dy + \int_{0}^{\infty} e^{-y^2 + \frac{Y}{\sqrt{T}} \cdot y - \lambda_1 y\sqrt{T}}\,dy$$

$$= \frac{\sqrt{\pi}}{2}\, e^{(Y^2/4T + \lambda_1^2 T/4)} \left\{ e^{\lambda_1 Y/2} \operatorname{erf}_c \frac{Y + \lambda_1 T}{2\sqrt{T}}\right.$$

$$\left. + e^{-\lambda_1 Y/2} \operatorname{erf}_c \frac{-Y + \lambda_1 T}{2\sqrt{T}} \right\} \qquad (4.34)$$

Also

$$\int_{-\infty}^{\infty} e^{-y^2} \cdot \frac{Y}{\sqrt{T}} f(y)dy$$

$$= \frac{1}{\sqrt{T}}\left[\int_{-\infty}^{0} y\ e^{-y^2+Yy/\sqrt{T}+\lambda_1 y\sqrt{T}}\ dy + \int_{0}^{\infty} y\ e^{-y^2+Yy/\sqrt{T}-\lambda_1 y\sqrt{T}}\ dy\right]$$

$$= \frac{1}{\sqrt{T}}\left[-\frac{1}{2}\int_{-\infty}^{0} (-\ 2y + \frac{Y}{\sqrt{T}} + \lambda_1\sqrt{T})\ e^{-y^2 + \frac{Yy}{\sqrt{T}} + \lambda_1 y\sqrt{T}}\ dy\right.$$

$$+ \frac{Y + \lambda_1 T}{2\sqrt{T}} \int_{-\infty}^{0} e^{-y^2 + \frac{Yy}{\sqrt{T}} + \lambda_1 y\sqrt{T}}\ dy$$

$$- \frac{1}{2}\int_{0}^{\infty} (-\ 2y + \frac{Y}{\sqrt{T}} - \lambda_1\sqrt{T})\ e^{-y^2 + \frac{Yy}{\sqrt{T}} - \lambda_1 y\sqrt{T}}\ dy$$

$$\left. - \frac{(-\ Y + \lambda_1 T)}{2\sqrt{T}} \int_{0}^{\infty} e^{-y^2 + \frac{Yy}{\sqrt{T}} - \lambda_1 y\sqrt{T}}\ dy\right]$$

$$= \frac{\sqrt{\pi}}{2}\ e^{(Y^2/4T\ +\ \lambda_1^2 T/4)} \left\{\frac{(Y + \lambda_1 T)}{2\sqrt{T}}\ e^{\lambda_1 Y/2}\ \mathrm{erf}_c\ \frac{Y + \lambda_1 T}{2\sqrt{T}}\right.$$

$$\left. - \frac{(-\ Y + \lambda_1 T)}{2\sqrt{T}}\ e^{-\lambda_1 Y/2}\ \mathrm{erf}_c\ \frac{-Y + \lambda_1 T}{2\sqrt{T}}\right\} \qquad (4.35)$$

These may then be used to evaluate the remaining integrals in (4.26), i.e.

$$\int_{-\infty}^{\infty} e^{-y^2}[H(y) - H(-y)]f(y)dy = \int_{-\infty}^{0} -e^{-y^2 + \frac{Y}{\sqrt{T}}y + \lambda_1 y\sqrt{T}}\, dy$$

$$+ \int_{0}^{\infty} e^{-y^2 + \frac{Y}{\sqrt{T}}y - \lambda_1 y\sqrt{T}}\, dy$$

$$= -\frac{\sqrt{\pi}}{2}\, e^{(Y^2/4T + \lambda_1^2 T/4)} \left\{ e^{\lambda_1 Y/2} \operatorname{erf}_c \frac{Y + \lambda_1 T}{2\sqrt{T}} \right.$$

$$\left. - e^{-\lambda_1 Y/2} \operatorname{erf}_c \frac{-Y + \lambda_1 T}{2\sqrt{T}} \right\} \qquad (4.36)$$

and

$$\int_{-\infty}^{\infty} e^{-y^2} \frac{Y}{\sqrt{T}} [H(y) - H(-y)]f(y)dy = \int_{-\infty}^{0} -\frac{1}{\sqrt{T}} \cdot y\, e^{-y^2 + \frac{Y}{\sqrt{T}} \cdot y + \lambda_1 y\sqrt{T}}\, dy$$

$$+ \int_{0}^{\infty} \frac{1}{\sqrt{T}} \cdot y \cdot e^{-y^2 + \frac{Y}{\sqrt{T}} \cdot y - \lambda_1 y\sqrt{T}}\, dy$$

$$= \frac{1}{\sqrt{T}} \left[1 - \frac{\sqrt{\pi}}{2}\, e^{(Y + \lambda_1 T)^2/4T}\, \frac{(Y + \lambda_1 T)}{2\sqrt{T}} \operatorname{erf}_c \frac{Y + \lambda_1 T}{2\sqrt{T}} \right.$$

$$\left. - \frac{\sqrt{\pi}}{2}\, e^{(-Y + \lambda_1 T)^2/4T}\, \frac{(-Y + \lambda_1 T)}{2\sqrt{T}} \operatorname{erf}_c \frac{-Y + \lambda_1 T}{2\sqrt{T}} \right. \qquad (4.37)$$

The required form of (4.26) is then obtained by means of (4.34) to (4.37). To facilitate the simplification, the following substitutions will be made:

$$\phi = \frac{Y + \lambda_1 T}{2\sqrt{T}}, \qquad \psi = \frac{- Y + \lambda_1 T}{2\sqrt{T}} \tag{4.38}$$

Then,

$$\frac{\partial\theta}{\partial Y} = \frac{\frac{\sqrt{\pi}}{2\sqrt{T}}\left[e^{\phi^2}\operatorname{erf_c}\phi - \lambda_1\sqrt{\pi T}\, e^{\phi^2 + \psi^2}\operatorname{erf_c}\phi\operatorname{erf_c}\psi + e^{\psi^2}\operatorname{erf_c}\psi\right]}{2\cdot\frac{\pi}{4}\left[e^{\phi^2}\operatorname{erf_c}\phi + e^{\psi^2}\operatorname{erf_c}\psi\right]^2} \tag{4.39}$$

or on rearranging,

$$\frac{\partial\theta}{\partial Y} = \frac{e^{-Y^2/4T}}{\sqrt{4\pi T}}\cdot\frac{e^{-\lambda_1^2 T/4}\left\{e^{\lambda_1 Y/2}\operatorname{erf_c}\frac{Y + \lambda_1 T}{2\sqrt{T}} + e^{-\lambda_1 Y/2}\operatorname{erf_c}\frac{- Y + \lambda_1 T}{2\sqrt{T}} - \lambda_1\sqrt{\pi T}\, e^{Y^2/4T + \lambda_1^2 T/4}\operatorname{erf_c}\frac{Y + \lambda_1 T}{2\sqrt{T}}\operatorname{erf_c}\frac{- Y + \lambda_1 T}{2\sqrt{T}}\right\}}{\frac{1}{2}\left\{e^{\lambda_1 Y/2}\operatorname{erf_c}\frac{Y + \lambda_1 T}{2\sqrt{T}} + e^{-\lambda_1 Y/2}\operatorname{erf_c}\frac{- Y + \lambda_1 T}{2\sqrt{T}}\right\}^2} \tag{4.40}$$

Symmetry of the Solution

Consider the integral

$$\int_{-\infty}^{\infty} e^{-y^2} f(y)dy = \int_{-\infty}^{\infty}\exp\left\{- y^2 + Yy/\sqrt{\tilde{T}} - (\lambda_1/2)(2\sqrt{\tilde{T}}\cdot y\operatorname{erf} y\sqrt{\tilde{T}}/T_o + 2\sqrt{\frac{T_o}{\pi}}\cdot(e^{-y^2\tilde{T}/T_o} - 1))\right\} \tag{4.41}$$

Making the change of variable

$$\eta = -y \tag{4.42}$$

and using the fact that y erf $y\sqrt{\tilde{T}}/T_o$ is an even function of y, it follows that

$$\int_{-\infty}^{\infty} e^{-y^2} f(y)dy = -\int_{\infty}^{-\infty} \exp\left\{-\eta^2 - \frac{Y\eta}{\sqrt{\tilde{T}}} - \left(\frac{\lambda_1}{2}\right)\left(2\sqrt{\tilde{T}} \cdot \eta \text{ erf } \eta \sqrt{\frac{T}{T_o}}\right.\right.$$

$$\left.\left. + 2\sqrt{\frac{T_o}{\pi}} \cdot \left(e^{-\eta^2\tilde{T}/T_o} - 1\right)\right)\right\} \tag{4.43}$$

Since η is only a dummy variable, one may write y in place of η giving, on reversing the limits of integration,

$$\int_{-\infty}^{\infty} e^{-y^2} f(y)dy = \int_{-\infty}^{\infty} \exp\left\{-y^2 - \frac{Yy}{\sqrt{\tilde{T}}}\right.$$

$$\left. - \left(\frac{\lambda_1}{2}\right)\left(2\sqrt{\tilde{T}} \cdot y \text{ erf } y \sqrt{\frac{\tilde{T}}{T_o}} + 2\sqrt{\frac{T_o}{\pi}} \cdot \left(e^{-y^2\tilde{T}/T_o} - 1\right)\right)\right\} dy$$

$$\tag{4.44}$$

Comparison of (4.41) and (4.44) immediately shows that the integral is an even function of Y. Similar considerations applied to the remaining integrals in (4.26) indicate that $\partial G/\partial Y$ is also an even function of Y.

APPENDIX V

EVALUATION OF INTEGRALS OF THE FORM $\int_{-\infty}^{\infty} e^{-y^2} f(y)dy$

Integrals of this type may be approximated by omitting the term $R_n(f)$ from the quadrature formula

$$\int_{-\infty}^{\infty} e^{-y^2} f(y)dy = \sum_{k=1}^{n} A_{kn} \cdot f(y_{kn}) + R_n(f) \qquad (5.1)$$

Krylov$^{(109)}$ has derived an expression for the coefficients A_{kn}, viz.

$$A_{kn} = \frac{2^{n+1} n! \pi^{1/2}}{[H_n'(y_{kn})]^2} \qquad (k = 1, 2, \ldots n) \qquad (5.2)$$

in which $H_n(y)$ is the Hermite polynomial of degree n defined by

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n(e^{-y^2})}{dy^n} \qquad (5.3)$$

The nodes (y_{kn}) of equation (5.1) are the roots of

$$H_n(y) = 0 \qquad (5.4)$$

and a real number (η) exists such that the remainder term may be written

$$R_n(f) = \frac{n! \pi^{1/2}}{2^n (2n)!} f^{(2n)}(\eta) \qquad (5.5)$$

Hence, $E_n(f)$ is zero whenever $f(y)$ is a polynomial of degree $\leq 2n - 1$. The y_{kn} and A_{kn} have been tabulated for $n = 1\ (1)\ 20$.(109)

APPENDIX VI

DERIVATION OF THE EXPRESSION FOR THE VELOCITY OF A SHARP BOUNDARY

For electrophoresis without diffusion, the transport equation becomes

$$\frac{\partial\theta}{\partial\tilde{T}} = -\left[\sum_{i=0}^{\infty}(i+1)y_i\theta^i\right]\frac{\partial\theta}{\partial X} \qquad \tilde{T} \geq 0,\ -\infty < X < \infty \qquad (6.1)$$

subject to an initial condition similer to (1.2), viz.

$$\theta(X,0) = \frac{1}{2}\,\mathrm{erf}_c\,\frac{-X}{2\sqrt{T_0}} \qquad (6.2)$$

(for the descending boundary).

The solution of (6.1) and (6.2) may then be written in the implicit form$^{(110)}$

$$\theta = \frac{1}{2}\,\mathrm{erf}_c\,-\frac{1}{2\sqrt{T_0}}\left(X - \sum_{i=0}^{\infty}(i+1)y_i\theta^i\tilde{T}\right) \qquad (6.3)$$

Differentiating,

$$\frac{\partial\theta}{\partial X} = \frac{\dfrac{1}{2\sqrt{\pi T_0}}\exp -\dfrac{1}{4T_0}\left(X - \sum\limits_{i=0}^{\infty}(i+1)y_i\theta^i\tilde{T}\right)^2}{1 + \dfrac{1}{2\sqrt{\pi T_0}}\left\{\exp -\dfrac{1}{4T_0}\left(X - \sum\limits_{i=0}^{\infty}(i+1)y_i\theta^i\tilde{T}\right)^2\right\}\left\{\sum\limits_{i=1}^{\infty}i(i+1)y_i\theta^{i-1}\right\}} \qquad (6.4)$$

Thus, where $X \neq \sum_{i=0}^{\infty} (i + 1)y_i\theta^i\tilde{T}$,

$$\lim_{T_o \to 0} \frac{\partial\theta}{\partial X} = 0 \tag{6.5}$$

but at the point where $X = \sum_{i=0}^{\infty} (i + 1)y_i\theta^i\tilde{T}$, $\lim_{T_o \to 0} \frac{\partial\theta}{\partial X}$ does not exist. This demonstrates the fact that in the limit of negligible diffusion, there is only one point where $\partial\theta/\partial X$ is non-zero, i.e. the boundary remains sharp. If X_B denotes this limiting boundary position, it follows from (6.3) that $\theta = \frac{1}{2}$ there, i.e.

$$X_B = \sum_{i=0}^{\infty} \frac{(i + 1)y_i}{2^i}\tilde{T} \tag{6.6}$$

or

$$v = u_oE_o \sum_{i=0}^{\infty} \frac{(i + 1)y_i}{2^i} \tag{6.7}$$

A similar result holds for the ascending boundary (remembering that the <u>effective</u> y_i values for ascending and descending boundaries are not, in general, equal - c.f. Section 4 (iv) of Chapter 2).

<u>NOTE</u>:

(i) Although no diffusion term is included in (6.1), the diffusion coefficient enters the problem via the initial condition (6.2). Governing equations and auxiliary conditions must be considered together and reduction to a single independent variable is therefore not possible.

(ii) Since equation (6.2) is a standard result, no derivation has been given. It may be remarked, however, that the electrophoretic term is not involved for $\tilde{T} < 0$ and, by omitting u_e and E_e from the dimensional table (see Appendix III), one obtains the dimensionless similarity variable $X^* = x/\sqrt{Dt}$, suggesting that solutions of the diffusion equation should be of the form $\theta = \theta(X^*)$. Since $X^* = X/\sqrt{T}$, (6.2) is of this form. Thus dimensional methods yield a similarity variable equivalent to the one introduced by Boltzmann(111) in solving non-linear diffusion equations (reducing them to ordinary differential equations).

(iii) If the diffusion coefficient is omitted from the dimensional analysis, a single independent variable $Y^* = x/u_e E_e t (= X/T)$ is obtained but no continuous solution of the form $\theta = \theta(Y^*)$ exists.

APPENDIX VII

DIMENSIONAL ANALYSIS OF THE POTENTIAL EQUATION

The boundary-value problem considered in Chapter 4 reads:

$$\frac{1}{r}\frac{d}{dr}\left(r\,\frac{d\Psi_3(r)}{dr}\right) = \frac{8\pi NC_1{}^{o}q}{\varepsilon_3}\cdot\sinh\frac{q\Psi_3(r)}{kT} \qquad r_o + r_1 \leqslant r \leqslant \infty \qquad (7.1)$$

$$\Psi_3(r_o + r_1) = \zeta - \frac{4\pi\sigma r_o}{\varepsilon_3}\cdot\ln\left(\frac{r_o + r_1}{r_o}\right) \qquad (7.2)$$

$$\lim_{r\to\infty}\Psi_3(r) = 0 \qquad (7.3)$$

$$\Psi_3'(r_o + r_1) = -\frac{4\pi\sigma r_o}{\varepsilon_3(r_o + r_1)} \qquad (7.4)$$

As discussed in Section 6 of Chapter 3, one of the parameters appearing above is dependent on the remainder and in constructing dimensionless monomials it will be convenient to omit σ.

Due to the presence of the exponential Boltzmann factors, the usual fourfold basis of electromagnetic phenomena is insufficient and a fivefold basis (viz. mass M, length L, time T, charge Q and temperature θ) is required. The form factor Ψ_3/ζ is one dimensionless monomial, the remainder being determined from the following dimensional table*.

	ψ_3	ε_2	C_1^*	q	k	T	r	N
M	1	- 1	1	0	1	0	0	- 1
L	2	- 3	- 3	0	2	0	1	0
T	- 2	2	0	0	- 2	0	0	0
Q	- 1	2	0	1	0	0	0	0
θ	0	0	0	0	- 1	1	0	0

Using columns one, two, three, five and six, a non-zero determinant (Δ_2) is given by

$$\Delta_2 = \begin{vmatrix} 1 & -1 & 1 & 1 & 0 \\ 2 & -3 & -3 & 2 & 0 \\ -2 & 2 & 0 & -2 & 0 \\ -1 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 \end{vmatrix} \tag{7.5}$$

indicating that the choice of a fivefold basis was correct. Giving the exponents of q, r and N the values 1, 0 and 0 respectively, one obtains the monomial

$$\pi_1 = \frac{\psi_3 q}{kT} \tag{7.6}$$

while the values 0, 1 and 0 for these exponents (in the same order) yield

$$\pi_2 = \frac{\psi_3^2 \varepsilon_2 r}{kT} \tag{7.7}$$

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*It will be noted that the symbols for the absolute temperature and the dimension of time are the same. This is in accordance with standard notation and the meaning of what follows should be clear.

Finally, exponents of 0, 0 and 1 for q, r and N respectively give

$$\pi_3 = \frac{NC_1^{o}k^3T^3}{\psi_3^6\varepsilon_2^3} \qquad (7.8)$$

To express the solution of (7.1) to (7.4) in physically meaningful terms, a new set of monomials will be derived by taking products of powers of the above monomials. Thus, since π_2 contains both the dependent and independent variables, a more suitable monomial is $\pi_2 \cdot \pi_3^{1/3}$ $(= N^{1/3} C_1^{o\,1/3} r)$ which then serves as a new independent variable (η). Using this and the dependent variable $\Theta = \pi_1$, the potential equation becomes

$$\frac{1}{\eta}\frac{d}{d\eta}\left(\eta\frac{d\Theta}{d\eta}\right) = \frac{8\pi(NC_1^{o})^{1/3}q^2}{\varepsilon_2 kT}\cdot\sinh\Theta \qquad (7.9)$$

Further, eliminating ψ_3 from π_1 and π_3,

$$\pi_1^2 \cdot \pi_3^{1/3} = \frac{(NC_1^{o})^{1/3}q^2}{\varepsilon_2 kT} \qquad (7.10)$$

Thus, parameters will not appear explicitly in the differential equation if a new variable R, viz.

$$R = \sqrt{8\pi}\cdot\pi_1\cdot\pi_3^{1/6}\cdot\eta \qquad (7.11)$$

$$= \sqrt{\frac{8\pi q^2 N C_1^{\,0}}{\epsilon_2 kT}} \cdot r \qquad (7.12)$$

is introduced, giving

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{d\Theta}{dR}\right) = \sinh\Theta \qquad (7.13)$$

It is interesting to note that the coefficient of r in equation (7.12) is the reciprocal of the Debye-Hückel radius, i.e. this radius is used as a scale factor in reducing r to the dimensionless coordinate R.

It now remains to consider the boundary conditions (7.2) to (7.4). The form factor

$$\pi_4 = \psi_3/\zeta \qquad (7.14)$$

given above is divided into π_1 to obtain a normalised zeta-potential Z_0, viz.

$$Z_0 = \frac{q\zeta}{kT} \qquad (7.15)$$

The parameters r_0 and r_1 are reduced to dimensionless form by dividing each by the Debye-Hückel radius, (r_{DH}), giving

$$R_0 = \frac{r_0}{r_{DH}} = \kappa r_0 \qquad (7.16)$$

$$R_1 = \frac{r_1}{r_{DH}} = \kappa r_1 \qquad (7.17)$$

The problem may now be stated thus:

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{dW}{dR}\right) = \frac{1}{Z_o}\sinh Z_o W \qquad (7.18)$$

$$W(R_o + R_1) = 1 - \frac{4\pi\sigma r_o}{e_2\zeta}\ln\left(\frac{r_o + r_1}{r_o}\right) \qquad (7.19)$$

$$\lim_{R\to\infty} W(R) = 0 \qquad (7.20)$$

$$W'(R_o + R_1) = -\frac{4\pi\sigma r_o}{e_2(r_o + r_1)}\cdot\frac{1}{\zeta\kappa} \qquad (7.21)$$

where W has been written in place of w_2.

It will be noticed that free parameters have been left in the boundary conditions (c.f. Section 6 of Chapter 3) to enable one to compute σ directly from the solution of (7.18).

APPENDIX VIII

DIFFERENTIATION OF $K_o(R)$

(i) By definition,$^{(112)}$ the cylinder functions of order m are solutions $w = Z_m(z)$ of Bessel's differential equation

$$\frac{d^2w}{dz^2} + \frac{1}{z}\frac{dw}{dz} + \left(1 - \frac{m^2}{z^2}\right) w = 0 \qquad (8.1)$$

where m is any real number. They also satisfy the recurrence relation

$$Z_{m+1}(z) = - z^m \frac{d}{dz} [z^{-m} Z_m(z)] \qquad (8.2)$$

Typical functions satisfying (8.1) and (8.2) are the Hankel functions of the first kind and order m, $H_m^{(1)}(z)$.

(ii) When $z = iR$ (R real), (8.1) reduces to the modified Bessel equation

$$\frac{d^2w}{dR^2} + \frac{1}{R}\frac{dw}{dR} - \left(1 + \frac{m^2}{R^2}\right) w = 0 \qquad (8.3)$$

whose solutions bounded as $R \to \infty$ are the modified Bessel functions of the second kind and order m, $K_m(R)$. These are related to the Hankel functions by

$$K_m(R) = \frac{\pi}{2} i^{m+1} H_m^{(1)} (iR) \qquad (8.4)$$

(iii) When m = 0, (8.2) becomes

$$H_1^{(1)} (z) = - \frac{d}{dz} H_o^{(1)} (z) \qquad (8.5)$$

Hence by (8.4)

$$K_o'(R) = - K_1(R) \qquad (8.6)$$

APPENDIX IX

INTEGRATION OF THE POTENTIAL EQUATION IN THE ABSENCE OF COIONS

To solve

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{dW_1}{dR}\right) = \frac{1}{2Z_o} e^{Z_o W_1} \qquad (9.1)$$

one first maps the pairs (R, W_1) on to the corresponding pairs (U, V) by means of the transformations$^{(80)}$

$$V = 2\ln R + Z_o W_1 \qquad (9.2a)$$

$$U = \ln R \qquad (9.2b)$$

In this way, (9.1) is reduced to

$$\frac{d^2V}{dU^2} = \frac{1}{2} e^V \qquad (9.3)$$

which, on multiplying by 2 dV/dU, integrates to

$$\left(\frac{dV}{dU}\right)^2 = e^V + a_1 \qquad (9.4)$$

where a_1 is a constant of integration. For the second integration, let

$$e^V = a_1 \tan^2 \phi \qquad (9.5)$$

Equation (9.4) then becomes

$$\operatorname{cosec} \phi \cdot \frac{d\phi}{dU} = \pm \frac{1}{2}\sqrt{a_1} \qquad (9.6)$$

and, on integration,

$$\ln \left\{ \operatorname{cosec} \phi - \cot \phi \right\} = \pm \frac{1}{2} \sqrt{a_1} \cdot W + a_2 \qquad (9.7)$$

where a_2 is the second constant of integration. Writing this in terms of the original variables (by (9.2) and (9.5)) and solving for W_1,

$$W_1 = \frac{1}{Z_0} \ln \left\{ \frac{\pm 2\sqrt{a_1} \cdot e^{a_2} R^{\pm \frac{1}{2} \sqrt{a_1}}}{R[e^{2a_2} R^{\pm \sqrt{a_1}} - 1]} \right\}^2 \qquad (9.8)$$

or

$$W_1 = \frac{1}{Z_0} \ln \left\{ \frac{\pm \sqrt{a_1}}{R \sinh \left[a_2 \pm \frac{1}{2} \sqrt{a_1} \ln R \right]} \right\}^2 \qquad (9.9)$$

Introducing new constants β_1 and β_2 defined by

$$\beta_1 = \frac{1}{2} \sqrt{a_1} \qquad (9.10a)$$

$$\beta_2 = e^{2a_2/\sqrt{a_1}}, \qquad (9.10b)$$

equation (9.9) gives

$$W_1 = \frac{1}{Z_0} \ln \left\{ \frac{4\beta_1^2}{R^2 \sinh^2 [\beta_1 (\ln R \pm \ln \beta_2)]} \right\} \qquad (9.11)$$

Finally, since β_2 is arbitrary so far (being determined by boundary conditions applied to (9.1)), it will be convenient to select $+ \ln\beta_2$ from (9.11), giving

$$W_1 = \frac{1}{Z_0} \ln \left\{ \frac{4\beta_1^2}{R^2 \sinh^2 [\beta_1 \ln (\beta_2 R)]} \right\} \qquad (9.12)$$

APPENDIX X

ALGORITHM FOR COMPUTING σ (BOUNDARY-LAYER METHOD)

Relations Giving the Parameters σ, R_2, β_2, β_3, β_5

It follows immediately from (136d) that $\beta_4 = 0$ while, by (136a)

$$1 - \frac{4\pi\sigma r_o}{e_2 \zeta} \ln\left(\frac{r_o + r_1}{r_o}\right)$$

$$= \frac{1}{Z_o} \ln\left\{\frac{4\beta_3{}^2}{(R_o + R_1)^2 \sin^2 [\beta_3 \ln (\beta_2 \ (R_o + R_1))]}\right\}, \quad (10.1)$$

by (136b)

$$\frac{1}{Z_o} \ln\left\{\frac{4\beta_3{}^2}{R_2{}^2 \ \sin^2 [\beta_3 \ln (\beta_2 R_2)]}\right\} = \beta_5 \ K_o(R_2), \quad (10.2)$$

by (136c)

$$\frac{2}{Z_o R_2}\left\{1 + \beta_3 \cot [\beta_3 \ln (\beta_2 R_2)]\right\} = \beta_5 \ K_1(R_2), \quad (10.3)$$

and by (137),

$$\frac{R_2{}^2 \ \sin^2 [\beta_3 \ln (\beta_2 R_2)]}{8\beta_3{}^2 Z_o} = \frac{1}{Z_o} \sinh [Z_o \beta_5 K_o(R_2)] - \beta_5 K_o(R_2) \quad (10.4)$$

Finally, from (140) and (125),

$$\frac{2}{Z_0}\left\{1+\beta_3\cot\left[\beta_3\ln\left(\beta_2\left(R_0+R_1\right)\right)\right]\right\}=\frac{4\omega\sigma r_0}{\epsilon_2\zeta}\,, \qquad (10.5)$$

Z_0 and ζ following from (7.15) and (113).

Reduction to Simpler Form

(i) Multiplying (10.2) and (10.4) by Z_0 and eliminating β_3,

$$\frac{R_2^2\sin^2\left[\beta_3\ln\left(\beta_2R_2\right)\right]}{8\beta_3^2}=\sinh\ln\left\{\frac{4\beta_3^2}{R_2^2\sin^2\left[\beta_3\ln\left(\beta_2R_2\right)\right]}\right\}$$

$$-\ln\left\{\frac{4\beta_3^2}{R_2^2\sin^2\left[\beta_3\ln\left(\beta_2R_2\right)\right]}\right\} \qquad (10.6)$$

Let

$$\frac{4\beta_3^2}{R_2^2\sin^2\left[\beta_3\ln\left(\beta_2R_2\right)\right]}=e^{A} \qquad (10.7)$$

Then (10.6) becomes

$$2\,e^{A}\left\{\sinh A-A\right\}=1 \qquad (10.8)$$

(ii) Dividing (10.3) by (10.2), Z_0 and β_3 are again eliminated thus:

$$\frac{2\left\{1+\beta_3\cot\left[\beta_3\ln\left(\beta_2R_2\right)\right]\right\}}{R_2\ln\left\{\frac{4\beta_3^2}{R_2^2\sin^2\left[\beta_3\ln\left(\beta_2R_2\right)\right]}\right\}}=\frac{K_1(R_2)}{K_0(R_2)} \qquad (10.9)$$

Let $\beta_3\ln\left(\beta_2R_2\right)=\beta_4$ (10.10)

Then substituting (10.7) and (10.10) in (10.9),

$$\cot \beta_6 = \left(\frac{R_2 A}{2} \; \frac{K_1(R_2)}{K_0(R_2)} - 1 \right) \Big/ \beta_3 \qquad (10.11)$$

Also by (10.7) and (10.10),

$$4\beta_3{}^2 (1 + \cot^2 \beta_6) = R_2{}^2 \, e^A \qquad (10.12)$$

Thus, eliminating β_6 from (10.11) and (10.12),

$$\beta_3 = \sqrt{\frac{R_2{}^2 e^A}{4} - \left[\frac{R_2}{2} \; A \; \frac{K_1(R_2)}{K_0(R_2)} - 1 \right]^2} \qquad (10.13)$$

Finally by (10.10),

$$\beta_2 = \frac{1}{R_2} \, e^{\beta_6/\beta_3} \qquad (10.14)$$

APPENDIX XI

PIECEWISE LINEARISATION OF THE POISSON-BOLTZMANN EQUATION ($n = 2$)

Equation (122) will be approximated by the system

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{dW_1}{dR}\right) = aW_1 + b \qquad R_o + R_1 \leq R \leq R_2 \qquad (11.1a)$$

$$\frac{1}{R}\frac{d}{dR}\left(R\frac{dW_2}{dR}\right) = cW_2 \qquad R_2 \leq R \leq \infty, \qquad (11.1b)$$

a, b and c being chosen so that the right-hand members of equations (11.1) suitably approximate the function $(\frac{1}{Z_o})\sinh Z_oW$. Rather than use equations of the form (102), the constants will be chosen in such a way that the difference between the right-hand members of (11.1) and the function $(\frac{1}{Z_o})\sinh Z_oW$ has zero integral over $[R_o + R_1, \infty]$ i.e.

$$\int_0^{\frac{1}{2}\cdot W(R_o+R_1)} \left(cW - \frac{1}{Z_o}\cdot\sinh Z_oW\right)dW$$

$$+ \int_{\frac{1}{2}\cdot W(R_o+R_1)}^{W(R_o+R_1)} \left(aW + b - \frac{1}{Z_o}\cdot\sinh Z_oW\right)dW = 0 \qquad (11.2)$$

(R_2 has been chosen so that $W(R_2) = \frac{1}{2}W(R_o + R_1)$ in the manner of equations (100)) Also, the right-hand members of (11.1) will be set equal at R_2, i.e.

$$\frac{c}{2} W(R_o + R_1) = \frac{a}{2} W(R_o + R_1) + b \qquad (11.3)$$

and finally, at $R = R_o + R_1$, the right-hand side of (11.1a) will be equated to $(\frac{1}{Z_o}) \cdot \sinh Z_o W$, i.e.

$$aW(R_o + R_1) + b = \frac{1}{Z_o} \cdot \sinh Z_o W \qquad (11.4)$$

For brevity, W_o will be written in place of $W(R_o + R_1)$. Equations (11.2) to (11.4) then yield the following solution for the constants a, b and c:

$$a = \frac{3}{Z_o W_o} \sinh Z_o W_o + \frac{4}{(Z_o W_o)^2} (1 - \cosh Z_o W_o) \qquad (11.5a)$$

$$b = -\frac{2}{Z_o} \sinh Z_o W_o - \frac{4}{Z_o^2 W_o} (1 - \cosh Z_o W_o) \qquad (11.5b)$$

$$c = -\frac{1}{Z_o W_o} \sinh Z_o W_o - \frac{4}{(Z_o W_o)^2} (1 - \cosh Z_o W_o) \qquad (11.5c)$$

Integrating equations (11.1),

$$W_1 = AK_o(R\sqrt{a}) + BI_o(R\sqrt{a}) - b/a \qquad (11.6a)$$

$$W_2 = CK_o(R\sqrt{c}) \qquad (11.6b)$$

where A, B and C are constants of integration which must satisfy the boundary condition

$$W_1(R_o + R_1) = W_o \qquad (11.7)$$

as well as the continuity relations for potential and field, viz.

$$W_1(R_2) = W_2(R_2) \qquad (11.8a)$$

$$W_1'(R_2) = W_2'(R_2). \qquad (11.8b)$$

Finally, R_2 must be chosen so that

$$W_1(R_2) = W_2(R_2) = \frac{1}{2} \cdot W_o \qquad (11.9)$$

If the constants A, B, C and R_2 are determined in this way, one has the following algorithm for calculating σ*:

(i) Choose a first approximation to σ (e.g. by Gorin's method).

(ii) Calculating W_o from (113) and (123), i.e.

$$W_o = 1 - \frac{4\sigma r_o}{F'\eta u} \cdot \ln\left(\frac{r_o + r_1}{r_o}\right). \qquad (11.10)$$

---

*With the aid of (123) and (125). In differentiating W_1, it should be noted that $K_o'(R) = -K_1(R)$ as in Appendix VIII, whereas $I_o'(R) = I_1(R)$ as in Sneddon$^{(39)}$. The statement by Sneddon that the Bessel functions I_n and K_n satisfy analogous recurrence relations is misleading.

(iii) Calculate Z_o from (113) and (7.15), viz.

$$Z_o = \frac{\pi q F' \eta u}{e_2 kT} \qquad (11.11)$$

(iv) Calculate a, b and c from equations (11.5).

(v) Select a first approximation to R_2.

(vi) Calculate A, B and C from the following relations:

$$A = \frac{(W_o/2 + b/a) \cdot I_o((R_o + R_1)\sqrt{a}) - (W_o + b/a) \cdot I_o(R_2\sqrt{a})}{K_o(R_2\sqrt{a}) \cdot I_o((R_o + R_1)\sqrt{a}) - K_o((R_o + R_1)\sqrt{a}) \cdot I_o(R_2\sqrt{a})}$$

(11.12a)

$$B = \frac{-(W_o/2 + b/a) \cdot K_o((R_o + R_1)\sqrt{a}) - (W_o + b/a) \cdot K_o(R_2\sqrt{a})}{K_o(R_2\sqrt{a}) \cdot I_o((R_o + R_1)\sqrt{a}) - K_o((R_o + R_1)\sqrt{a}) \cdot I_o(R_2\sqrt{a})}$$

(11.12b)

$$C = \frac{W_o}{2K_o(R_2\sqrt{c})} \qquad (11.12c)$$

$$C = \sqrt{\frac{a}{c}} \cdot \frac{1}{K_1(R_2\sqrt{c})} \left\{ A \cdot K_1(R_2\sqrt{a}) - B \cdot I_1(R_2\sqrt{a}) \right\} \qquad (11.12d)$$

(vii) If the values of C from (11.12c) and (11.12d) do not coincide, further approximations to R_2 are inserted at (v) and (vi) is repeated until (11.12c) and (11.12d) yield sufficiently close estimates of C.

(viii) Calculate a second approximation to σ by means of (113), (125) and (11.6a), viz.

$$\sigma = \frac{(R_o + R_1)uF'\eta}{4r_o} \cdot \sqrt{a} \cdot \left\{ A\,K_1((R_o + R_1)\sqrt{a}) - BI_1((R_o + R_1)\sqrt{a}) \right\} \tag{11.13}$$

(ix) If the value from (viii) does not equal that introduced in (i), the second approximation is inserted at (i) and the whole calculation repeated until no variation in σ (to a given degree of accuracy) is observed.

APPENDIX XII

CONVERSION OF UNITS IN CHARGE CALCULATIONS

Viscosity (η)

1 poise = 1 gm/cm.sec = 1×10^{-8} gm/(A sec).

Mobility (u)

1 cm^2/volt.sec = $\frac{3}{4.8} \times 10^{12}$ (electronic charge).sec/gm.

Friction factor (F')

Dimensionless.

Dielectric constant (ϵ_s)

1 (e.s.u. charge)^2 · sec^2/cm^3.gm = $\frac{1}{(4.8)^2} \times 10^{-4}$ (electronic charge)^2 sec^2/A^{3}gm.

Electronic Charge (q)

q = 1 electronic charge.

Boltsmann's constant

$k = 1.38 \times 10^{-16}$ gm cm^2/sec^2 $^\circ$K = 1.38 gm A^2/sec^2 $^\circ$K.

The last set of units in each case yield the charge density (σ) in electronic charge /A^2.

NOTE: For aqueous solutions of electrolyte at 273°K and ionic strength I,

$$\kappa = 0.324\sqrt{I} \quad (A^{-1}) \tag{12.1}$$

and

$$(R_o + R_1) = 0.324\,(r_o + r_1)\sqrt{I} \tag{12.2}$$

(where r_o and r_1 are in A).

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