FINE PARTICLE DEPOSITION IN
SMOOTH CHANNELS

by
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to the required standard

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ABSTRACT

Previous research on particle deposition in channels has emphasized the mass transfer aspects of the process. Little attention has been paid to the problem of determining whether or not particles, which have been transported to the channel walls, will actually adhere there. This adhesion step is complicated in most practical deposition situations by the presence of turbulent flow, chemical interactions, polydisperse particles, and wall roughness. Thus, as a first step towards providing a more fundamental understanding of the adhesion process, a theoretical and experimental study of a simplified deposition system was undertaken.

In this idealized system, a dilute aqueous suspension of spherical, uniformly-sized, colloidal particles flows in steady, fully-developed laminar motion through geometrically simple channels. Under these circumstances, deposition onto the walls of the channels takes place by convective diffusion in a force field arising from the electrical double layer, London-van der Waals, and viscous interactions between each suspended particle and the wall. Because the range of these interaction forces is confined to a narrow region near the channel walls, their influence on the deposition process can be treated approximately by assuming convective diffusion in the bulk of the suspension with a first-order reaction at the walls. Explicit expressions for the surface reaction coefficient are derived in terms of the parameters which affect these interactions.
The resulting extended Graetz problem is solved for both parallel-plate and cylindrical channels. Through the use of confluent hypergeometric functions combined with asymptotic techniques, an evaluation of these series solutions is made possible which is more accurate than all previous solutions, especially for the deposition of colloids and for cylindrical channels. Simple Leveque-type asymptotic solutions are also obtained for the case of large Peclet numbers, and when the reaction rate constant is infinite, these reduce to the corresponding well-established results for convective diffusion. These solutions describe only the initial state of the deposition process.

To assess the derived model, an experimental investigation of the same idealized deposition system was carried out using uniform, spherical, silica particles (0.40, 0.60, and 0.65 μm dia.) and a parallel-plate channel (0.08 mm gap-thickness) constructed from plate glass and coated with different plastics to achieve a variety of surface chemical conditions. The use of particles doped with the γ-emitter Co⁵⁸, in conjunction with a collimated scintillation detector mounted on the outside of the channel, greatly facilitated the measurement of particle deposition. In addition, the tracer technique, when used with a second suspension of identical, but non-radioactive particles, allowed a separate measurement of particle release from the surface.

It was found that, under the conditions of the present experiments, the re-entrainment of previously deposited particles was essentially non-existent. Thus, the declining rate of particle accumulation with time observed for most runs could only be interpreted as a declining deposition rate.

The measured initial rates of deposition of negatively charged particles onto positively charged plastic substrates were found to be in
reasonable quantitative agreement with those predicted by the above theory if it was assumed that the process was mass-transfer controlled. For this case, the decrease in accumulation with time was best interpreted by a model which accounted for the change in surface area available for further deposition as the walls became progressively covered. It was shown that this surface coverage effect is enhanced by double layer exclusion (due to the repulsive interaction of the diffuse layers surrounding each particle), geometric exclusion (due to the finite size of particles and their random distribution on the particle wall), and hydrodynamic exclusion (due to the movement of fluid around the deposited particles). The maximum surface coverages attained never exceeded 10%.

For negative particles and negative walls, the initial deposition rates were generally much less than for positive substrates, and the process was found to be surface-reaction rate controlled. For this case, the theory provided an accurate qualitative description of the experimental results; e.g. decreasing the double layer thickness (by adding neutral salts) or decreasing the magnitude of the surface zeta potentials (by lowering the suspension pH) both served to increase the initial deposition rate. However, the measured values were generally much greater than those predicted theoretically. The evidence suggests that when repulsive electrical double layer interactions control the rate of particle deposition, deposition occurs preferentially onto areas of locally-favourable potential or geometry (or both). Thus, it was typically observed that the deposition rates fell off quickly at very low surface coverages as these preferred sites were presumably filled.
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A.2 Dimensionless particle deposition rate $J_D$ in a cylindrical channel as a function of dimensionless axial distance $\bar{y}$ for selected values of dimensionless reaction rate constant $K$. The solid lines refer to the modified Graetz solution and the dashed lines to the modified Leveque approximation for small $\bar{y}$.

A.3 Dimensionless mean particle concentration $\theta_m$ in a cylindrical channel as a function of dimensionless axial distance $\bar{y}$ for various selected values of dimensionless reaction rate constant $K$. The solid lines refer to the modified Graetz solution and the dashed lines to the modified leveque approximation for small $\bar{y}$.

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B.2 Schematic representation of a complex recirculating system.
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A problem of widespread interest is that of predicting and controlling the rate at which a fine particle, suspended in a liquid, deposits on a foreign surface. Such knowledge is of importance to a variety of practical situations. These may be broadly classified into three categories according to the size of the foreign surface. In the first category, deposition takes place on a surface whose macroscopic dimensions approach those of the particle. Such a process is known as coagulation if the interacting particles are composed of the same material or heterocoagulation if they are different. In the second category, deposition takes place on a surface which is finite but large relative to the size of the particle. Examples of applications in this category include the collection of suspended particles on a coarser medium in filtration, the attachment of ore particles to gas bubbles in froth flotation, and the deposition of "size" on cellulose fibres in the manufacture of paper. In the third category, deposition takes place on an infinitely extended surface such as might be found in the case of a suspension flowing in a channel. Applications involving deposition in channels include the particulate fouling of heat exchangers, the contamination of nuclear power plants, and thrombus formation in the human arterial tree.

For convenience, it is usually assumed that the deposition process takes place in two separate steps:
i) a transport step whereby a particle in the bulk suspension is transferred to the interface region. For submicron particles, this step is essentially a convective-diffusion process.

ii) an adhesion step in which a particle in the interface region becomes attached to the collector surface. This step is controlled by the various interaction forces which arise at small distances of separation between the particle and the collector.

It is of interest to observe the different emphasis which has been placed on each of these two steps with reference to the three categories of particle deposition listed above.

In the first category, which has long been a topic of interest to surface and colloid chemists, the adhesion step has received a great deal of attention. However, the role of convection in the process of coagulation has been almost entirely ignored. In the third category, a field popular with chemical engineers and fluid dynamicists, the transport step is well understood for a variety of flow situations but almost no attention has been paid to the surface chemical phenomena which influence the adhesion step. However, in the second category, particularly in the filtration field, a united effort by scientists from many backgrounds has, in recent years, led to a much improved apprehension of both aspects of the deposition process.

The primary objective of the present investigation is to gain a better understanding of the role played by the adhesion step in the process of particle deposition in channels. Towards this end, it will be necessary to borrow heavily from the experimental techniques of colloid chemistry and from some of the recent theoretical advances in the field of particle filtration. It is hoped that, by providing an alternative method of examining some of the basic concepts of coagulation and filtration theory, the present investigation will contribute reciprocally to these fields.
The deposition of particles from a flowing suspension onto channel walls is generally a rather complex process. For a start, the flow in most practical applications is turbulent. Due to the lack of a universal mathematical description of the turbulent flow field, there is not yet available a completely satisfactory model for the transport step in this regime, even though the problem has been extensively investigated. Fluid turbulence also affects the adhesion process by creating momentarily intense local shear rates at the channel wall. In addition, the adhesion step is influenced not only by the various physical and chemical interaction forces which act on particles in close proximity to the wall, but also by such factors as particle shape and surface roughness, which can promote mechanical entrapment. It is apparent that to develop a fuller understanding of the adhesion process, it will be necessary to begin by studying simpler deposition situations in which many of the complexities of "real" systems have been eliminated.

Consider the following idealized deposition system. In this system, an aqueous suspension of spherical, uniformly-sized, submicron particles moves in laminar flow through a channel consisting of two very smooth flat plates on which the particles may deposit but do not chemically interact. Under these circumstances, because the flow field can be precisely defined, the transport step is amenable to exact analysis. Furthermore, the only factors of importance to the adhesion process are the physical interaction forces of which there are three in aqueous solutions, namely:

i) viscous interaction force due to the increased resistance to movement experienced by a particle near a foreign surface. This force reduces the mobility of a particle and hence tends to retard deposition.

ii) London-van der Waals dispersion force due to the instantaneous existence of dipoles caused by the short period movement of electrons in atoms and molecules. This force is generally attractive.
iii) electrical double layer interaction force due to the presence of the atmospheres of excess charge which surround all surfaces in contact with ionic or polar media. This force can be attractive or repulsive depending upon the signs of the charge layers involved in the interaction.

These are precisely the forces which form the basis of the DLVO theory of colloid coagulation (1,2). A theory for the kinetics of coagulation was first developed in 1917 by Smoluchowski (3), who assumed that every Brownian collision between particles led to permanent contact. In 1934, Fuchs (4) extended this analysis to include the possibility of "slow" coagulation, by treating the process as one of diffusion over a generalized potential energy barrier. However, it was not until the 1940's that the specific nature of this potential energy field was fully appreciated. Working independently, Derjaguin and Landau (1) and Verwey and Overbeek (2) succeeded in obtaining a solution for the repulsive interaction energy between two identical spherical double layers. By combining this solution with an expression derived by Hamaker (5) for the van der Waals attraction between two spheres, they were able to completely specify in terms of measurable parameters the overall interaction energy field required to solve the Fuchs' equation. Because of its success in providing an accurate qualitative (and in some cases, quantitative) explanation of many phenomena observed in the study of colloid stability, the DLVO theory has gained a wide acceptance.

Subsequent years have seen a great deal of activity in this area. Starting with the innovations of Derjaguin (6), the theory of the interaction of double layers has been extended to include the interaction between particles of different sizes (including the sphere-plate geometry of interest to channel deposition) and having different surface potentials. Significant improvements in the understanding of the van der Waals interaction have come about as a result of the pioneering work of Lifshitz (7). Recently,
the DLVO theory has been modified to account for the existence of the viscous interaction forces between two approaching colloid particles (8,9). Thus, the stage was set for the appearance of a comprehensive model of the adhesion step for extended surfaces based on the DLVO theory of colloid coagulation. This innovation has recently come about in the particle filtration field.

Before discussing the relevance of this innovation to the present problem, it should be noted that the division of the deposition process into two steps is a conceptual device used to gain a fuller appreciation for the complexity of the problem. In general, the two steps are not separable and a solution to the complete problem of diffusion in both a potential energy and a velocity field is required. For the idealized deposition system chosen here, both fields are easily specified. But because the energy field contributes many non-linear terms to the defining equation, an analytic solution is not possible. Recently, however, Ruckenstein and Priewe (10) and Spielman and Friedlander (11) have demonstrated that, as long as the interaction energy field is confined to a narrow region near the surface of the collector, particle filtration can be approximated as a two-step process: a mass transfer step involving only convection and diffusion in the bulk of the suspension; and an adhesion step, the treatment of which is an extension of the DLVO theory, at the collector surface. The adhesion step for extended surfaces is a kinetic process whose rate is directly proportional to the concentration of particles in the interface region. Thus, it may be represented as a first-order reaction at the collector surface. The reaction rate equation provides one of the boundary conditions required for solving the bulk convective-diffusion problem. These authors derive explicit expressions for the first-order rate constant in terms of the parameters which control the
electrical double layer, London-van der Waals and viscous interaction
forces.

In the theory section of the present investigation (Chapter 2),
the approximation developed above for filtration collectors is applied to
the analogous problem of deposition in a parallel-plate channel. First,
the theory of the various interaction forces involved in the adhesion step
is briefly reviewed (Sect. 2.1.1). This is followed by a short qualitative
discussion on how the parameters which affect these forces might be expected
to influence the deposition rate (Sect. 2.1.2). Then a quantitative theory
of particle deposition in the presence of physical interaction forces is
presented. The arguments of the above authors are restated in order to
establish the range of applicability of the first-order reaction boundary
condition for the channel problem. A useful approximation for the reaction
rate constant is obtained for large repulsive energy barriers and then ex­tended to include the effect of particle inertia (Sect. 2.2.1). Existing
solutions to the resulting convective mass transfer problem are cited and
new solutions more suited to colloid systems are obtained (Sect. 2.2.2).
Because colloidal particles are characterized by small Brownian diffusivities,
simple approximate expressions for large Peclet numbers are also developed
(Sect. 2.2.3). In addition, the entire analysis is repeated for the related
problem of deposition in a cylindrical channel (Appendix A, Sect. A.1).

Experimentally, there has been no recorded attempt to make system­
matic measurements of fine particle deposition as a function of surface
interaction forces in channels. Such measurements have, however, been carried
out for filtration collectors consisting of packed beds of spheres (12,13,
14,15). In general, the observed experimental trends could be explained very
well on the basis of overall interaction energy curves calculated from the
DLVO model. However, because of the method used for obtaining filtration measurements in each case (a comparison of inlet and outlet suspended particle concentrations) and because of the inherent difficulties in modelling the complex hydrodynamics of a packed bed, these results do not provide any direct information about particle deposition rates.

The only documented experiments in which particle deposition was systematically measured under well-defined convection and surface-chemical conditions, are several studies made using a rotating disc collector (16, 17, 18). Marshall and Kitchener (16) investigated the accumulation of carbon black particles (0.18 μm dia.) on a disc rotating in an aqueous suspension of these particles as a function of particle and collector surface (zeta) potentials and the thickness of the double layers. To obtain a smooth collector having a wide variety of surface potentials, they developed a technique for coating different plastics onto the disc. The concentration of accumulated particles was measured as a function of time by rinsing the disc, drying it in a dessicator, and counting the residual particles under a microscope using dark-ground illumination. Marshall and Kitchener found that the deposition was greatly reduced under conditions where the electrical double layer interaction was repulsive compared to when it was attractive. However, their results did not agree very well with predictions based on a simplified treatment of the deposition problem. Amongst the reasons for this disagreement, they cite the following: non-spherical particles, unstable slightly-coagulating suspension, and errors caused by the ex-situ technique for determining deposited particle concentrations.

The experimental methods of Marshall and Kitchener were subsequently improved upon by Hull and Kitchener (17). The latter authors instituted the
use of a stable colloid consisting of 0.31 μm dia. polystyrene spheres and an in-situ microscopic measurement of particle concentration. Hull and Kitchener found that when the particles were negatively charged and the plastic film positively charged, the deposition rate was closely in agreement with the Levich (19) theory of diffusion-controlled transport to the disc. However, with negative particles and negative films, although deposition was greatly reduced and qualitatively followed the DLVO theory, the measured rates were always greater than those predicted from their simplified analysis. A more detailed theoretical treatment by Ruckenstein and Prieve (10) failed to resolve these differences. Hull and Kitchener concluded that the source of these discrepancies was the heterogeneous nature of all real surfaces; deposition occurred preferentially onto areas of locally favourable potential or geometry.

Clint et al. (18) used a rotating disc to study the deposition of 0.21 μm dia. polystyrene spheres onto a smooth polystyrene substrate. Because particles and substrate were similarly charged, measurable deposition occurred only under conditions where the particles themselves were coagulating. Thus, their results were not readily analyzable.

Although the rotating disc system represents a situation where the role of convection is well understood, it does have at least one experimental drawback. The results obtained by the above authors depict only the overall accumulation process which, in fact, may be the net outcome of the two competing processes of deposition and release. The rotating disc system cannot be readily modified to accommodate both deposition and release rate measurements under the conditions where both processes are occurring. In addition, the microscopic technique used for obtaining deposited particle concentrations is extremely time-consuming. As a consequence, the above
investigators were only able to measure enough points on each accumulation curve to establish an initial deposition rate. Their results give little information as to how the accumulation rate is affected when the substrate becomes significantly covered with particles. For example, the highest coverage obtained in these experiments was only ~0.4%, by Hull and Kitchener (17).

In Chapter 3 of the present study, an experimental method is described for measuring particle deposition in a parallel-plate channel under conditions of laminar flow and known double layer properties. The technique takes advantage of several of the experimental innovations introduced by the above investigators. For example, in order to obtain a variety of surface potential combinations, the smooth glass test sections are overlaid with plastics using a modified version of the coating apparatus employed by Marshall and Kitchener (Sect. 3.3). The idea of using a stable suspension of spherical particles was borrowed from Hull and Kitchener. However, in the present experiment, the particle material is silica which has been radioactively-tagged with a γ-emitter, Co$^{58}$ (Sect. 3.2). The use of radioactive particles in conjunction with a collimated scintillation detector mounted on the outside of the channel allows a simple, and in many cases, continuous measurement of the concentration of deposited particles with time. Because of the ease of the continuous analysis, any number of accumulation measurements can be made during a run. Thus, the measurements can be extended to significant surface coverages without sacrificing the more detailed information required at the start of the run to establish an initial deposition rate. In addition, the suspension of radioactive particles can be used with a second suspension of identical, but non-radioactive particles to yield separate deposition and release rate measurements under the dynamic conditions
when both processes are occurring (see Sect. 3.4). The electrokinetic methods used for obtaining the particle and substrate surface (zeta) potentials are described in Sect. 3.5.

The results of the experiments are discussed in Chapter 4 with reference to the developed theory of particle deposition. The conclusions and suggestions for extending this work are presented in Chapters 5 and 6, respectively.
2.1 Interaction Between a Spherical Particle and a Plane Surface

2.1.1 Types of Interaction Forces

2.1.1.1 Electrical Double Layer Interaction

In general, all solids in contact with an aqueous medium acquire an electrical charge, usually because of the ionization of slightly soluble surface groups or because of the preferential adsorption of specific ions from solution. To maintain electroneutrality, the liquid phase must acquire a net compensating charge opposite in sign to that fixed on the solid surface. Electrostatic attraction attempts to cause this compensating charge in the liquid to line up parallel to the fixed charge on the solid surface. However, because of diffusion effects, the layer of charge in the liquid assumes an equilibrium distribution such that the excess charge concentration falls from a maximum at the interface to zero at distances sufficiently removed from the surface. This system of two charge layers, a fixed charge on the surface of the solid and a smeared-out or diffuse layer in the liquid next to the solid, is the Gouy-Chapman model of the electrical double layer.

The structure of the double layer can be obtained theoretically by solving the Poisson-Boltzmann equation. This mathematical development has been treated in standard texts (20,21) and hence will not be included here. It shows that all of the properties of the Gouy-Chapman double layer
model are defined by the specification of two parameters: \( \psi_0 \), the surface potential, and \( \kappa \), the reciprocal double layer thickness. For low surface potentials (\( \psi_0 \leq 25 \text{ mV} \)), \( 1/\kappa \) is the distance at which the potential of the diffuse layer has fallen to \( 1/e \) of the surface value, \( e \) being the base of the natural logarithms.

The Gouy-Chapman model has been modified by Stern (20) to include the discrete size of ions and the existence of an immobilized layer of adsorbed counterions at the surface. In this model, the potential falls linearly across the adsorbed layer, from the surface value \( \psi_0 \) to the Stern potential, \( \psi_0^* \), and then decreases in accordance with the Gouy-Chapman description to zero potential (electroneutrality) in the bulk solution. The distribution of ions (or potential) in the diffuse layer is now determined by \( \psi_0^* \) and not \( \psi_0 \). The Stern potential is important physically because it is closely related to the zeta potential calculated from electrokinetic measurements, and for many practical situations, the two can be considered identical (see Sect. 3.5.1).

When two double layers are brought into contact, for example when a particle approaches a plane surface, there is an electrostatic interaction of the ions in the diffuse layers. The potential energy of interaction can be determined through force (22) or free energy (2) considerations from a knowledge of the distribution of space charge (or electrical potential) between the two interacting bodies and from the electrostatic boundary conditions at their surfaces. All utilizable solutions for the interaction of dissimilar double layers assume that the distribution is given by the solution of the Poisson-Boltzmann equation and further that either a constant surface potential or a constant surface charge density
boundary condition applies. However, the Poisson-Boltzmann equation neglects effects such as finite ion volume, variation in the dielectric constant with ion concentration, and discreteness of charge which may strongly influence the distribution (20). Furthermore, it has not yet been established which boundary condition best applies in real situations. The boundary condition is determined by the dynamics of the interaction. If the time taken for the re-establishment of electrochemical equilibrium between the surface and the bulk solution is small compared to the time taken for a Brownian collision, then it can be assumed that the potential at the surface/medium interface remains constant during the interaction. On the other hand, if the equilibrating process takes much longer than the Brownian encounter, then a constant charge density during interaction is the correct assumption. It has been argued (23,24) that in reality both interface charge density and interface potential change during the course of the interaction and that the boundary conditions need to be amended to reflect these changes.

Thus, because all of the available solutions are subject to the above limitations, only the appropriate analytical expressions for the double layer interaction energy will be considered here. In addition to the assumption of either a constant potential or a constant charge density boundary condition, an analytic solution for the interaction energy requires further simplifying approximations. First, it is necessary to adopt the linearized form of the Poisson-Boltzmann equation. Hence, in principle, the interaction energy thus calculated is valid only for small potentials, i.e. $\psi_0 \leq 25$ mv for a univalent counterion. Secondly, since spherical double layers generally result in an intractable problem, interactions
involving particles are usually resolved by adopting Derjaguin's approximation (22) at small separations and the linear superposition approximation (2) at large separations.

Derjaguin suggested that the interaction between double layers on spherical particles may be assumed to be made up of contributions from infinitesimally small pairs of concentric parallel rings each of which can be considered a flat plate. Since expressions for the interaction energy per unit area of two parallel plates are available, the overall double layer interaction is obtained by integration. This method is only valid for circumstances in which the double layer thickness and the separation between the two surfaces are of the same order of magnitude, but in which both are small compared to the size of the particles. Hogg et al. [25] have used this approximation in conjunction with the linearized form of the Poisson-Boltzmann equation to derive an expression for the energy of the double layer interaction between two dissimilar spheres (dissimilar in size and surface potential) in a symmetrical electrolyte for the case where the interfacial potentials of both surfaces remain constant during the interaction. When one of the particle radii becomes infinite, a situation corresponding to the interaction between a sphere and a plate, their expression for the interaction energy, $\phi_{\text{edl}}$, reduces to

$$\phi_{\text{edl}} = \frac{e a}{4} \left\{ 2\psi_1 \psi_2 \ln \frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} + (\psi_1^2 + \psi_2^2) \ln \left[ 1 - e^{-2\kappa h} \right] \right\}$$

[2.1]

In this equation, obtained independently by Ives and Gregory (12), $\varepsilon$ is the dielectric constant of the medium, $a$ is the particle radius, $\psi_1$ and $\psi_2$ are the Stern potentials of the particle and the plate, respectively, $h$ is
the separation between the particle surface and the surface of the plate, and $\kappa$, the reciprocal double layer thickness, is given by

$$\kappa = \left( \frac{8\pi n e_0 z^2}{e k T} \right)^{\frac{1}{2}}$$

[2.2]

where $n$ is the counterion concentration (number of ions/cm$^3$), $z$ is the valency of the ion, $e_0$ is the electronic charge, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. For the case where the charge densities at both surfaces remain constant during the interaction, Wiese and Healy (26) give

$$\phi_{\sigma-\sigma}^{\text{edl}} = \frac{e a}{4} \left\{ 2\psi_1 \psi_2 \ln \left[ \frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} \right] - (\psi_1^2 + \psi_2^2) \ln \left[ 1 - e^{-2\kappa h} \right] \right\}$$

[2.3]

and for the two alternative situations where the interaction is between one surface at constant potential and a second surface at constant charge density, Kar et al. (27) obtain

$$\phi_{\psi-\sigma}^{\text{edl}} = \frac{e a}{4} \left\{ 2\psi_1 \psi_2 \left( \frac{\pi}{2} - \tan^{-1} \sinh \kappa h \right) - (\psi_2^2 - \psi_1^2) \ln \left[ 1 + e^{-2\kappa h} \right] \right\}$$

[2.4]

when the particle surface (surface 1) remains at constant potential and

$$\phi_{\sigma-\psi}^{\text{edl}} = \frac{e a}{4} \left\{ 2\psi_1 \psi_2 \left( \frac{\pi}{2} - \tan^{-1} \sinh \kappa h \right) + (\psi_2^2 - \psi_1^2) \ln \left[ 1 + e^{-2\kappa h} \right] \right\}$$

[2.5]

when the plane surface (surface 2) remains at constant potential. Eqs. [2.3], [2.4], and [2.5], like Eq. [2.1], represent the sphere-plate
interaction only. The more generalized forms for dissimilar spheres are given in the cited references.

At separations large compared to the double layer thickness, the electrical double layer on one surface is not significantly affected by the proximity of the second surface. Thus, the potential profile between the two surfaces may be approximated by a linear superposition of the non-interactive profiles from each surface. Bell et al. (28) have used this linear superposition approximation to derive the following expression for the sphere-plate interaction

$$\phi_{\text{edl}} = \varepsilon a\psi_1\psi_2 e^{-\kappa h}$$  \[2.6\]

Since the two interacting surfaces are assumed to have a negligible influence over each other, Eq. [2.6] is representative of the double layer interaction energy at large separations regardless of whether the constant potential or the constant charge boundary condition is used.

For the general case of two dissimilar spheres, the expressions obtained using Derjaguin's approximation for small separations do not yield the correct distance relationship for the interaction energy, as given by the linear superposition approximation, at large separations. However, for the special case of the sphere-plate interaction, it can be proven that Eqs. [2.1], [2.3], [2.4] and [2.5] all reduce to Eq. [2.6] as $\kappa h$ becomes large. This result is illustrated in Fig. 2.1. The four expressions for the interaction energy, representing all possible permutations of the boundary conditions, all converge to within 1% of the value given by Eq. [2.6] for $\kappa h \geq 5$. This fortuitous circumstance, which, presumably, is the result of one of the surfaces being planar, suggests that the expressions obtained using Derjaguin's approximation may be used here to represent the interaction
Figure 2.1. Effect of surface boundary conditions on electrical double layer interaction as a function of dimensionless separation distance between a sphere and a plate. $\psi_1 = -20$ mv, $\psi_2 = -10$ mv, $a = 0.25$ µm, $\varepsilon = 80$ (H₂O).
energy at all separation distances. It is, in fact, possible to test this hypothesis for the constant potential-constant potential case. In an attempt to find a physically more satisfying alternative to Derjaguin's approximation, McCartney and Levine (29) developed a new technique based on an integral equation governing a surface-distribution of electric dipoles, which they used to derive the energy of interaction between two identical spheres when their surface potentials remain constant. This technique has been extended by Bell et al. (29) to the case of dissimilar spheres. For the sphere-plate interaction, their equation can be reduced to

$$\phi_{ed1} = \frac{2a}{2(a+h)} \left\{ \frac{1 + \left( \frac{a}{a+h} \right)^{\frac{1}{2}} e^{-\kappa h}}{1 - \left( \frac{a}{a+h} \right)^{\frac{1}{2}} e^{-\kappa h}} \ln \left[ 1 + \left( \frac{a}{a+h} \right)^{\frac{1}{2}} e^{-\kappa h} \right] + \left( \psi_1^2 + \psi_2^2 \right) \ln \left[ 1 + \left( \frac{a}{a+h} \right)^{\frac{1}{2}} e^{-2\kappa h} \right] \right\}$$

[2.7]

where

$$\Lambda = \left( \frac{a+h}{a} \right)^{\frac{1}{2}} + \left( \frac{a}{a+h} \right)^{\frac{1}{2}}$$

[2.8]

Although the integral equation method has the same restrictions on $\kappa a$ as Derjaguin's approximation (i.e. $\kappa a \geq 5$), it has the advantage that for the general case of dissimilar spheres it does yield the correct variation with distance for all separations. Thus, it can be assumed that Eq. [2.7] is representative of the sphere-plate interaction energy at intermediate separations. It can be easily shown that for $h \to 0$, Eq. [2.7] reduces to Eq. [2.1] and for $\kappa h \gg 1$ to Eq. [2.6]. Figure 2.1 demonstrates that the values
for the interaction energy obtained from either Derjaguin's approximation (Eq. [2.1]) or from the integral equation method (Eq. [2.7]) are in good agreement over the whole range of $\kappa h$. It will therefore be assumed that all of the expressions derived using Derjaguin's approximation (i.e. Eqs. [2.1], [2.3], [2.4] and [2.5]) provide an adequate estimate of the interaction energy at all separations.

It can be seen from Figs. 2.1 and 2.2 that the results obtained for the interaction energy at small separations are widely divergent depending upon which particular pair of boundary conditions are chosen. In general the assumption of constant charge density leads to a greater repulsion than the constant potential case. As might be expected, the two situations involving mixed potentials lead to interaction energies which are intermediate between the unmixed cases, with the boundary condition on the planar surface (surface 2) dominating the interaction (i.e. $\phi^{\sigma-\sigma} > \phi^{\psi-\sigma} > \phi^{\sigma-\psi} > \phi^{\psi-\psi}$).

Recently, attempts have been made to provide a more realistic description of the boundary conditions on the interacting surfaces. These require knowledge of the specific mechanism by which charge is generated on each surface. For example, for the case where surface charge arises from the presence of single or multiple ionizable groups, Ninham and Parsegian (30) and Prieve and Ruckenstein (31), respectively, have numerically evaluated the interaction energy between two plane surfaces separated by an electrolyte solution. The boundary conditions were formulated by assuming the groups on the surfaces always remained in ionic equilibrium with the solution.

Derjaguin's approximation for spherical double layers is not restricted to small potentials. It requires only that the value of the interaction energy between two parallel plates be known as a function of distance.
Figure 2.2. Electrical double layer interaction energy between a sphere (surface 1) and a plate (surface 2) for various initial surface potential combinations assuming constant potential (solid lines) or constant charge density (dashed lines) boundary conditions for both surfaces. $\psi_1 = -20$ mv, $a = 0.25$ μm, $\varepsilon = 80$ (H$_2$O).
Such values have been extensively tabulated by Devereau and deBruyn (32) for the interaction of two plates at constant potential for surface potentials up to 250 mv. Hogg et al. (25) have used these tabulated results in the integration required by Derjaguin's method to obtain the interaction energy of dissimilar spheres at high potentials. They found that their analytical expression (from which Eq. [2.1] was derived) gave a reasonably good estimate of the energy for surface potentials as high as 50-70 mv. Numerical and approximate analytical methods for obtaining interaction energies for dissimilar surfaces at even higher potentials have been reviewed by Bell et al. (28) for the constant potential boundary condition and by Bell and Peterson (33) for the constant charge density case.

2.1.1.2 London-van der Waals Interaction

The idea of an attractive force between two neutral atoms was introduced by van der Waals in 1873 to explain the properties of non-ideal gases and liquids. But it was not until 1930, after the advent of quantum mechanics, that London was able to place this attraction on a sound theoretical foundation. The London-van der Waals force arises from the rapidly fluctuating dipole moment generated in a neutral atom by the motion of electrons around its nuclei. The electric field of this instantaneous dipole polarizes a nearby neutral atom and the returning field of the induced dipole - the reflected or reaction field - then interacts with the first atom resulting in an attractive force between them. London showed that the energy of attraction between two atoms varies inversely as the sixth power of their distance of separation, and is (to a first approximation) independent of the interaction with other atoms. Thus, because these attractive forces are additive,
the total interaction energy between two condensed bodies consisting of aggregates of atoms or molecules can be determined simply by summing the contributions of all interacting pairs. In this way, Hamaker (5) obtained the van der Waals attraction energy, $\phi_{\text{vdw}}$, for the interaction of a number of geometrically simple bodies, including the following expression for the sphere-plate system:

$$
\phi_{\text{vdw}} = -\frac{A}{6} \frac{2a(h+a)}{h(h+2a)} + \ln \left( \frac{h}{h+2a} \right)
$$

[2.9]

where $A$ is the Hamaker constant. It should be noted that this attraction decays comparatively slowly with increasing distance, a property which explains the long-range character of these forces.

Eq. [2.9] only applies at very small distances of separation ($h \rightarrow 0$) and even then only as a first approximation for bodies whose thicknesses exceed molecular dimensions. The London picture of the attractive force between two Bohr atoms is valid as long as the time taken for the field to travel from the first atom to the second and back is small compared to the time taken for the electron to rotate around the nucleus. As the separation increases, the correlation of the two interacting dipoles becomes retarded and hence, the attractive force is less than that predicted by London. The effect of retardation was worked out by Casimir and Polder (34). They found that for distances of separation $h \ll \frac{\lambda}{2\pi}$, where $\lambda$ is the wavelength characteristic of the atom dipole fluctuations, the energy of interaction between two atoms decreased as $1/h^6$ as before but for large separations, $h \gg \frac{\lambda}{2\pi}$, it decreased as $1/h^7$. If $\phi^{a-a}$ is the interaction energy between two atoms as given by London, then the retarded energy, $\phi^{a-a}_{\text{ret}}$, can be given in terms of $\phi^{a-a}$ and a correction function, $f(p)$, as follows
\[ \phi_{\text{ret}} = \phi_{\text{ret}} \cdot f(p) \]  

where \( p = \frac{2\pi h}{\lambda} \). By fitting the results of Casimir and Polder, Overbeek (35) gives the following approximate expressions for \( f(p) \):

\[
 f(p) = \begin{cases} 
 1.01 - 0.14p & \text{if } p < 3 \\
 2.45/p - 2.04/p^2 & \text{if } p \geq 3 
\end{cases}
\]  

Recently, Clayfield et al. (36) have repeated Hamaker's calculations using Eq. [2.10] with Eq. [2.11] to represent the atom-pair interaction and derive the following expression for the sphere-plate case:

\[ \phi_{\text{vdw}} = -2A I_{s-p} \]  

where for \( h > \rho \)

\[
 I_{s-p} = I_1 = \frac{a^3}{15h^2(h+2a)^2} \left[ D - \frac{2E(h+a)}{3h(h+2a)} \right]
\]  

for \( h + 2a > \rho > h \)

\[
 I_{s-p} = I_1 + \frac{\rho'}{12} \left( 4a - \rho' \right) \left[ -\frac{B}{4\rho^4} + \frac{C}{3\rho^3} + \frac{D}{5\rho^5} - \frac{E}{6\rho^6} \right] \\
 + \rho^2 \left[ a - \frac{\rho'}{3} \right] \left[ -\frac{B}{12\rho^4} + \frac{C}{6\rho^2} + \frac{D}{20\rho^6} - \frac{E}{30\rho^8} \right] \\
 + \frac{B}{12} \left[ -\ln \left( \frac{\rho}{h} \right) + \frac{\rho'}{h \rho^2} \left( h^2 + \frac{3h \rho'}{2} + a \rho' \right) \right]
\]
\[
\begin{align*}
&+ \frac{C}{6} \left[ -2(a+h) \ln \left( \frac{\rho}{h} \right) + \rho' + \frac{(2a+h)\rho'}{\rho} \right] \\
&+ \frac{D}{60} \frac{\rho'^2}{h^3 \rho^3} \left[ h(\rho' - 3a) - a\rho' \right] \\
&+ \frac{E \rho'^2}{360 h^3 \rho^3} \left[ h^2(12a - 4\rho') + h \rho'(8a - \rho') + 2a\rho'^2 \right]
\end{align*}
\]

for \( \rho > h+2a \)

\[
I_{s-p} = 4a^3(\rho'-a) \left[ - \frac{B}{4\rho^4} + \frac{C}{3\rho^3} + \frac{D}{5\rho^5} - \frac{E}{6\rho^6} \right] \\
\quad \quad + \frac{4a^3}{3} \left[ - \frac{B}{12\rho^3} + \frac{C}{6\rho^3} + \frac{D}{20\rho^4} - \frac{E}{30\rho^5} \right] \\
\quad \quad + \frac{B}{12} \left[ - \ln \left( \frac{h+2a}{h} \right) + \frac{2a}{h} (a+h) \right] \\
\quad \quad + \frac{C}{3} \left[ 2a - (a+h) \ln \left( \frac{h+2a}{h} \right) \right]
\]

where: \( \rho = 3\lambda/2\pi \) , \( \rho' = \rho - h \)

\( B = 1.01 \) , \( C = 0.14(2\pi/\lambda) \)

\( D = 2.45 \lambda/2\pi \) , \( E = 2.04(\lambda/2\pi)^2 \)

The frequency of electronic fluctuations in atoms is of the order of \( 10^{15} \) to \( 10^{16} \) per second and hence \( \lambda \) may range from 300 to 3000 Å. Overbeek (35) recommends a value of \( \lambda = 1000 \) Å for most materials. Figure 2.3 demonstrates
how the Hamaker interaction is weakened by retardation effects as a function of the separation distance and for the range of $\lambda$-values suggested above. It should be noted that for the interaction of macroscopic particles with thick plates, the attraction between some of the molecular pairs will always be retarded and hence, strictly speaking, Eq. [2.9] is never valid, even when the two bodies are in contact. This fact is frequently overlooked by many colloid scientists, who assume that Hamaker's equations for macroscopic bodies can be used for separations $h < \frac{\lambda}{2\pi}$, a condition that, strictly speaking, only applies to interactions between atoms or molecules.

Thus, if it can be assumed that the interactions between individual molecules embedded in macroscopic bodies are additive, then Eq. [2.12] provides the correct relationship with distance for the overall interaction between a sphere and a plate. However, in order to estimate the interaction energy for a real situation, it is still necessary to specify a value for $A$, the Hamaker constant. For the interaction of a particle (material 1) with a flat plate (material 2) in an aqueous medium (material 3), the "effective" Hamaker constant is given by (5)

$$A = \frac{1}{\varepsilon_{\lambda}} \left( A_{12} - A_{13} - A_{23} + A_{33} \right) \quad [2.13]$$

where $A_{ij}$ is the Hamaker constant for the interaction of material $i$ with material $j$ in a vacuum. The influence of the medium on the transmission of the London forces must be accounted for by dividing by $\varepsilon_{\lambda}$, the dielectric constant of the medium at a frequency which is characteristic for the system (35). Thus, Eq. [2.13] really only applies when the characteristic wavelength of each of the materials involved is approximately the same. The various methods of calculating the $A_{ij}$ from optical dispersion data have
Figure 2.3. Retardation of London-van der Waals interaction energy for a sphere and a plate as a function of separation distance $h$ and characteristic wavelength $\lambda$. 
been reviewed by Gregory (37) and more recently by Visser (38). For those materials for which the necessary optical data are available, the predictive methods yield a range of $A_{ij}$ values. Thus, application of Eq. [2.13] will yield at best only a very approximate estimate of the Hamaker constant. Experimentally determined values of $A$, particularly in liquid media, are also not very reliable. For example, two carefully conducted coagulation studies (39,40) using polystyrene latices as a model colloid resulted in a range of values of $A$ for polystyrene in water of $1.0 \times 10^{-14} - 1.5 \times 10^{-13}$ ergs.

Aside from the difficulty in specifying the Hamaker constant, the Hamaker approach to calculating van der Waals forces using the assumption of pairwise additivity of individual interatomic interactions has fallen on strong criticism. Although this assumption may be valid for dilute gases, it is intrinsically unsound for condensed systems. Lifshitz (7) has developed a physically more satisfactory approach for calculating the interaction energy between condensed bodies. He derived expressions for the interaction between two infinite parallel plates of different materials placed in a vacuum by treating them as continua and assuming that the attraction was due to a fluctuating electromagnetic field in the gap, arising from all electric and magnetic polarizations within the two plates. Thus the van der Waals interaction energy including retardation effects could be determined explicitly just from consideration of the bulk properties of the materials, namely, the optical characteristics of each material with respect to the whole electromagnetic spectrum. The theory of Lifshitz has been generalized by Dzyaloshinskii et al. (41) to take into account the presence of a dielectric medium between the two plates.
Owing to the mathematical complexity of the continuum theory, results for other body shapes are not easy to obtain. Mitchell and Ninham (42) developed an infinite set of linear equations for which they derived asymptotic approximations that are exact at the limits of contact and infinite separation between two identical spheres. The same problem has been treated by Smith et al. (43) using numerical methods. Recently, Langbein (44) has derived an expression for the energy of interaction between two dissimilar spheres (of which the sphere-plate geometry is a special case) in terms of a multiply-infinite series which in principle is exact but in practise is extremely difficult to evaluate. Even if a more tractable expression for the sphere-plate case were available, the evaluation of the van der Waals energy still requires the complete optical spectra over all wavelengths for all the materials of interest. Unfortunately these data are not available for at least two of the materials used in the experiments to be described. Thus the retarded Hamaker Equation [2.12] will be used here to represent the van der Waals interaction. It is somewhat comforting to note that for parallel plates, the Lifshitz theory and the retarded Hamaker theory as worked out by Overbeek (35) give the same distance relationship for the energy at both small and large separations.

2.1.1.3 Viscous Interaction

When a particle moves relative to a continuous medium, either by virtue of an applied force or because of Brownian motion, its movement is retarded by friction created by the viscosity of the medium. For submicron spherical particles in an infinite liquid, the coefficient of dynamic friction, \( f \), is given by Stokes' Law as
\[ f = 6\pi\mu a \]  

[2.14]

where \( \mu \) is the bulk viscosity of the medium. However, when a similar immersed sphere approaches a plane solid surface, it experiences an increased resistance to motion because the friction between the fluid and the wall increases the force required to push the fluid out of its path. Thus, in the vicinity of the planar surface, this "viscous interaction" between the particle and the wall requires that the expression for the Stokes' friction coefficient be rewritten as

\[ f = 6\pi\mu a\alpha \]  

[2.15]

where \( \alpha \), the Stokes' Law correction factor, is given by Brenner (45) as

\[
\alpha(h) = \frac{4}{3} \sinh \Omega \sum_{n=1}^{\infty} \frac{n(n+1)}{(2n-1)(2n+3)} \left[ \frac{2 \sinh(2n+1)\Omega + (2n+1)\sinh^2\Omega}{4 \sinh^2(n+\frac{1}{2})\Omega - (2n+1)^2 \sinh^2\Omega} \right] - 1 
\]  

[2.16]

where \( \Omega = \cosh^{-1}\left(\frac{h+a}{a}\right) \)

The Brownian diffusion coefficient, \( D \), of the particle is given by the Stokes-Einstein equation (46)

\[ D = \frac{kT}{f} \]  

[2.17]

Thus, at small separations, the viscous interaction between the particle and the wall also affects the diffusion coefficient which must be rewritten as

\[ D = D_\infty / \alpha \]  

[2.18]
where $D_\infty$ is the diffusion coefficient in the bulk fluid where Stokes' Law applies. Thus, the viscous interaction manifests itself through the friction coefficient and thereby, through the coefficient of Brownian diffusion.

2.1.1.4 Other Forces

As well as the three already discussed, there are other forces present which may also affect the deposition process. Most of these act in a direction perpendicular to the channel walls. Included in this group are the Born repulsion force between the electron clouds of interacting molecules, the "steric" forces due to the presence of adsorbed layers of ordered water molecules, and a "lift" force caused by the action of fluid shear on the particle. In addition, the fluid motion creates a "drag" force on the particle which tends to carry it in a direction parallel to the deposition surface.

Born repulsion is a short-range molecular interaction resulting from the overlap of the electron clouds surrounding individual molecules on the two approaching surfaces. London (47) has shown, by invoking the Pauli exclusion principle, that the Born repulsion energy between two interacting molecules or atoms has a $1/h^{12}$ dependence on the distance of separation. However, the correct extension of these results to macroscopic bodies has not been carried out because of the extreme difficulties encountered. Whereas the London-van der Waals forces are sufficiently long-range that the separated surfaces may be treated as being homogeneous and flat, the Born forces are too short-range to permit these simplifications. Thus, a meaningful theory must account for the extreme heterogeneity of geometry and energy presented by both interacting surfaces.
Although the Born forces cannot be accounted for in a quantitative way, their qualitative inclusion in the analysis leads to an important result. At very small distances of separation, the overall interaction energy, as will be demonstrated, is dominated by the London-van der Waals attraction. When Born effects are not included, this attraction energy assumes an infinitely large negative value as \( h \) approaches zero. Under these conditions, a particle which manages to adhere to a wall is irreversibly removed from the suspension. The effect of the Born repulsion is to determine the closest distance of approach, \( h_0 \), between the two surfaces. Since the interaction energy is finite for all \( h > 0 \), it is therefore theoretically possible for a particle bound to the plane surface at \( h_0 \) to diffuse back into the suspension. Thus, inclusion of the Born repulsion leads to the possibility of particle release. Frens and Overbeek (48) have used this concept to explain the redispersal of coagulated suspensions when conditions are altered to increase the double layer repulsion.

It has been reported (49,50) that silica sols demonstrate an anomalous resistance to coagulation, their stability extending into regions of electrolyte concentration and pH where the DLVO theory predicts coagulation should take place. The degree of anomalousness increases with decreasing particle size and increasing concentrations of hydroxyl groups on the particle surface as determined by the method of manufacture and the subsequent surface pretreatment. On this basis, Harding (51) attributes this exceptional resistance to coagulation of silica particles to the presence of structured, immobilized water layers on their surfaces. For example, NMR studies by Pearson and Derbyshire (52) suggest that about three monolayers of water molecules may be regarded as being firmly bound to the \( \text{SiO}_2 \) surface. These layers of ordered water on one or both of the interacting surfaces act as a
"steric" barrier, limiting the distance of closest approach of the two bodies. Thus, "steric" factors act in the same way as the Born repulsion forces. They both push the distance of minimum separation, $h_0$, out to a position where the overall interaction is finite. When $h_0$ is of the order of molecular dimensions where the London-van der Waals predominate, it then corresponds to the position of a finite minimum in the potential energy curve at which a deposited particle might escape from the surface by diffusion. However, for surfaces surrounded by many layers of immobilized water, $h_0$ may in fact extend out to distances where the interaction energy is dominated by an electrical double layer repulsion. In this case coagulation or deposition is no longer possible and the suspension is said to be "sterically" stabilized.

An additional force which acts in a direction perpendicular to the bounding walls of a channel is the lift force which arises from the interaction between a solid spherical particle and the rate of shear of the flowing fluid. The first systematic study of its existence was carried out by Segre and Silberberg (53), who observed that small, neutrally bouyant spheres in Poiseuille flow through a tube slowly migrate across streamlines to an equilibrium position 0.6 tube radii distant from the axis. The same observations have more recently been made for the case of Poiseuille flow through parallel-plate channels (54,55). It has also been demonstrated (54,56) that the lift force is enhanced and the equilibrium position changed in vertical channels when the spheres are not neutrally bouyant, i.e. when the particle velocity is significantly different from the undisturbed fluid velocity. For more dense particles in a downflow (or less dense particles in an upflow), increasing the density difference shifts the equilibrium position further away from the axis and eventually to the channel walls.
For the reverse situation(s), increasing the density difference shifts the equilibrium position towards the centre-line.

In the attempt to obtain a theoretical interpretation of these results, it was early recognized (57) that no sideways force on a single rigid spherical particle can be derived on the basis of the creeping flow equations, even in the presence of bounding walls. A transverse lift force can only exist theoretically if fluid inertial effects are taken into account. Thus, Cox and Brenner (58) have derived expressions for the inertia-induced migration velocity of a sphere in a general channel flow by making a double expansion of the flow field in terms of two small-valued parameters, the particle Reynolds number and the ratio of the particle radius to the characteristic channel width. Their results, however, are not given explicitly, but instead are left in a form involving very complex volume integrals. Recently, Vasseur and Cox (59) have succeeded in numerically evaluating these volume integrals for the case of neutrally and non-neutrally bouyant spheres in Poiseuille flow through a vertical channel consisting of two parallel plane walls. This simplest of all Poiseuille flows was also investigated by Ho and Leal (60) using the method of reflections, but their analysis is restricted to neutrally buoyant spheres.

For submicron spheres, the restrictions on the particle Reynolds number and the particle to channel size ratio, as required by the perturbation analysis of Cox and Brenner, will generally be met. Thus, it would appear that the results of Vasseur and Cox are applicable to the present study. Unfortunately, this is not the case. To obtain a solution to the equations of fluid motion, their analysis considers the particle to be acting as an isolated point force within the flowing fluid. This assumption not only requires that the particle be small compared to the size of the channel,
but also that its size be small relative to the distance of separation between the particle and the nearest channel wall, i.e. $h/a \gg 1$. Thus, this solution is not applicable at close distances of approach between the particle and the wall. Unfortunately, it is precisely this region which is of the utmost importance to the study of particle deposition. In fact, as will be shown later, under the experimental conditions used here, almost all of the changes in particle concentration due to deposition take place within a region $h/a \leq 10$. Thus, there is at present no available analysis for estimating the lift force due to fluid shear in the vicinity of a flat wall.

How important is the shear-induced lift force to the deposition process? Since the Reynolds number of submicron spheres is very small, the lift force must also be correspondingly minute. Thus, the flux of particles due to the lateral migration caused by these forces might be considered to be negligible. However, in laminar flow the only other mechanism available for transporting particles across streamlines is diffusion due to Brownian motion. Because the Brownian diffusivities of particles in the size range of 0.1-1.0 μm are also very small, it is quite conceivable that particle transport via shear-induced migration could compete very successfully with Brownian diffusion. Ho and Leal (60) have investigated the relative importance of these two mechanisms for the case of neutrally-bouyant spheres in a parallel-plate channel. They have calculated the final concentration distribution which is established in an infinitely long channel when no deposition takes place. Under these conditions Brownian motion tends to cause a uniform dispersion across the channel, whereas the lateral migration force tends to cause the particles to crowd towards a preferred equilibrium position. On the basis of the parameter, $G = \rho v_m^2 a^4 / 2b k T$, where $\rho$ is the density of the fluid, $v_m$ is the average velocity of the Poiseuille flow, and $b$ is
the half thickness of the channel, they found that for $G \geq 10$, particle transport is inertia controlled and for $G \leq 0.01$, it is diffusion controlled. Typical values of $G$ encountered experimentally in this work range from 0.01 to 0.1. Since the particles used here are non-neutrally bouyant spheres which endure even greater lift forces than their neutrally-bouyant counterparts, it is probable that the shear induced migration force contributes a non-negligible component to the rate of mass transfer in particle deposition. Unfortunately, because a description of this force is not currently available in the region of most importance to particle deposition, its effect will not be included in the analysis to be presented here.

One further condition which must be met before a particle can deposit on the channel wall is that the net adhesive force acting at $h_0$ must exceed the effect of the drag force created by the flowing fluid. Goldman et al. (61) and O'Neill (62) have shown that the drag force exerted on a fixed sphere in contact with a plane in a slow linear shear flow acts parallel to the wall and is 70% greater than the Stokes' Law prediction. The inclusion of any force which has a component perpendicular to the adhesion force immediately leads to a conceptual problem. If the sphere and the wall are perfectly smooth such that they meet at a single point of contact, the transverse component will cause the particle to roll along the surface regardless of the size of the adhesion force. However, the problem is easily reconciled once it is realized that submicroscopic roughness elements and surface deformations cause a significant increase in the contact area (63). In this case, the influence of forces such as viscous drag can be analyzed by carrying out a torque balance around the downstream point of contact between the particle and the wall.
Unfortunately, there is not yet available a reliable method for predicting the extent of the contact area for a given particle-wall combination. Thus, a different approach is required to determine the importance of the drag force under the present experimental circumstances. If it is assumed that a suspended particle in the vicinity of the wall travels at the same velocity as the fluid streamline which passes through its centre [in fact, the particle lags behind the fluid in this region (61)], it then becomes possible to estimate the kinetic energy imparted to the particle by the flowing fluid. For the range of experimental conditions employed in the present investigation, this contribution was found to vary from $10^{-4}$ to $10^{-2}$ kT. Since this energy is several orders of magnitude smaller than the expected potential energy of attraction at $h_0$ [particle adhesion energies found experimentally for aqueous systems typically range from 10-100 kT (64,65)], it seems very unlikely that viscous drag will be playing a prominent role in the present investigation. A similar argument can be applied to demonstrate that gravitational effects in vertical channels can also be neglected under the present circumstances.

2.1.2 Overall Interaction Energy Curves

The overall potential energy for the interaction between a spherical particle and a planar surface is obtained simply by summation of the separate electrical double layer (Eq. [2.1], [2.3], [2.4] or [2.5]) and London-van der Waals (Eq. [2.12]) energy curves. Were the expressions available, the potential energies due to Born and "steric" repulsion and to inertia-induced lift forces could be similarly superimposed to provide a more complete picture of the overall interaction. As mentioned before, viscous interaction is accounted for hydrodynamically. An examination of the above equations reveals
that total energy curves, derived on the basis of double layer and dispersion interaction forces, are a function of the following parameters: sign and magnitude of the Stern potentials of each surface; double layer thickness, which is in turn controlled by the concentration and valence of the electrolyte (Eq. [2.2]); and the system Hamaker constant, which depends on the materials of the two interacting solids and on the medium separating them (Eq. [2.13]). In addition, they are largely affected by the particular pair of boundary conditions, either constant surface potential or constant surface charge density, which are assumed to apply during the interaction. Figures 2.4-2.7 demonstrate how the overall interaction energy is influenced by all of these factors.

Figure 2.4, for example, shows the effect of altering the surface Stern potential, $\psi_2$, when the values of $\psi_1$, $1/\kappa$ and $A$ are fixed. Eq. [2.1] is used here to represent the double layer interaction. When the Stern potentials of the two surfaces are of opposite sign, the overall interaction energy is everywhere attractive. However, when the two potentials are of the same sign, the potential energy is repulsive everywhere except at very small distances of separation where it is dominated by the London-van der Waals force. In other words, repulsive electrical double layer interactions give rise to the existence of a potential energy barrier which diffusing particles must overcome if they are to deposit on the channel wall. Once a particle has diffused over this potential energy barrier, it falls into a very deep potential well and hence is subsequently restricted from diffusing back, or "releasing," from the wall. It can be seen from Fig. 2.4 that, as the magnitudes of the potentials of two similarly-charged surface increase, the height of the potential barrier also increases, and hence the rate of deposition should decrease.
Figure 2.4. Effect of plate potential on overall interaction energy as a function of separation distance between a sphere and a plate. \( \phi_{edx} \) (Eq. 2.1), \( \psi_1 = -20 \text{ mv}, a = 0.25 \mu\text{m}, \kappa a = 50, \epsilon = 80, A = 5 \times 10^{-14} \text{ergs}, \lambda = 1000 \text{Å}. \)
The effect of a variable double layer thickness \((1/\kappa)\) on the overall energy is illustrated in Fig. 2.5. This figure demonstrates that as the diffuse layers are compressed into the region where the van der Waals energy predominates, the height and thickness of the energy barrier decrease until (at \(\kappa a = 500\)) the barrier disappears altogether. Thus, it is expected that increasing the concentration of electrolyte should result in an enhanced rate of particle deposition. In addition, this effect should be very sensitive to the valence of the counterions (see Eq. [2.2]). At intermediate values of \(\kappa a\) the double layer interaction falls off rapidly enough that the London energy dominates at both small and large separations. Hence, for \(\kappa a = 100\) and 200, the interaction energy curves exhibit the usual maximum but also have a second potential energy minimum at larger distances of separation. If this "secondary minimum" is more than a few \(kT\) units deep, it represents a stable potential well into which particles will readily deposit. However, because the well is only of finite depth, particles collected here are not irreversibly attached to the wall. They could diffuse back into the bulk suspension (favored for \(\kappa a = 100\)) or over the potential barrier to become permanently fixed to the wall (favored for \(\kappa a = 200\)). Thus, deposition into a secondary minimum should be characterized by reversible "release" from the walls. In addition, a change in conditions such as a decrease in the electrolyte concentration, should cause a spontaneous redispersal of all particles held in the secondary minimum.

Figure 2.6 shows the dependence of the overall energy on the system Hamaker constant. The range of A-values chosen represent those typically encountered for solids immersed in aqueous solutions. As A increases, the maximum of the potential energy curve decreases. Hence, it is expected that the rate of deposition will correspondingly increase. Figure 2.7
Figure 2.5. Effect of double layer thickness \(1/\kappa\) on overall interaction energy as a function of separation distance between a sphere and a plate. \(\phi_{\text{ed}}\) (Eq. [2.1]), \(\psi_1 = -20\ \text{mv}, \psi_2 = -10\ \text{mv}, \alpha = 0.25\ \mu\text{m}, \epsilon = 80, A = 5 \times 10^{-14}\ \text{ergs}, \lambda = 1000\ \text{Å}.\)
Figure 2.6. Effect of Hamaker constant $A$ on overall interaction energy as a function of separation distance between a sphere and a plate. $\phi_{edl}$ (Eq. [2.1]), $\psi_1 = \pm 20$ mV, $a = 0.25$ $\mu$m, $\kappa a = 50$, $\varepsilon = 80$, $\lambda = 1000$ Å.
Figure 2.7. Effect of electrostatic boundary conditions on overall interaction energy as a function of separation distance between a sphere and a plate. \( \psi-\psi \) (Eq. [2.1]), \( \sigma-\sigma \) (Eq. [2.3]), \( \psi-\sigma \) (Eq. [2.4]), \( \sigma-\psi \) (Eq. [2.5]), \( \psi_1 = -20 \text{ mv}, \psi_2 = -20 \text{ mv}, a = 0.25 \text{ \mu m}, \kappa a = 50, \varepsilon = 80, A = 5 \times 10^{-14} \text{ ergs}, \lambda = 1000 \text{ Å}. \)
illustrates the effect of altering the boundary conditions of the double layer interaction on the overall energy curve. Under conditions where the diffuse layer parameters and the Hamaker constant are fixed, the constant charge-constant charge boundary condition leads to the largest barrier towards particle deposition and the constant potential-constant potential condition the least.

Thus, examination of the overall energy curves obtained by superimposing the electrical double layer and London-van der Waals interaction energies provides a qualitative interpretation of the effect of the relevant parameters on particle deposition. A quantitative theory for particle deposition in a parallel-plate channel will be derived in the following section.

2.2 Theory of Particle Deposition in a Parallel-Plate Channel

2.2.1 First Order Reaction Approximation

Consider a vertical parallel-plate channel of width $2b$ (Fig. 2.8) through which an incompressible fluid flows with a steady laminar motion.

\[ v = \frac{3}{2} \left( 1 - \frac{y^2}{b^2} \right) v_m \]

\[ x = 0 \]

Figure 2.8. Parallel-Plate Channel. Particle suspension with a fully-developed laminar velocity profile flows from a region where the walls act as perfect reflectors ($x < 0$) to a region where deposition can occur ($x > 0$).
Let $x$ be the distance in the direction of fluid flow parallel to the channel walls and $y$ the distance normal to these walls, which are specified by $y = b$ and $y = -b$; $y = 0$ is the median plane. The velocity profile of the flow is fully established and therefore parabolic. Suspended within the fluid are spherical particles of radius $a$ whose velocity in the direction of flow is assumed to be that of the undisturbed fluid; i.e. the particles are sufficiently fine that gravitational and wall effects can be neglected. $C = C(x,y)$ denotes the particle concentration at any point $x,y$; more precisely, $C(x,y)dV$ is the time average number of particle centres in the volume element $dV$. Maximum suspension concentrations are assumed to be dilute enough that hydrodynamic interactions between particles can be considered negligible.

Up to the position $x = 0$, the walls of the channel act as particle reflectors and hence, for $x \leq 0$, the suspension is homogeneous at the constant concentration $C_0$. Beyond $x = 0$ deposition can occur and the mathematical problem is to find out how the particle concentration distribution $C$ changes subject to convective diffusion in the potential energy field $\phi = \phi(y)$. If it is assumed that diffusion in the $x$-direction can be neglected and also (for the moment) that each particle maintains its terminal drift velocity in the interaction force field, $-d\phi/dy$, then a particle balance over a differential volume in the channel yields the following partial differential equation:

$$
\frac{3}{2} \left( 1 - \frac{y^2}{b^2} \right) v_m \frac{\partial C}{\partial x} = \frac{\partial}{\partial y} \left[ D \frac{\partial C}{\partial y} + C \frac{\partial \phi}{\partial y} \right] \tag{2.19}
$$

Here $v_m$ is the mean or bulk velocity of the fluid. The potential energy $\phi$ between each particle and the channel walls is considered to be the sum of the electrical double layer and the London-van der Waals interaction energies only. For want of a suitable mathematical description, the effects
of Born and "steric" repulsion and of shear-induced lift forces have been excluded from this analysis. The viscous interaction between a particle and a wall is accounted for by using the separation-dependent friction coefficient, \( f \), given by Eq. [2.15]. By substituting for \( f \) from Eq. [2.17], Eq. [2.19] can be rewritten in a more workable form as

\[
\frac{3}{2} \left( 1 - \frac{y^2}{b^2} \right) v_m \frac{\partial C}{\partial x} = \frac{3}{2} \left( 1 - \frac{y^2}{b^2} \right) \frac{\partial}{\partial y} \left[ \frac{\partial C}{\partial y} + \frac{\partial C}{\partial x} \frac{\partial \phi}{\partial y} \right]
\]

Eq. [2.20] is subject to the boundary conditions

\[
C(0,y) = C_0
\]

\[
\left[ \frac{\partial C(x,y)}{\partial y} \right]_{y=0} = C'(x,0) = 0
\]

denoting differentiation with respect to \( y \) by a prime, and

\[
C(x,b-a) = 0
\]

The initial condition, [2.21], signifies that the suspension is homogeneous at the constant concentration \( C_0 \) at \( x = 0 \). The second boundary condition, [2.22], is a symmetry condition about the median plane. The third boundary condition, [2.4], which follows from an examination of the overall potential energy curves, states that all particles that come into contact with the wall (i.e. particles with centres at \( y = b-a \)) are irreversibly removed from the system. The present analysis therefore excludes the possibility of the release of particles previously deposited in either a primary or secondary minimum back into the suspension. Thus, it describes only the initial state
of the deposition process when the number of deposited particles is still small. This restriction is necessary in any event because when the channel wall becomes significantly covered with particles, the deposition environment will become profoundly altered. The inclusion of either particle release or a surface-coverage dependent deposition rate in the analysis leads to a much more complex mathematical problem which is unsteady with respect to time.

Because $\phi$ and $D$ are complicated functions of the space variable $y$, Eq. [2.20] is intractable as it stands. Fortunately, the nature of the physical problem allows simplifying assumptions to be made. As can be seen in Figs. 2.4-2.7, surface interactions are restricted to a region close to the channel wall. The double layer thickness, $\kappa^{-1}$, is a measure of the region of double layer interaction. Viscous and London-van der Waals interactions are significant over separations of the order of the particle radius. Thus, if it is assumed that both the double layer thickness and the particle size are small compared with the channel dimension (i.e., $\kappa b \gg 1$, $b/a \gg 1$), then the velocity and potential energy fields of the above problem can be approximately uncoupled by dividing the flow channel into two regions:

1. a wall region where the convective terms can be neglected, and

2. a core region where the potential energy and viscous interaction terms can be neglected.

The junction of the two regions is located at a distance $y = b-a-\delta$ from the centre-plane of the channel, where $\delta$ is defined to be the closest distance of separation at which all surface interactions can be considered negligible.

Thus, for the wall region (subscript 1), Eq. [2.20] may be written
\[
\frac{\partial}{\partial y} \left[ \frac{D}{kT} \frac{\partial C_1}{\partial y} + \frac{D_C}{kT} \frac{\partial \phi}{\partial y} \right] = 0
\]  

[2.24]

with boundary conditions

\[ C_1 \left( x, b-a \right) = 0 \quad , \quad C_1 \left( x, b-a-\delta \right) = C_\delta (x) \]  

[2.25]

where \( C_\delta (x) \) is the particle concentration at the junction of the two regions.

For the core region (subscript 2), Eq. [2.20] becomes

\[
\frac{3}{2} \left( 1 - \frac{y^2}{b^2} \right) v_m \frac{\partial C_2}{\partial x} = D_\infty \frac{\partial^2 C_2}{\partial y^2}
\]  

[2.26]

with boundary conditions

\[ C_2 \left( 0, y \right) = C_0 \quad , \quad C_2 \left( x, 0 \right) = 0 \]  

[2.27]

and

\[ C_2 \left( x, b-a-\delta \right) = C_\delta (x) \]  

[2.28]

where \( D_\infty \) is the constant particle diffusion coefficient outside the region of viscous interaction. To complete the description of this new problem, the additional condition of equal particle fluxes at the junction of the two regions is required:

\[ J_1 \left( x, b-a-\delta \right) = -D_\infty C_2' \left( x, b-a-\delta \right) \]  

[2.29]

where \( J_1 \) is the particle flux in the wall region.
The differential equation [2.24] for the wall region is easily solved by integrating once, multiplying both sides of the new expression by \( e^{\phi/kT} \), and then integrating a second time. Upon application of the boundary conditions [2.25], the following solution for \( C_1 \) is obtained:

\[
C_1(x,y) = \frac{C_\delta(x) e^{-\phi/kT} \int_0^h \alpha e^{\phi/kT} dh}{\int_0^\delta \alpha e^{\phi/kT} dh}
\]  

[2.30]

where \( h(= b-a-y) \) is the separation distance as before and \( \alpha \), the Stokes' Law correction factor, is given by Eq. [2.16]. The particle flux in the wall region can be expressed as

\[
J_1(x,y) = -\left[ D \frac{\partial C_1}{\partial y} + \frac{DC_1}{kT} \frac{\partial \phi}{\partial y} \right]
\]  

[2.31]

By differentiating Eq. [2.30] and substituting into [2.31], it is found that the flux into the wall region at the junction, \( y = b-a-\delta \), is

\[
J_1(x, b-a-\delta) = \frac{D_\infty C_\delta(x)}{\int_0^\delta \alpha e^{\phi/kT} dh}
\]  

[2.32]

Thus, by substituting Eq. [2.32] into [2.29], the following explicit relationship for \( C_\delta(x) \) may be obtained

\[
C_\delta(x) = -\left[ \int_0^\delta \alpha e^{\phi/kT} dh \right] C_2'(x, b-a-\delta)
\]  

[2.33]
Hence, the third boundary condition for the core region, [2.28], combined with Eq. [2.33] becomes, in terms of fluxes,

\[ D_{\infty} C_2'(x, b-a-\delta) = \frac{-D_{\infty}}{\int_0^\delta \alpha \cdot e^{\phi/kT} \, dh} \cdot C_2(x, b-a-\delta) \quad \text{[2.34]} \]

The integral in Eq. [2.34] is a constant. Thus, when surface interactions are confined to a narrow zone near the channel walls, transfer within this thin layer appears to the core region as a first order reaction at the walls, for which the surface rate constant, \( K_1 \), is given by

\[ K_1 = \frac{D_{\infty}}{\int_0^\delta \alpha \cdot e^{\phi/kT} \, dh} \quad \text{[2.35]} \]

Eq. [2.35] is identical to the expression for the reaction rate constant derived by Ruckenstein and Prieve (10). Under the conditions which permitted the uncoupling of the velocity and potential energy fields of the original problem, [2.20], \( b-a-\delta = b \). Thus the boundary condition for the core region, [2.34], combined with Eq. [2.35], can be approximately rewritten as

\[ D_{\infty} C_2'(x,b) = -K_1 C_2(x,b) \quad \text{[2.36]} \]

A more formal solution to the core region problem would effectively account for the finite size of the particles and the thickness of the wall region by considering a channel whose dimensions had been symmetrically reduced by \( a+\delta \).

To eliminate the complication of specifying the distance \( \delta \) in Eq. [2.34], Spielman and Friedlander (11) suggest the use of an effective wall concentration, \( C_2(x, b-a) \) for the core region. By expanding \( C_2(x,y) \) and
\( C'_2(x,y) \) in a Taylor's series about \( y = b-a \) and neglecting second and higher derivatives of \( C_2 \) with respect to \( y \), Eq. [2.34] can be shown to be equivalent to

\[
D_\infty C'_2(x, b-a) = \frac{-D_\infty}{\int_0^\infty \left[\alpha e^{\phi/kT} - 1\right] dh} \cdot C_2(x, b-a)
\]  \[2.37\]

Because the integral in Eq. [2.37] is also a constant, Spielman and Friedlander's analysis yields the following alternative expression for the surface rate constant:

\[
K_1 = \frac{D_\infty}{\int_0^\infty \left[\alpha e^{\phi/kT} - 1\right] dh}
\]  \[2.38\]

Since \( b/a \gg 1 \), then \( b-a \approx b \), and hence, Eqs. [2.37] and [2.38] also combine to give Eq. [2.36]. In this case, since the wall region thickness \( \delta \) has already been accounted for, a more formal solution need only consider a core region whose overall dimensions have been reduced by one particle diameter.

Because the viscous interaction between the particle and the wall is not accounted for by Spielman and Friedlander, \( \alpha \equiv 1 \) in their analysis. This implies that at large particle-wall separations (\( h \geq \delta \)) for which \( \phi \to 0 \), \( \alpha e^{\phi/kT} \to 1 \) and the upper limit of integration \( \delta \) can be replaced by \( \infty \) in Eq. [2.38]. However, at large \( h \), \( \alpha \to 1 + (9a/8h) + O(h^{-2}) \) (45), and so the integral becomes logarithmically dependent on \( \delta \), diverging as \( \delta \to \infty \). Thus, when hydrodynamic interactions are accounted for, the limit of integration in Eq. [2.38] should not be extended to \( \infty \), and it becomes necessary to evaluate \( \delta \) for each new deposition situation. In fact, the analysis can
only be applied to those situations where it can be shown that the integral in either Eq. [2.35] or [2.38] is insensitive to the value of $\delta$ taken over a reasonable range. Extensive evaluations of these two integrals for a wide range of the relevant parameters, indicate that the above condition is met only when the interaction energy has a repulsive maximum, $\phi_{\text{max}}$, whose height is greater than approximately $5kT$. Under these conditions both Eqs. [2.35] and [2.38] yield closely similar values for the surface reaction rate constant $K_i$. When $\phi_{\text{max}} \leq 5kT$ the complete transport equation [2.19] must be solved. For example, Prieve and Ruckenstein (66) have used numerical methods to obtain solutions of the complete transport equation describing deposition onto a spherical collector in the presence of London-van der Waals and viscous interaction forces.

2.2.1.1 Approximation of $K_i$ for Large Potential Barriers

Since both $\alpha$ and $\phi$ are rather complicated functions of $h$, further analytic reduction of Eq. [2.35] or [2.38] is not generally possible, and hence the integral appearing in each of these equations must be evaluated numerically. However, if the maximum of the potential energy barrier (located at $h_{\text{max}}$) is large relative to the thermal energy of the particles (i.e. $\phi_{\text{max}} \gg kT$), then Ruckenstein and Prieve (10) have shown that the following simplification can be made. Due to this strong inequality, the principle contribution to the integral in either of the foregoing equations arises from a very small region near $h_{\text{max}}$. An approximation for $\phi(h)$ in the vicinity of $h_{\text{max}}$ can be obtained by expanding $\phi$ in a Taylor's series about $h = h_{\text{max}}$. Since $(d\phi/dh)_{h=h_{\text{max}}} = 0$, truncation after the second order term yields
\[ \phi(h) \sim \phi_{\text{max}} - \frac{\gamma}{2}(h - h_{\text{max}})^2 \]  

[2.39]

where \( \gamma = -\left(\frac{\partial^2 \phi}{\partial h^2}\right)_{h=h_{\text{max}}} \)

Because \( \alpha(h) \) is a slowly varying function compared to the exponential term, it is reasonable to replace it by its value \( \alpha_m \) at \( h=h_{\text{max}} \) and assume it is constant around \( h_{\text{max}} \). Combining this approximation with Eq. [2.39] and using the relationship \( \int_0^Z e^{-u^2} du = \frac{\sqrt{\pi}}{2} \text{erf}(z) \), one obtains

\[
\int_0^\delta \alpha e^{\phi/kT} dh = \left(\frac{\pi kT}{2\gamma}\right)^{\frac{1}{2}} \alpha_m e^{\frac{\phi_{\text{max}}}{kT}} \left\{ \text{erf}\left[\frac{\gamma}{2kT}\left(\delta - h_{\text{max}}\right)\right] + \text{erf}\left[\frac{\gamma}{2kT} h_{\text{max}}\right] \right\}
\]

[2.40]

The magnitude of \( \gamma \) is a measure of the sharpness of the maximum in the potential energy curve. It can be demonstrated that when \( \phi_{\text{max}}/kT >> 1 \), then \( \left(\frac{\gamma}{2kT}\right)^{\frac{1}{2}} h_{\text{max}} >> 1 \). Thus since \( \delta >> h_{\text{max}} \), the arguments of both error functions appearing in Eq. [2.40] will be large. When the argument of an error function is greater than \( \sim 2 \), it can be replaced by infinity. Since \( \text{erf}(\infty) = 1 \), Eq. [2.40] becomes

\[
\int_0^\delta \alpha e^{\phi/kT} dh = \left(\frac{\pi kT}{\gamma}\right)^{\frac{1}{2}} \alpha_m e^{\frac{\phi_{\text{max}}}{kT}}
\]

[2.41]

In addition, when \( \phi_{\text{max}} >> kT \), it can also be shown that \( \left(\frac{2\pi kT}{\gamma}\right)^{\frac{1}{2}} \alpha_m e^{\frac{\phi_{\text{max}}}{kT}} >> \delta \). Thus,

\[
\int_0^\delta \left[ \alpha e^{\phi/kT} - 1 \right] dh = \int_0^\delta \alpha e^{\phi/kT} dh - \delta = \left(\frac{2\pi kT}{\gamma}\right)^{\frac{1}{2}} \alpha_m e^{\frac{\phi_{\text{max}}}{kT}}
\]

[2.42]
Thus, when the repulsive energy maximum is sufficiently large, the surface rate constants of Ruckenstein and Prieve (Eq. [2.35]) and Spielman and Friedlander (Eq. [2.38]) can be combined with Eqs. [2.41] and [2.42], respectively, to yield the common expression

$$K_1 = \frac{D_m}{D_m} \left( \frac{\gamma}{2\pi kT} \right)^{\frac{1}{2}} e^{-\phi_{\text{max}}/kT}$$

[2.43]

since $\alpha_m = D_0/D_m$. Under these conditions, the reaction rate constant has the Arrhenius form, where $\phi_{\text{max}}$ is the "activation energy" for deposition and $D_m \left( \frac{\gamma}{2\pi kT} \right)^{\frac{1}{2}}$ is the "frequency factor." This result is not surprising, as the interaction energy profile strongly resembles the plot of energy against "reaction coordinates" used in the theory of rate processes. A comparison of the $K_1$-values obtained from a numerical integration of either Eq. [2.35] or [2.38] and those calculated from Eq. [2.43] show that, over a wide variety of conditions, all three expressions yield the same value for $\phi_{\text{max}} \approx 10 kT$.

2.2.1.2 Effect of Particle Inertia

In deriving the mass transfer equation [2.19] it was necessary to assume that particles experiencing the field of force created by their interaction with the channel walls always travel at their terminal velocities. In other words, it was assumed that the particles are essentially "massless" such that accelerative effects could be ignored. While it is true that the mass of a submicron particle is very small, it is also true, as can be observed from Figs. 2.4-2.7, that for the interaction of similarly-charged double layers, large changes in the interaction force field occur over very small distances. Thus, it is conceivable that particle inertia plays a
non-negligible role in colloid deposition. If the effect of particle inertia is to be included in the problem of particle deposition, the wall region mass transfer equation based on "massless" particles, Eq. [2.24], is no longer valid. Eq. [2.24] must be replaced by the more general diffusion expression, the Fokker-Planck equation, which is valid for rapidly-changing potential energy fields.

Chandrasekhar (67) gives an excellent review of the derivation of the latter differential equation from the statistical theory of Brownian motion and provides a few solved examples of its practical application. One such example considers the escape of harmonically-bound particles over a simplified potential energy barrier which can be represented by a parabolic relationship such as Eq. [2.39]. Thus, the solution which follows below is essentially that given by Chandrasekhar except where modified to account for changes in co-ordinates used and differences in boundary conditions assumed.

Consider the typical potential energy curve depicted in Fig. 2.9. For the one-dimensional, steady-state wall region problem being considered here, the Fokker-Planck equation may be written

\[ \frac{\partial}{\partial h} \left( \frac{\partial \phi}{\partial h} \right) + \frac{\partial}{\partial \delta} \left( \frac{\partial \phi}{\partial \delta} \right) = 0 \]

Figure 2.9. Typical overall interaction energy curve when electrical double layer interaction is sufficiently repulsive.
where $W(x,h,u)dhdu$ is a probability function and is defined as the number of particles per unit area at a separation distance between $h$ and $h+dh$ and with an instantaneous velocity between $u$ and $u + du$ at any longitudinal position $x$, $m$ is the mass of a particle, and

$$\beta(h) = \frac{6\pi u a x(h)}{m} \quad [2.45]$$

Chandrasekhar has shown that when the force on a particle does not change appreciably over distances of the order $\left[\frac{1}{\beta(\frac{m}{kT})}\right]$, Eq. [2.24] (with $y = b-a-h$) can be derived as a special case of Eq. [2.44].

Chandrasekhar proceeds to find a solution to Eq. [2.44] as follows. First, he notes that the Maxwell-Boltzmann distribution, $W = B \cdot \exp\left[-\frac{(mu^2 + \phi)}{2kT}\right]$, satisfies Eq. [2.44]. Here, $B = B(x)$ is a normalization factor which is constant at any given position $x$ in the channel. However, this equilibrium distribution cannot be valid for all values of $h$, for if it were, there would be no net diffusion across the barrier at $h_{\text{max}}$. If this barrier is high enough (i.e. $\phi_{\text{max}} >> kT$), particles in the vicinity of the boundary between the core and wall regions will have sufficient time to establish a balance between the interaction forces and Brownian motion, before their population changes significantly. Thus, it is expected that the Maxwell-Boltzmann distribution will be realized to a high degree of accuracy in the neighbourhood of $\delta' \leq h \leq \delta$. Hence, the required solution should have the form
\[ W = B \cdot F(h,u) \exp \left( -\frac{m \nu^2}{2kT} + \frac{\phi}{kT} \right) \]  

[2.46]

where \( F(h,u) \) is nearly unity in the region \( \delta' \leq h \leq \delta \) and approaches zero for values of \( h \) appreciably less than \( h = h_{\text{max}} \)

\[ \text{i.e.} \quad F(h,u) \approx 1 \quad \delta' \leq h \leq \delta \]

and \( F(h,u) = 0 \quad h << h_{\text{max}} \)

It will be assumed here that \( \phi_{\text{max}} \geq 10 \text{ kT} \) so that in the vicinity of \( h_{\text{max}} \), the interaction energy can be represented by the approximate parabolic expression, Eq. [2.39]. Thus, when \( h - h_{\text{max}} \approx 0 \), the Fokker-Planck equation [2.44] can be rewritten as

\[ u \frac{\partial W}{\partial H} + \gamma H \frac{\partial W}{\partial u} = \beta_m \frac{\partial}{\partial u} \left[ uW + \frac{kT}{m} \frac{\partial W}{\partial u} \right] \]  

[2.47]

where \( \beta_m = \beta(h_{\text{max}}) \), which is assumed to be constant in this region, and

\[ H = h - h_{\text{max}} \]  

[2.48]

The appropriate form for \( W \) valid in the region \( H \approx 0 \) is obtained by substituting Eqs. [2.39] and [2.48] into Eq. [2.46]. Thus,

\[ W = B e^{-\frac{\phi_{\text{max}}}{kT}} F(H,u) \exp \left( -\frac{m \nu^2}{2kT} - \frac{\gamma H^2}{2kT} \right) \]  

[2.49]

Substitution of Eq. [2.49] into Eq. [2.47] yields the following differential equation for \( F(H,u) \)

\[ u \frac{\partial F}{\partial H} + \gamma H \frac{\partial F}{\partial u} = \beta_m \left[ \frac{kT}{m} \frac{\partial^2 F}{\partial u^2} - u \frac{\partial F}{\partial u} \right] \]  

[2.50]
which must satisfy the boundary conditions

\[ F(H, u) \to 1 \quad \text{as} \quad H \to \infty \]
\[ F(H, u) \to 0 \quad \text{as} \quad H \to -\infty \]  \[\text{(2.51)}\]

Following Chandrasekhar, the solution to this boundary-value problem can be shown to be

\[ F(H, u) = \left( \frac{P - \beta_m}{2\pi q} \right)^{\frac{1}{2}} \int_{\xi}^{\infty} \exp \left[ - \left( \frac{P - \beta_m}{2q} \right) \xi^2 \right] d\xi \]
\[ = \frac{1}{2} \left\{ 1 - \text{erf} \left[ \left( \frac{P - \beta_m}{2q} \right)^{\frac{1}{2}} \xi \right] \right\} \]  \[\text{(2.52)}\]

where

\[ p = \frac{\beta_m}{2} + \left( \frac{\beta_m^2}{4} + \frac{\gamma}{m} \right)^{\frac{1}{2}} \]
\[ q = \frac{\beta_m kT}{m} \]
\[ \xi = u - pH \]  \[\text{(2.53)}\]

Eq. [2.52] satisfies the conditions \( F \to 1 \) as \( \xi \to -\infty \) (\( H \to \infty \)) and \( F \to 0 \) as \( \xi \to \infty \) (\( H \to -\infty \)). Combining Eqs. [2.52] and [2.49] yields the solution for \( W(H, u) \) in the region near \( h_{\text{max}} \) (\( H \sim 0 \))

\[ W = \frac{B}{2} \left\{ 1 - \text{erf} \left[ \left( \frac{P - \beta_m}{2q} \right)^{\frac{1}{2}} \xi \right] \right\} + \frac{\phi_{\text{max}}}{kT} \exp \left[ - \left( \frac{mu^2}{2kT} - \frac{\gamma H^2}{2kT} \right) \right] \]  \[\text{(2.54)}\]

In the region \( \delta' < h < \delta \), a Maxwell-Boltzmann distribution is obtained, and hence
\[ W = B \exp \left[ -\frac{\mu u^2}{2kT} - \frac{\phi}{kT} \right] \]  \hspace{1cm} \text{[2.55]}

Integration of Eq. [2.55] over all values of \( u \) yields \( W^*(h)dh \), the number of particles per unit area between \( h \) and \( h + dh \). Therefore,

\[
W^*(h)dh = \int_{-\infty}^{\infty} W(h,u)dhdu
= B \left( \frac{2\pi kT}{m} \right)^{\frac{1}{2}} e^{-\frac{\phi}{kT}} dh
\]  \hspace{1cm} \text{[2.56]}

Thus, by definition, \( W^*(h) \equiv C_1(x, b-a-h) \), the number of particles per unit volume at any position \( h(\delta' \leq h \leq \delta) \). At \( h = \delta, \phi = 0 \) and \( C_1(x, b-a-\delta) = C_0(x) \) (Eq. [2.25]). Substitution of these quantities into Eq. [2.56] yields the following expression for the normalization constant \( B \):

\[
B = \left( \frac{m}{2\pi kT} \right)^{\frac{1}{2}} C_0(x)
\]  \hspace{1cm} \text{[2.57]}

Thus, the final expression for \( W \) valid in the neighbourhood near \( h_{\text{max}} \), obtained by combining Eqs. [2.54] and [2.57], is

\[
W = \left( \frac{m}{8nkT} \right)^{\frac{1}{2}} \left\{ 1 - \text{erf} \left[ (p - \beta \frac{m}{2q})^{\frac{1}{2}} \xi \right] \right\} - \frac{\phi_{\text{max}}}{kT} \exp \left[ -\frac{\mu u^2}{2kT} + \frac{\gamma H^2}{2kT} \right] C_0(x)
\]  \hspace{1cm} \text{[2.58]}

The particle flux in the wall region, \( J_1(x,y) = -J_1(x,h) = -J_1(x,H) \), which is constant for all \( h \), is evaluated at \( h = h_{\text{max}} \) using the relationship

\[
J_1(x,y) = -\int_{-\infty}^{\infty} W(x, H=0, u)du
\]  \hspace{1cm} \text{[2.59]}
Substituting Eq. [2.58] into Eq. [2.59] and integrating by parts yields

\[
J_1(x, y) = \left(\frac{kT}{2\pi m}\right)^\frac{1}{2} \left(\frac{p - \frac{\beta_m}{\beta}}{p}\right)^\frac{1}{2} e^{-\frac{\phi_{\text{max}}}{kT}} C_\delta(x)
\]

\[
= \left(\frac{kT}{2\pi m}\right)^\frac{1}{2} \left[\left(1 + \frac{4\gamma}{m\beta_m^2}\right)^\frac{1}{2} - 1\right] - \frac{\phi_{\text{max}}}{kT} C_\delta(x)
\]  

[2.60]

after substituting for \( p \) according to Eq. [2.53]. Upon multiplying the numerator and denominator of Eq. [2.60] by \( \left(1 + \frac{4\gamma}{m\beta_m^2}\right)^\frac{1}{2} - 1 \), the following simplification results

\[
J_1(x, y) = \left(\frac{kT}{2\pi m}\right)^\frac{1}{2} \left(\frac{m\beta_m^2}{4\gamma}\right)^\frac{1}{2} \left[\left(1 + \frac{4\gamma}{m\beta_m^2}\right)^\frac{1}{2} - 1\right] - \frac{\phi_{\text{max}}}{kT} C_\delta(x)
\]  

[2.61]

By comparison with Eqs. [2.32] and [2.35], the reaction rate constant, \( K_1 \), for the case where particle inertia is not neglected can be written immediately as

\[
K_1 = \left(\frac{kT}{2\pi m}\right)^\frac{1}{2} \left(\frac{m\beta_m^2}{4\gamma}\right)^\frac{1}{2} \left[\left(1 + \frac{4\gamma}{m\beta_m^2}\right)^\frac{1}{2} - 1\right] - \frac{\phi_{\text{max}}}{kT} C_\delta(x)
\]  

[2.62]

If \( \frac{4\gamma}{m\beta_m^2} \ll 1 \), the approximation \((1 + z)^\frac{1}{2} \approx 1 + \frac{z}{2} - \frac{z^2}{8} + \cdots \) can be used to show that Eq. [2.62] reduces to

\[
K_1 = \frac{kT}{m\beta_m} \left(2\pi kT\right)^\frac{1}{2} \frac{\phi_{\text{max}}}{kT}
\]

and hence, via Eqs. [2.45], [2.15], and [2.17], to
which is identical to Eq. [2.43] derived earlier for the case where particle inertia was neglected. Thus Eq. [2.62] provides the precise condition for the approximate validity of Eq. [2.63]. Since $\frac{4y}{m^2} = \frac{4\eta}{f^2}$, where $f = 6\pi \mu a$, a greater particle mass, a sharper energy barrier, or a smaller Stokes' friction coefficient are all factors which tend to make particle inertia a more important consideration, as might be expected. As particle inertia becomes more important, Eq. [2.62] indicates that the surface reaction rate constant and hence the rate of deposition of particles onto the channel wall will increase. Thus, the effect of inertia is to help particles surmount the potential energy barrier and thereby improve their probability of arriving at the wall.

In summary, it has been shown in this section that when $Kb \gg 1$ and $b/a \gg 1$, the problem of particle deposition in a parallel-plate channel with surface interactions resulting in a potential energy maximum, $\phi_{\max} > 5kT$, is reduced to the convective-diffusion problem [2.26] and [2.27] in the core with a first order reaction boundary condition [2.36] at the walls. From knowledge of the specific interactions leading to the repulsive maximum, the reaction rate constant, $K_1$, can be evaluated by integrating either Eq. [2.35] or [2.38]. Both expressions yield the same value when $\phi_{\max} > 5kT$. When $\phi_{\max} > 10kT$, the potential energy barrier can be approximated by a parabolic equation. Under these conditions both Eqs. [2.35] and [2.38] can be integrated analytically to yield Eq. [2.43]. In deriving Eqs. [2.35] and [2.38] from the solution of the wall region problem, it was necessary to assume that the inertia of the particles undergoing Brownian motion was
negligible. When inertia is accounted for, the more complex differential equation \[2.44\] for the wall region must be solved. This solution, carried out only for the case of a parabolic energy barrier (i.e. \(\phi_{\text{max}} \geq 10 kT\)), yields Eq. \[2.62\] for the surface reaction rate constant. Equation \[2.43\] is a special case of Eq. \[2.62\]. The solution of the core-region boundary-value problem is considered in the next section.

2.2.2 Solution to Core Region Problem

In dimensionless terms, the convective-diffusion equation \[2.26\] and corresponding boundary conditions, \[2.27\] and \[2.36\], for the core region can be rewritten

\[
\left(1 - \eta^2\right) \frac{\partial \theta}{\partial \eta} = \frac{\partial^2 \theta}{\partial \eta^2} \tag{2.64}
\]

with

\[
\theta(0, \eta) = 1 \tag{2.65}
\]
\[
\theta'(\gamma, 0) = 1 \tag{2.66}
\]
\[
\theta(\gamma, 1) + \frac{1}{K} \theta'(\gamma, 1) = 0 \tag{2.67}
\]

where \(\theta = \theta(\gamma, \eta) = C_2/C_0\), \(K = bK_1/D_\infty\), \(\eta = y/b\), and if \(Pe = \frac{4v_m b}{D_\infty}\) is the Peclet number, \(\gamma = (1/Pe)(8x/3b)\). In this section the prime denotes differentiation with respect to \(\eta\).

When the dimensionless reaction rate constant \(K = \infty\), the infinite sink wall condition results. Under these circumstances, the differential equation \[2.64\] and its accompanying boundary conditions constitute the classical "Graetz problem," named after the mathematician who originally examined the analogous problem of heat transfer in a channel with a constant wall temperature. The Graetz problem has been extensively invesigated in
the literature, and the results are well summarized by Drew (68), Jakob (69), and Sellars et al. (70).

When $K \neq \infty$, corresponding to the case where surface interactions affect the progress of particle deposition, the "extended Graetz problem" which ensues has also been treated in the literature. Sideman et al. (71) gave a solution to the analogous problem of heat transfer with constant wall resistance, and Colton et al. (72) dealt with the corresponding situation of mass transfer in a parallel plate duct formed from two semi-permeable membranes.

By separation of variables, the solution to Eq. [2.64] may be written as

$$\theta(\gamma, \eta) = \sum_{n=1}^{\infty} Y_n(\eta) e^{-\lambda_n^2 \gamma}$$

[2.68]

where $Y_n(\eta)$ and $\lambda_n$ are the eigenfunctions and corresponding eigenvalues, respectively, of

$$\frac{d^2 Y}{d \eta^2} + \lambda^2 \left( 1 - \eta^2 \right) Y = 0$$

[2.64]

with boundary conditions

$$Y'(0) = 0$$

[2.70]

$$Y(1) + \frac{1}{K} Y'(1) = 0$$

[2.71]

Because their Brownian diffusivities are very small, colloidal particles are characterized by large Peclet numbers. Hence, commonly encountered values of the dimensionless longitudinal distance $\gamma$, which is
inversely proportional to Pe, are correspondingly small. The convergence of the series solution [2.68] is slowest when $\gamma \to 0$. Thus, for colloid systems, many terms of Eq. [2.68] will be required to provide an accurate solution.

Traditionally, the eigenfunction equation [2.69] has been solved by assuming the existence of a simple power series solution in $\eta$ for $Y(\eta)$, eg. (71,72). Substitution of this series in Eq. [2.69] yields a recurrence relationship for its coefficients. Although this series converges, the absolute values of the successive terms (which alternate in sign) go through an extremely large maximum, making it very difficult to evaluate eigenvalues $\lambda_\eta$ and coefficient $D_\eta$ beyond $n = 5$. Recently, Walker and Davies (73) showed that if a solution to Eq. [2.69] is expressed in terms of confluent hypergeometric functions, it then becomes possible to evaluate many more $\lambda_\eta$ and $D_\eta$. The use of confluent hypergeometric functions, proposed some time ago by Lauwerier (74) for differential equations of this type, will be adopted here.

When the transformation, $z = (2\lambda)^{\frac{1}{2}} \eta$, is made, Eq. [2.69] becomes Weber's equation

$$\frac{d^2Y}{dz^2} + \left(\frac{z^2}{4} - \frac{\lambda}{2}\right)Y = 0 \tag{2.72}$$

The general solution in terms of the variable $\eta$ is (75, p. 686)

$$Y(\eta) = A_1 e^{-\frac{\lambda \eta^2}{2}} M\left(\frac{1-\lambda}{4}, \frac{1}{2}, \lambda \eta^2\right)$$

$$+ A_2 (2\lambda)^{\frac{1}{2}} \eta e^{-\frac{\lambda \eta^2}{2}} M\left(\frac{3-\lambda}{4}, \frac{3}{2}, \lambda \eta^2\right) \tag{2.73}$$

where $A_1$ and $A_2$ are arbitrary constants and $M(a,b,x)$ is a confluent hypergeometric function of the first kind. Slater (76) has written an excellent
treatise on this function and its properties. Using the relationships
\[
\frac{d}{dx} M\left(a, b, x\right) = \frac{a}{b} M\left(a+1, b+1, x\right)
\]
and
\[
M\left(a, b, 0\right) = 1
\]
it is easily shown that the first boundary condition, Eq. [2.70], implies that \(A_2 = 0\). Thus, if the confluent hypergeometric function is expanded in its infinite series form, the solution to Eq. [2.69] may be written
\[
Y(n) = e^{-\frac{\lambda \eta^2}{2}} \left[ 1 + \sum_{i=1}^{\infty} \frac{(1-\lambda) \cdots (4i-3-\lambda)}{(2i)!} \lambda^i \eta^{2i} \right]
\]
where the constant \(A_1\) is absorbed into the coefficients \(D_n\) in Eq. [2.68].

The eigenvalues are the roots of the second boundary condition [2.71], which reads
\[
F(\lambda) = Y(1) + \frac{1}{K} Y'(1)
\]
\[
= e^{-\frac{\lambda}{2}} \left[ 1 - \frac{\lambda}{K} + \sum_{i=1}^{\infty} \frac{(1-\lambda) \cdots (4i-3-\lambda)}{(2i)!} \lambda^i \left( 1 + \frac{2i-\lambda}{K} \right) \right] = 0
\]
Eq. [2.75] is solved by means of a Newton-Raphson iteration technique. In practise, a good first approximation to any eigenvalue is obtained simply by adding 4 to the previous one. Using this scheme, Eq. [2.75] yields at least 50 eigenvalues before convergence problems begin leading to excessive computing time. This notable improvement in calculating the \(\lambda_n\) (and \(D_n\)), using Eq. [2.74] in place of the conventional power series solution referred
to above, can be attributed to the presence of the exponential term as a separate factor in Eq. [2.74]. When expanded in series form, this exponential term displays oscillatory instabilities similar to those of the conventional series when \( \lambda \) becomes large.

When \( n \gg 50 \), the convergence of \( F(\lambda) \) is unacceptably slow and higher eigenvalues can only be obtained if an asymptotic expansion is used. For the case where \( \lambda \to \infty \), Eq. [2.75] can be written (see Appendix A, Sect. A.2)

\[
F(\lambda) = - \frac{2^{5/6} \pi(1/2)}{3^{2/3} \pi(2/3)} \sin \left( \frac{\lambda \pi}{4} - \frac{5\pi}{12} \right) \lambda^{1/6} 
- \frac{2^{7/6} \pi(1/2)}{3^{4/3} \pi(4/3)} \sin \left( \frac{\lambda \pi}{4} - \frac{\pi}{12} \right) \lambda^{5/6} = 0
\]  

[2.76]

The coefficients, \( D_n \), are found by substituting Eq. [2.68] into the initial condition [2.65] and employing the usual orthogonality relationships. Thus,

\[
D_n = \frac{\int_0^1 (1-n^2) Y_n(n) \, dn}{\int_0^1 (1-n^2) Y_n^2(n) \, dn}
\]  

[2.77]

Sideman et al. (71) have shown that

\[
\int_0^1 (1-n^2) Y_n(n) \, dn = - \frac{1}{\lambda_n^2} Y_n'(1)
\]  

[2.78]

and

\[
\int_0^1 (1-n^2) Y_n^2(n) \, dn = \frac{1}{2\lambda_n} Y_n'(1) \left[ \frac{\partial Y_n(1)}{\partial \lambda} + \frac{1}{K} \frac{\partial Y_n'(1)}{\partial \lambda} \right] \bigg|_{\lambda=\lambda_n}
\]  

[2.79]
Hence,

\[
D_n = -2 \left\{ \lambda_n \left[ \frac{\partial Y_n(1)}{\partial \lambda} + \frac{1}{K} \frac{\partial Y'_n(1)}{\partial \lambda} \right] \right\}^{-1}
\]

\[= -2 \left\{ \lambda_n \left[ \frac{\partial F(\lambda)}{\partial \lambda} \right] \right\}^{-1}
\]

[2.80]

where, from Eq. [2.75]

\[
\frac{\partial F(\lambda)}{\partial \lambda} = e^{\frac{\lambda}{2}} \left[ \frac{1}{2} (\lambda - 1) - \frac{1}{K} \sum_{i=1}^{\infty} \frac{(1-\lambda) \cdots (4i-3-\lambda)}{(2i)!} \right]
\]

\[
\cdot \lambda^i \left[ \frac{1}{\lambda} - \frac{1}{2} - \sum_{j=1}^{i} \frac{1}{4j-3-\lambda} \left( 1 + \frac{2i-\lambda}{K} - \frac{1}{K} \right) \right]
\]

[2.81]

The corresponding asymptotic form easily follows from Eq. [2.76].

The two quantities of practical interest which may now be obtained from the solution are the particle deposition rate and the mean particle concentration as a function of the longitudinal distance down the channel.

In dimensionless terms, the local particle deposition rate, \( J_D \), is given by

\[
J_D(\gamma) = -\theta'(\gamma, \eta) = - \sum_{n=1}^{\infty} D_n \gamma'_n(1) e^{-\lambda_n^2 \gamma}
\]

[2.82]

using Eq. [2.68], where \( Y'_n(1) \) is readily obtained from Eq. [2.74]. For large \( \lambda_n \), the asymptotic form is used (Appendix A, Sect. A.2), namely,

\[
Y'_n(1) = \frac{-2^{7/6} \Gamma(1/2)}{3^{4/3} \Gamma(4/3)} \sin \left\{ \frac{\lambda n \pi}{4} - \frac{\pi}{12} \right\}^{-5/6} \lambda_n
\]

[2.83]
The dimensionless mean concentration, $\theta_m$, is found by integrating the concentration profile over the channel cross section. Hence,

$$\theta_m(\gamma) = \frac{3}{2} \int_0^1 (1-n^2) \theta(\gamma, n) \, dn$$  \hspace{1cm} [2.84]

By substituting Eqs. [2.68] and [2.78] into Eq. [2.84] it can be easily shown that

$$\theta_m(\gamma) = -\frac{3}{2} \sum_{n=1}^{\infty} \frac{D_n}{\lambda_n^2} \left( \frac{Y_n'(1)}{\lambda_n^2} \right) e^{-\lambda_n^2 \gamma}$$  \hspace{1cm} [2.85]

It is noteworthy that the approach adopted here can theoretically yield more accurate solutions than are currently available in the literature for the special case $K = \infty$. The relevant expressions are easily obtained from the above formulas by dropping all terms with $K$ in the denominator. Because of the importance of this case, the exact values for the first 50 $\lambda_n$ and $D_n$, as well as the terms $E_n = -D_n Y_n'(1)$ and $F_n = -\frac{3}{2} D_n Y_n'(1)/\lambda_n^2$ appearing in Eqs. [2.82] and [2.85], respectively, are compiled in Table 2.1.

A computer program for evaluating particle deposition rates and mean particle concentrations as a function of $\gamma$ and $K$ is listed in Appendix D, Sect. D.1. A separate program is required for the special case $K = \infty$. In the computations, the first 50 terms of Eqs. [2.82] and [2.85] are evaluated exactly; additional terms, if required, are found approximately by using the appropriate asymptotic forms. In general, the asymptotic and exact eigenvalues and coefficients are in close agreement in the region $n \sim 50$. For example, for $K = 1.0$ the following exact (vs. asymptotic values) are obtained: $\lambda_{50} = 196.365 \ (196.368)$, $D_{50} = -0.00015233 \ (-0.00015207)$, and $D_{50} Y_{50}'(1) = -0.00035094 \ (-0.00035022)$. As $n$ becomes larger, the
Table 2.1
First Fifty Eigenvalues and Coefficients for $K = \infty$
Parallel-Plate Channel.

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<td>0.3758939</td>
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<td>-0.0047606</td>
<td>0.3477308</td>
<td>0.0000133</td>
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</tbody>
</table>
agreement between each asymptotic and exact term improves, while its contribution to the converged value of the series diminishes. On the basis of this information, it has been estimated that the maximum error which results from using asymptotic forms for $n > 50$ occurs only in the fifth significant figure of the computed quantity of interest. Thus, particle deposition rates and mean concentrations correct to four significant figures can be evaluated, provided a sufficient number of terms in Eqs. [2.82] and [2.85], respectively, are chosen. Table 2.2 indicates the approximate number of terms ($N$) required to yield a solution with four-figure accuracy for various values of $\gamma$ and for all $K$.

Table 2.3 compares values of $J_D$ and $\theta_m$ obtained using the analysis presented here with those computed from other solutions available in the literature for the two cases $K = 1.0$ and $K = \infty$. The table shows, for example, that the solution of Sideman et al. (71) involving five exact terms should only be used to predict values for $\gamma \gtrsim 10^{-2}$. Table 2.2 indicates that the series solutions of Walker and Davies (73) extended to 50 exact terms can be used for $\gamma \gtrsim 10^{-4}$. The analysis presented by Colton et al. (72) provides for the evaluation of any number of terms of which the first five are exact, the remainder being supplied by the first-order asymptotic expansion

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$10^0$</th>
<th>$10^{-1}$</th>
<th>$10^{-2}$</th>
<th>$10^{-3}$</th>
<th>$10^{-4}$</th>
<th>$10^{-5}$</th>
<th>$10^{-6}$</th>
<th>$10^{-7}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>1</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>1000</td>
<td>5000</td>
</tr>
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</table>
### Table 2.3
Comparisons of Deposition Rates and Mean Concentrations in a Parallel Plate Channel

<table>
<thead>
<tr>
<th>K</th>
<th>γ</th>
<th>( J_D )</th>
<th>( \theta_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>( 10^0 )</td>
<td>0.2428</td>
<td>0.2428</td>
</tr>
<tr>
<td></td>
<td>( 10^{-1} )</td>
<td>0.6111</td>
<td>0.6111</td>
</tr>
<tr>
<td></td>
<td>( 10^{-2} )</td>
<td>0.7828</td>
<td>0.7831</td>
</tr>
<tr>
<td></td>
<td>( 10^{-3} )</td>
<td>0.8647</td>
<td>0.8885</td>
</tr>
<tr>
<td></td>
<td>( 10^{-4} )</td>
<td>0.8787</td>
<td>0.9450</td>
</tr>
<tr>
<td></td>
<td>( 10^{-5} )</td>
<td>0.8802</td>
<td>0.9733</td>
</tr>
<tr>
<td></td>
<td>( 10^{-6} )</td>
<td>0.8803</td>
<td>0.9869</td>
</tr>
<tr>
<td></td>
<td>( 10^{-7} )</td>
<td>0.8803</td>
<td>0.9933</td>
</tr>
<tr>
<td>8</td>
<td>( 10^0 )</td>
<td>0.1015</td>
<td>0.1015</td>
</tr>
<tr>
<td></td>
<td>( 10^{-1} )</td>
<td>1.339</td>
<td>1.339</td>
</tr>
<tr>
<td></td>
<td>( 10^{-2} )</td>
<td>3.033</td>
<td>3.041</td>
</tr>
<tr>
<td></td>
<td>( 10^{-3} )</td>
<td>4.954</td>
<td>6.680</td>
</tr>
<tr>
<td></td>
<td>( 10^{-4} )</td>
<td>5.381</td>
<td>14.51</td>
</tr>
<tr>
<td></td>
<td>( 10^{-5} )</td>
<td>5.428</td>
<td>31.38</td>
</tr>
<tr>
<td></td>
<td>( 10^{-6} )</td>
<td>5.433</td>
<td>67.73</td>
</tr>
<tr>
<td></td>
<td>( 10^{-7} )</td>
<td>5.433</td>
<td>146.0</td>
</tr>
</tbody>
</table>
first suggested by Sellars et al. (70) (see Appendix A, Sect. A.2). The close agreement shown in Table 2.3 between the computed results of Colton et al. and those obtained from the present analysis (i.e., Eqs. [2.82] and [2.85]) attests to the fact that the asymptotic forms provide an exceptionally good approximation to the exact forms, particularly for the special case \( K = \infty \). In fact, the present analysis leads to no significant improvement over that of Colton et al. for a parallel-plate channel but, because the former has so many more exact terms, it does demonstrate the accuracy of Colton's results. More importantly, the results obtained here can be used with confidence to determine the range of applicability of the useful approximate solution derived in the section following.

2.2.3 Approximate Solution for Large Peclet Numbers

When the Peclet number is large, the dimensionless longitudinal distance \( \gamma \) is correspondingly small, and hence, many terms of Eqs. [2.82] and [2.85] are required. In this case, simpler approximate forms which are asymptotically correct for small \( \gamma \) can be found.

Small \( \gamma \) corresponds to the entrance region of the channel where the particle concentration boundary layer is still developing. The simplest approximate form is obtained when this boundary layer lies entirely within the region near the wall where the parabolic velocity profile can be replaced by its tangent line at the wall. Thus, if virtually all of the changes in concentration in the direction normal to the wall take place in a region \( h << b \), where \( h = b-a-\gamma \) as before, then the two channel walls are effectively at infinite separation and the problem is reduced to one of particle deposition on a single wall in an infinite medium undergoing a simple shear flow.
To take advantage of the first-order reaction boundary condition, the present analysis requires that the concentration boundary layer thickness exceed the thickness of the wall region and that only particles in the core region be considered. For particles in the core, \( h \geq \delta \), and thus \( h \gg 1 \) and \( h/a \gg 1 \). This means that the approximation becomes valid when \( \gamma \) is small but not zero.

It is convenient to regard \( \theta = \frac{C_2}{C_0} \) as a function of \( \gamma \) and of \( \xi = h/b \). Using the conditions \( a/b \ll \xi \ll 1 \) appropriate to the above approximation, the convective-diffusion problem described by Eqs. [2.64]-[2.67] becomes

\[
2\xi \frac{\partial \theta}{\partial \gamma} = \frac{\partial^2 \theta}{\partial \xi^2}
\]

[2.86]

with the single-wall boundary conditions

\[
\theta(0,\xi) = 1, \quad \theta(\gamma,\infty) = 1
\]

and

\[
\theta(\gamma,0) = \frac{1}{K} \theta'(\gamma,0) = 0
\]

[2.87]

In this section, the prime denotes differentiation with respect to \( \xi \). The problem that results when \( K = \infty \) was first treated by Leveque (77), who found an entrance region solution to the original Graetz heat transfer problem. Colton et al. (72), using a perturbation technique, have given an approximate solution to the above problem which is valid only when the product \( K\gamma^{1/3} \ll 1 \). Leveque's method is extended here to provide a general solution for all \( K \).

By employing the similarity variable, \( X = \left(\frac{2}{9}\gamma\right)^{1/3} \xi \), Eq. [2.86] is transformed to the ordinary differential equation

\[
\frac{d^2 \theta}{dX^2} + 3X \frac{d \theta}{dX} = 0
\]

[2.88]

subject to the boundary conditions
\[ \theta(\infty) = 1 \]

\[ \theta(0) = \left( \frac{2}{1} \right)^{1/3} \left( \frac{d\theta}{dX} \right)_{X=0} = 0 \]  \hspace{1cm} [2.89]

The solution of Eq. [2.88] satisfying the conditions [2.89] is

\[ \theta(X) = \frac{\int_{0}^{X} e^{-u^3} du + \left( \frac{1}{K} \right) \left( \frac{2}{9\gamma} \right)^{1/3}}{\int_{0}^{\infty} e^{-u^3} du + \left( \frac{1}{K} \right) \left( \frac{2}{9\gamma} \right)^{1/3}} \]

or

\[ \theta(\gamma, \xi) = \frac{\int_{0}^{X} e^{-u^3} du + \left( \frac{1}{K} \right) \left( \frac{2}{9\gamma} \right)^{1/3}}{\Gamma(4/3) + \left( \frac{1}{K} \right) \left( \frac{2}{9\gamma} \right)^{1/3}} \]  \hspace{1cm} [2.90]

since

\[ \Gamma(4/3) = \int_{0}^{\infty} e^{-u^3} du \]

Tables of the function \( \int_{0}^{X} e^{-u^3} du \) are given by Abramowitz (78).

The dimensionless particle deposition rate is

\[ J_D(\gamma) = \theta'(\gamma, 0) = \frac{\left( \frac{2}{9\gamma} \right)^{1/3}}{\Gamma(4/3) + \left( \frac{1}{K} \right) \left( \frac{2}{9\gamma} \right)^{1/3}} \]  \hspace{1cm} [2.91]

In this case, the dimensionless mean concentration, \( \theta_m(\gamma) \), is obtained by equating the total number of particles removed from the fluid to the number deposited over the distance \( \gamma \). This yields
\[
\theta_m(\gamma) = 1 - \frac{3}{2} \int_0^\gamma J_D(\gamma) d\gamma 
\]

\[
= 1 - \frac{1}{K^2 \Gamma(4/3)^3} \ln \left[ 1 + \frac{\Gamma(4/3)K}{(2/9 \gamma)^{1/3}} \right] + \frac{1}{K \Gamma(4/3)^2 (2/9)^{1/3}} - \frac{1}{2 \Gamma(4/3)(2/9 \gamma)^{2/3}} \tag{2.92}
\]

For the special case \( K = \infty \), Eqs. [2.90] - [2.92] reduce to those obtained by Leveque (77). Also for this special case, Kennedy (79) has given a higher-order approximation for large Peclet numbers which explicitly accounts for the parabolic nature of the velocity profile. Approximate values of \( J_D \) and \( \theta_m \) obtained from Eqs. [2.91] and [2.92], respectively, are included in Table 2.3 for comparison with their exact (to 4 significant figures) counterparts. As expected, the exact and asymptotic solutions approach each other as \( \gamma \to 0 \).

The range of applicability of the results calculated using the simple approximate expressions [2.91] and [2.92] can be determined by comparison with those computed from the more accurate Eqs. [2.82] and [2.85], respectively. These comparisons have been carried out in Figs. 2.10 and 2.11.

Figure 2.10 shows the dimensionless particle deposition rate \( J_D \) plotted as a function of \( \gamma \), the dimensionless distance from the channel entrance, at various values of \( K \), the dimensionless reaction rate constant. In this plot, as in the subsequent one, the solid lines refer to the results obtained from the modified Graetz solution, which is accurate for all \( \gamma \), whereas the dashed lines represent those obtained from the modified Leveque approximation, which is asymptotically correct when \( \gamma \) becomes small. Figure 2.10 and Table
Figure 2.10. Dimensionless particle deposition rate $J_D$ in a parallel-plate channel as a function of dimensionless longitudinal distance $\gamma$ for various values of dimensionless reaction rate constant $K$. Solid lines refer to the modified Graetz solution and dashed lines to the modified Leveque approximation for small $\gamma$. 
2.3 demonstrate that the approximate Eq. [2.91] provides an adequate estimate of \( J_D \) for \( \gamma < 10^{-3} \) when \( K = \infty \) and for an even wider range of \( \gamma \) as \( K \) decreases.

In the entrance region of the channel, the particle deposition rate decreases with decreasing \( K \) as expected. However, because a high deposition rate corresponds to a high rate of depletion of particles in the suspension, at distances far down the channel, this relation between \( J_D \) and \( K \) is reversed, i.e., \( J_D \) increases as \( K \) decreases. When either \( \gamma \) or \( K \) becomes very small, the dimensionless deposition rate approaches \( K \) as predicted by Eq. [2.91].

In other words, under conditions where the resistance to deposition is sufficiently high the rate of particle deposition is surface reaction controlled. As either \( \gamma \) or \( K \) increases, diffusion in the core region becomes more prominent. In fact, if the ratio of deposition rate to mean concentration were plotted in place of \( J_D \) in Fig. 2.10, the range of surface reaction control for any \( K \) would correspond to the value of \( \gamma \) beyond which the curve would begin to deviate from the horizontal. When \( K = \infty \), surface interactions have no net effect on particle transport and deposition is completely diffusion controlled. This case is equivalent to the classical situation where surface interactions (except for the infinitely deep potential well at zero separation between the particle and wall) are not considered.

Figure 2.11 shows the dependence of the transverse mean particle concentration \( \theta_m \) on \( \gamma \) and \( K \) for the parallel-plate channel. When \( K = 0 \), there exists an infinite potential barrier to particle deposition at the channel wall and thus the mean particle concentration remains constant at the inlet value for all \( \gamma \). For any positive \( K \), \( \theta_m \) diminishes as \( \gamma \) increases, and the decrease in \( \theta_m \) becomes more pronounced with increase in \( K \), which corresponds to a decrease in the surface resistance to particle deposition. This trend continues until the second extreme case \( K = \infty \) is reached. Here, the
Figure 2.11. Dimensionless mean particle concentration $\theta_m$ in a parallel-plate channel as a function of dimensionless longitudinal distance $\gamma$ for various values of dimensionless reaction rate constant $K$. Solid lines refer to the modified Graetz solution and dashed lines to the modified Leveque approximation for small $\gamma$. 
asymptotic approximation, Eq. [2.92], becomes valid when \( \gamma \lesssim 10^{-2} \). An even wider range of \( \gamma \) is covered by this approximation for \( K < \infty \).

In the parallel-plate deposition experiments to be described in the following sections, all values of \( \gamma \) encountered are less than \( \sim 10^{-5} \). Thus, since it has been shown that the approximate expressions [2.91] and [2.92] are suitably accurate in this range, these equations, which can be applied far more easily than the more exact forms, will be used to analyze all of the experimental results obtained here.

Mercer and Mercer (80) have shown that, with an appropriately modified definition of \( \gamma \), the core-region convective-diffusion equation [2.64] also describes the problem of heat and mass transfer between parallel, circular discs. Thus, all of the results obtained here for a parallel-plate channel can also be applied to their situation. In addition, because of the many similarities involved, a complete analysis of the problem of particle deposition in a cylindrical channel is included here as Appendix A, Sect. A.1.
Chapter 3

EXPERIMENT

3.1 Introduction

The factor which has the largest influence on the design of the experiment is the method chosen to measure the rate of particle deposition. A review of the experimental work on particle deposition in channels from flowing fluids reveals the existence of a number of possible techniques.

The most commonly-encountered method is to operate the experiment for a set period of time, then dismantle the channel (or remove a section of the channel) and measure the concentration of residual particles on the collector surface. For example, in their now classic study of aerosol deposition in turbulent flow, Friedlander and Johnstone (81) employed a microscope to obtain surface concentrations. Goldsmith et al. (82) studied the diffusiophoresis and thermophoresis of radioactively-tagged nichrome particles in a collector consisting of two parallel plates covered with removable liners. At the end of each run, the liners were removed and cut into strips for gamma counting. Bartlett and Kabele (83) used a similar technique to investigate the dispersion of radioactive aqueous corrosion products. The main advantage of this discontinuous method is that the accumulation process is essentially "frozen" at the end of the time period, making it possible to obtain an accurate, unambiguous measurement of the local particle concentration at
that time. However, several points on the accumulation curve are required to establish a deposition rate. Thus, at best, the technique makes the gathering of rate information a rather tedious chore, particularly since the deposition conditions must be replicated for each timed segment. At worst, the dismantling and sample preparation steps can lead to the introduction of large uncertainties into each individual measurement.

Of the schemes which allow a continuous measurement of particle deposition, the predominant technique has been to measure the changes in the concentration of suspended particles over the length of a well-defined test section. Examination of Eq. [2.92] suggests that this method is most suited to aerosols (lower fluid viscosities, hence higher particle diffusivities) undergoing very slow flows. Thus, Nolan and Guerrini (84) using an Aitken counter, Thomas (85) using a Tyndallometer, and Chamberlain et al. (86) employing radioactive particles and measuring the activity emitted from filter papers, were able to study the efficiency of Brownian motion as a mechanism for removing fine particles from gas streams. For higher flow rates of more viscous media, collector-size limitations restrict the concentration-change technique to cases where deposition is enhanced by a large applied force. For example, Hiler et al. (87,88) studied the electrophoretic removal of charged colloidal clay particles from water flowing in an applied electric field by measuring changes in the suspension concentration using gravimetry or absorptiometry. Since the presence of surface forces is not expected to result in enhanced deposition but instead, in many cases, to reduced deposition, the concentration-change method will not be sensitive enough to be applicable here. In addition, the technique only allows the evaluation of average deposition rates, whereas it is the local rates that are required to substantiate the derived theory.
The continuous technique which has been used most successfully in studies of particle deposition in liquid media has been to pass a constant heat flux from the channel walls into the flowing fluid and measure changes in resistance to heat transfer with time. The change in thermal resistance from the clean-wall situation, as registered by higher wall temperatures, can then be related to the amount of material accumulated on the surface. The "fouling" of heat exchange surfaces has been investigated in this manner by a number of authors (89,90,91) for a wide variety of fluid-wall combinations. Watkinson (89) has also attempted to measure particle accumulation rates on the walls of small-diameter tubular test sections by measuring pressure-drop changes over the length of the test section using a sensitive differential pressure transducer. The latter technique, however, is not sufficiently responsive under laminar flow conditions. The thermal resistance method can be made quite sensitive if the depositing particles have a very low thermal conductivity. But it shares with the pressure drop measurement a certain ambiguity because it is difficult to assess how much the changing wall roughness contributes to the measured response. In addition, it gives rise to a number of other undesirable effects such as thermophoresis, natural convection, and variable fluid properties, which are not accounted for in the derived theory.

Another possible continuous technique would be to monitor the change in light transmittance due to scattering and absorption by particles which have accumulated on the walls of a transparent (e.g. glass) channel. Marshall (92) attempted to use this method to measure the surface concentration of carbon black particles which had been deposited onto a rotating glass disc. He found, however, that the variation in transmittance through different areas of the glass was as large as the changes caused by the artificially-prepared
deposits. Thus, it was not expected that this technique would be suited to the present application.

A radioactive tracer technique is adopted in this work. The particles are tagged with a radioactive $\gamma$-emitter and their accumulation is measured using a detector which is externally-mounted on the channel wall. Lister et al. (93) have demonstrated the feasibility of this technique in monitoring the accumulation of radioactive corrosion products on the walls of a tubular steel test section. The tracer method offers a means of obtaining a sensitive, unambiguous, and local measurement of surface particle concentration without the need of dismantling the channel. Furthermore, by employing a parallel-plate channel of large aspect ratio, the resolution of very small surface concentrations becomes possible, even when the background due to the suspension is present. Thus, when the rate of deposition is reasonably fast, the technique can be used to provide a continuous measurement of particle accumulation. When the potential energy barrier is sufficiently high that a significant reduction in the deposition rate results, a discontinuous measurement will be required. In this case, the suspension is flushed out of the channel prior to counting.

This radioactive tracer approach, as elaborated in Sect. 3.4, offers the additional advantage of separate deposition and release measurements under the dynamic conditions when both processes are occurring.

3.2 Particles

3.2.1 Introduction

To comply with the assumptions implicit in the derived theory, a model colloidal suspension of dispersed, sub-micron, uniformly-sized, spherical
particles was required. In addition, the radioactive tracer technique chosen for measuring deposition rates made it essential that the particles be tagged with a γ-emitter having an energy >100 kev. and a half-life >50 days. There are no commercially-available particles which meet all of these requirements. Thus, one of the first experimental problems was to develop a means of producing such a colloid system.

A literature search revealed that there are, at present, several organic and inorganic materials which can be prepared as uniform spheres in the size-range of interest. Those reported include polymer latices (94) and particles of elemental selenium (95), chromium hydroxide (96), aluminum hydroxide (97), silica (98), and titania (99). Procedures have already been established for the radioactive tagging of two of these materials. Black and Walsh (100) have described a method of producing radioactive spherical latex particles by the emulsion polymerization of $^{131}I$-labelled 2,4 iodostyrene monomers. However, although the γ-radiation of $^{131}I$ is suitably energetic (365 kev.), its half-life (8.07 days) is too short for the purposes of the present experiment. Flachsbart and Stöber (101) have developed a simple experimental procedure for incorporating radioactive contaminants into spherical silica particles. Because their procedures are applicable to a wide variety of radioactive metal salts, the contaminant selected can be tailored to the needs of the experiment.

It was primarily for this reason that the decision was made to further investigate the possible use of radioactive silica particles as a model colloid. Other reasons for this choice include the fact that silica suspensions are notably stable over a wide range of electrolyte conditions and that the surface chemistry of silica has been extensively studied (102, 103).
It is widely known that amorphous silica can be produced by the chemical reaction of tetra-esters of silicic acid (tetra-alkyl silicates) with water. This reaction has many important commercial applications including use in the binding of refractory and coating materials, in weatherproofing porous surfaces, in binding resins to glass, in the production of silica gels and films, and as a source of finely-divided silica for the paint and rubber industry (104). Due to the immiscibility of water and all alkyl silicates, the reaction must be carried out in a mutual solvent if homogeneous conditions are desired. The hydrolysis is catalyzed by acid or base solutions. Aelion et al. (105) have studied the hydrolysis of tetra-ethyl orthosilicate (TEOS) and have suggested that the overall reaction takes place via two consecutive steps:

i) hydrolysis of ester to silicic acid

\[
\text{Si(OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}
\]

ii) dehydration of silicic acid to form amorphous silica (particles or gel)

\[
\text{Si(OH)}_4 \rightarrow \text{SiO}_2\downarrow + 2\text{H}_2\text{O}
\]

They found that in the presence of hydroxyl ion catalyst and an excess of water both the hydrolysis and dehydration reactions were fast and complete. Under these conditions, the hydrolysis reaction is rate-controlling, the overall rate being first order with respect to the TEOS concentration and proportional to the amount of base present. The authors suggest that the base catalysis involves a nucleophilic displacement of the alkoxy group (C\text{H}_3\text{O}-) by the hydroxyl ion.

Stöber et al. (98) discovered that when the mutual solvent is an alcohol and ammonium hydroxide is used as a catalyst, the reaction between
a number of short-chain tetra-alkyl silicates and water under controlled experimental conditions produces silica spheres having a very narrow size distribution. By changing the alkyl group of either the alkyl silicate or the mutual solvent, they found that uniform particles could be reproducibly manufactured in a range of sizes from 0.05 to 2.0 μm; in general, the longer the alkyl chain, the larger the particles.

Using the production techniques developed by Stöber et al., Flachsbart and Stöber (101) attempted to prepare radioactivity-tagged particles by introducing a number of different isotopes as contaminants into the growing silica spheres. The tracer isotope (metal chloride dissolved in an HCl solution) was added simultaneously with the alkyl silicate to a previously ammoniated solution of water and alcohol. Subsequent leaching tests using acid- and base solutions revealed that, of all the radioactive metals employed, only those which formed precipitable hydroxide compounds in alkaline solutions were completely incorporated into the matrix of the silica particles. The list of successful candidate isotopes, their relevant nuclear properties, and the maximum concentrations with respect to the particle weight achieved by Flachsbart and Stöber is shown in Table 3.1. For fear of influencing the

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (days)</th>
<th>γ-Energy (keV)</th>
<th>Tracer Conc. (μg/g)</th>
<th>Tracer Act. (μCi/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{51}$</td>
<td>27.8</td>
<td>320</td>
<td>.003</td>
<td>0.12</td>
</tr>
<tr>
<td>Ce$^{141}$</td>
<td>32.5</td>
<td>145</td>
<td>.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe$^{59}$</td>
<td>45.1</td>
<td>1099</td>
<td>5</td>
<td>1.9</td>
</tr>
<tr>
<td>Be$^{7}$</td>
<td>53.4</td>
<td>478</td>
<td>.06</td>
<td>2.0</td>
</tr>
<tr>
<td>Sb$^{124}$</td>
<td>60.3</td>
<td>603</td>
<td>9</td>
<td>0.50</td>
</tr>
<tr>
<td>Co$^{58}$</td>
<td>71.3</td>
<td>811</td>
<td>.02</td>
<td>2.0</td>
</tr>
</tbody>
</table>
nucleation process, the authors restricted the amount of contaminant added to the reactant solution to yield initial concentrations below the solubility limit of the hydroxide. Thus, as can be seen from Table 3.1, the maximum tracer concentrations achieved are rather low. Flachsbart and Stöber suggest that the incorporation of the foreign material into the silica matrix takes place in two steps: adsorption of a soluble form of the hydroxide onto the growing silica surface followed by simultaneous dehydration of the silicic acid and the hydroxide to link the two together in the oxide form.

Thus, the groundwork for the manufacture of labelled silica spheres had been laid. However, before accepting this particle system as a suitable candidate for fulfilling the specific requirements of the deposition experiment, additional experimentation was needed not only to test out the techniques developed by Stöber et al. and Flachsbart and Stöber, but also to resolve other difficulties not considered by these authors. For example, the method used by Flachsbart and Stöber for tagging silica spheres severely limits the amount of radioactive material which can be introduced into the particles. Calculations based on the mass transfer theory developed earlier suggest that deposition measurements using a radioactive tracer method are only feasible if the specific activity of the particles can be increased about a thousand-fold over the values shown in Table 3.1. Thus, procedures must be developed for incorporating much larger amounts of the labelling material into the growing spheres without affecting their sphericity or uniformity of size.

Also, a means of obtaining a highly disperse suspension in water with little carry-over of contaminants from the production solution must be found. The latter prerequisite is not only needed to provide suitable control over the aqueous chemical environment but is also required in order to yield a low
suspension conductivity for those experiments in which streaming potentials will be measured (see Sect. 3.5.3.2). In addition, more information about the rate of dissolution and the morphology of particles produced by the method of Stöber et al. is required; the former because, in some experiments, it was desired to operate at particle concentrations near the solubility limit of silica, and the latter because Iler (103) has hypothesized that particles produced in this manner are actually spherical aggregates of much smaller particles, 10 nm or less in size.

One other possible disadvantage of using silica particles is that silica surfaces tend to adsorb several layers of water molecules which can form a "steric barrier" to particle deposition (see Sect. 2.4.1). However, coagulation studies (51) with particles produced by the techniques of Stöber et al. demonstrate that their stability behaviour can be explained by the DLVO theory, which does not account for "steric" factors.

3.2.2 Experimental Development of a Model Colloid

3.2.2.1 Production of Uniform Silica Spheres

The materials used were as follows. The methanol, ethanol, n-propanol, and n-butanol employed as solvents were of analytic reagent grade (Mallinkrodt). Water was distilled just prior to use. Anhydrous ammonia (99.9%, Canadian Liquid Air) was used to saturate the alcohol-water solutions. Tetra-ethyl orthosilicate was supplied either in reagent grade (ICN - K&K Laboratories) or in practical grade (b.p. 56-58 °C/10 mm, Matheson Coleman and Bell). Tetra-methyl and tetra-butyl orthosilicates were prepared by reacting reagent grade silicon tetrachloride (MC&B) with methanol or butanol, respectively, employing the methods evolved by Dearing and Reid (106).
In general, the following procedures were used to produce silica particles. Measured volumes of alcohol and freshly distilled water were poured into a 6-fluid-ounce glass bottle with a screw-on cap fitted with a teflon liner-seal. The bottle was then positioned in a specially constructed constant temperature bath which was maintained at 25.0 ± 0.1 °C for all production runs. The contents of the bottle were agitated by a magnetic stirrer. Ammonia from a cylinder was bubbled into the water-alcohol mixture through a glass frit until saturation was achieved. At this point, the alkyl silicate was pipetted into the bottle and the cap was screwed on tightly to prevent the escape of ammonia. After an invisible hydrolytic reaction forming silicic acid, the condensation of the supersaturated silicic acid was indicated by an increasing opalescence of the mixture starting 1-5 minutes after adding the tetra-alkyl silicate. The transition to a turbid white suspension occurred within a few more minutes.

As a standard procedure, samples for electron microscope examination were taken after 60 minutes of reaction, although in most cases the particles had reached their final size at times sooner than this. A copper transmission electron microscope carrier grid covered with a carbon film was positioned on a clean glass plate. The samples were prepared by placing a droplet of the suspension on the grid using a glass capillary to affect the transfer. After the droplet had evaporated to dryness, electron micrographs of the particles retained on the film were obtained using a Hitachi HU 11 A transmission electron microscope. The magnification of the microscope was periodically recalibrated by means of a germanium shadowed carbon replica (54864 lines/in., Ladd Research Industries). The average particle size and standard deviation were determined by manually measuring more than 200 particles from several random micrographs of the grid sample.
As there is not sufficient space or reason to report all of the results in detail, only an overview of the most important findings will be presented here.

First, it was found that the sphericity of the particles and their uniformity of size were very closely related. The electron micrographs indicated that particle samples which demonstrated the greatest degree of sphericity (i.e. largest fraction of perfect spheres) also had the narrowest distribution of particle diameters (i.e. lowest standard deviation). Maximal sphericity and uniformity of size were obtained by:

1) using extremely pure reactants. This fact is clearly shown in Fig. 3.1 which compares electron micrographs of particles produced by hydrolyzing practical grade TEOS (a) and reagent grade TEOS (b) in n-propanol. Thus, to assure the best results, all esters were redistilled in a specially-constructed vacuum fractionator prior to use. The 100 cm. x 18 mm. dia. glass column was packed with 5 mm. single-turn glass helices (Fenske packing) and was equipped with a magnetically-operated reflux head. Both column and reflux head were vacuum jacketed to prevent heat loss. Prior to each distillation, nitrogen dried with silica gel was passed through the column to remove all traces of water. Dried nitrogen was bubbled into the reboiler through a thin glass capillary during the distillation to promote boiling. By operating with a reflux ratio of 5:1, it was possible to extract a product having a boiling point range of only 0.1 °C at constant pressure after a maximum of two distillations. Virtually identical results were obtained from twice-distilled practical grade and once-distilled reagent grade tetra-ethyl orthosilicate.
Figure 3.1. Comparison of silica particles produced by hydrolyzing practical grade TEOS (a) and reagent grade TEOS (b) in n-propanol. Scale bars represent 1 μm.
ii) using maximum ammonium concentrations. Thus, the best results were obtained by completely saturating the alcohol-water mixture prior to adding the alkyl silicate. Since the solubility of ammonia in water is greater than in all alcohols (e.g. five times greater than in n-propanol), ammonia contents can be enhanced by using water concentrations greatly in excess of the stoichiometric requirements of the reaction. However, too much water leads to the non-uniform reaction conditions that the use of the mutual solvent was intended to avoid. For the TEOS/H₂O/n-propanol system investigated most thoroughly, optimal results were achieved using volume ratios of 1:5:25.

The condensation and polymerization to form particles having a spherical shape appears to be the natural tendency of amorphous silica. Presumably, the spherical shape results because the process of surface formation requires a minimization of surface energy and hence surface area. It is hypothesized here that since silica surfaces are highly negatively-charged under alkaline conditions, they are prevented from aggregating and hence continue to grow as individual spheres. However, when trace amounts of certain contaminants are present, some coagulation is possible. As a result, particle clusters (doublets, triplets, etc.) form at all stages of the reaction. Those that form before the reaction is complete continue to act as nuclei for particle growth. Subsequent precipitation attempts to cast them into the usual spherical mold. The non-spherical particles which can be seen in Fig. 3.1(a) were probably formed in this manner. Optical examination of the sol produced from the practical grade TEOS demonstrated that coagulation continued to occur with time after the reaction had been completed. The suspension produced using the reagent grade material, on the other hand, remained stable.
According to LaMer (107), particles of uniform size can be produced only if one of the following conditions is met:

i) slow growth of particles by controlled deposition on an appropriate number of foreign nuclei, or

ii) slow growth of particles by controlled deposition on nuclei homogeneously generated during a restricted nucleation period.

Since, in the case of the production of uniformly-sized silica sols by alkyl silicate hydrolysis, particle sizes can be duplicated from batch to batch, or varied in a replicable way by altering any of the production variables, it would appear that the homogeneous nucleation mechanism is operative here.

La Mer and Dinegar (108) have presented a theory of monodisperse sol production based on a limited homogeneous nucleation period. Before describing the theory, it is useful to first review what is known about the process of homogeneous or self-nucleation. Walton (109) states

"In solutions at normal temperatures, the molecules or ions of the solute are in constant motion and consequently are often within the sphere of influence of another molecule or ion. Hence, groups of molecules or ions are always present when the solute is present in any concentration other than trivial.

Prior to nucleation, there is a continuous formation and dissolution of ionic or molecular clusters in equilibrium with all other clusters. If the concentration of solute ions or molecules is high enough, the clusters become sufficiently large to become consolidated into small crystallites, whereupon the supposedly irreversible crystal growth ensues.

The largest cluster which may exist before spontaneous crystallization is usually referred to as the critical cluster or nucleus."

According to LaMer and Dinegar, the existence of a critical cluster implies the existence of a critical concentration, here termed $C_{\text{sat}}^*$, above which nucleation proceeds at an appreciable rate and below which nucleation is negligible.
It should be noted that $C_{\text{sat}}$ is always greater than $C_{\text{sat}}^*$, the concentration at which the solution is saturated and above which, by definition, spontaneous growth will occur (providing nuclei are available). The theory of La Mer and Dinegar is best summarized with reference to Fig. 3.2.

For the reactions under consideration, as the hydrolysis of the alkyl silicate proceeds, the concentration of Si(OH)$_4$ increases steadily to $C_{\text{sat}}$. If no foreign nuclei are present, the Si(OH)$_4$ concentration will continue to increase until the critical concentration for self-nucleation, $C_{\text{sat}}^*$, is reached. Above this concentration, nucleation proceeds at a rate proportional to the driving force, $C-C_{\text{sat}}^*$. As soon as some nuclei are present, particle growth will occur spontaneously under the control of a much larger driving force, $C-C_{\text{sat}}$. However, since the growth rate is also dependent on the surface area available, and hence, the number of nuclei present, nucleation will continue until such time that the growth rate is fast enough to lower the concentration of Si(OH)$_4$ below $C_{\text{sat}}^*$. Thus, when the difference between $C_{\text{sat}}^*$ and $C_{\text{sat}}$ is large and the rate of production of new Si(OH)$_4$ reasonably slow, the sudden appearance of nuclei relieves the supersaturation so rapidly and effectively that the region of nucleation (II) is restricted in time and no new nuclei are formed after the initial outburst. The nuclei produced during this limited period grow uniformly by a diffusion process (region III) and a sol of monodisperse particles is obtained. Note that the model predicts the existence of a lag time before any nuclei appear.

In order to check the validity of this hypothesis, it is necessary to show that the total number of particles in the reaction bottle remains constant with time following the nucleation period. Thus, the following pair of duplicate experiments were carried out. Using the TEOS/n-propanol system, 2-ml. samples were pipetted from the reaction bottle at various times during the reaction and were filtered immediately under vacuum through pre-weighed
Figure 3.2. Schematic representation, following La Mer (107), of sequence of events leading to production of monodisperse silica particles by homogeneous nucleation. Solid line refers to the variation with time of concentration of dissolved silicic acid. Cross-hatched region represents the variation with time of particle size range.
0.2 μm Celotate (alcohol-resistant, Millipore) filter membranes. The filtered samples were promptly washed with n-propanol, dried under vacuum for 48 hours, and weighed again to determine the mass of particles produced with time. The results obtained are shown in Fig. 3.3. The individual samples were then examined using the transmission electron microscope in order to determine the variation in particle size with time for each run. The final number concentration of particles can be predicted from the asymptotic values of the mass concentration and the particle size using a typical density value of 2.2 g/cm$^3$ for amorphous silica. Under the conditions used here, the change in volume due to the overall reaction between TEOS and water to produce silica and ethanol is negligible. Thus, if it is assumed that the number concentration of particles remains constant at all times during the run, it is possible to obtain an independent prediction of the variation in mass concentration with time from the particle size data. These predicted mass concentrations for each run are also plotted on Fig. 3.3. The close correlation between experimental and predicted mass concentrations demonstrates that the number concentration of particles remains constant during each run. Thus, the uniformity of the silica sols produced by the methods of Stöber et al. can be explained by the limited self-nucleation model of LaMer and Dinegar, according to which all particle nuclei are formed almost simultaneously and further precipitation contributes only to particle growth. Fig. 3.3 also exhibits the time lag predicted by the model.

These results strongly indicate that the silica particles grow as dense dehydrated units rather than as the aggregates of much smaller particles suggested by Iler (103). It is difficult to imagine a mechanism by which the latter process could take place. The view that the particles produced by
Figure 3.3. Mass of silica particles (per unit volume of solution) produced as a function of time for hydrolysis of TEOS in n-propanol. Open symbols represent measured mass concentrations while closed symbols represent values predicted from measured average diameters assuming that the number of particles produced remains constant throughout each run.
hydrolyzing alkyl silicates are solid spheres is supported by two further observations. First, an examination of a sol sample obtained from the TEOS/H$_2$O/n-propanol reaction system using an ETEC Autoscan scanning electron microscope revealed that, to the limit of resolution of the instrument (~150Å), the particles were all single smooth spheres. Secondly, measurements of the particle density failed to disclose the differences that would be expected between a solid and a porous sphere.

Particle densities were determined from settling rate measurements. It was observed that when a suspension of particles was allowed to settle in a well-sealed 12-ml. bottle, a fairly sharp interface between the supernatant and the sedimenting suspension was maintained. This is the expected behaviour for spheres of uniform size whose Stokes-Einstein diffusivities are negligibly small. Thus, dilute suspensions (<0.1% by volume) of silica particles were prepared by dispersing the dry powder in both water and n-propanol, and their terminal settling velocities, $u_s$, were determined by following the interface using a travelling microscope. Assuming prior knowledge of the average particle size, $a$, and the density, $\rho_p$, and viscosity, $\mu$, of the liquid medium and further, that Stokes' Law applies, the particle density, $\rho_s$, was estimated from the following expression

$$\rho_s = \rho_p + \frac{9\mu u_s}{2a^2 g}$$  \[3.1\]

where $g$ is the acceleration due to gravity. From a total of 23 separate measurements (14 in n-propanol, 9 in water) the average density of the silica
particles was found to be $2.18 \pm 0.04$ g/cm$^3$ (95% confidence). The density values reported for amorphous silica lie in the range of 2.17-2.20 g/cm$^3$ (110, p. B-137).

For a permeable sphere formed as an aggregate of much smaller identical spheres, the minimum possible voidage is 26%, attained in either a face-centred cubic or hexagonal close-packed structure. Thus, settling measurements in water and n-propanol would be expected to yield apparent density values of 1.89 and 1.84 g/cm$^3$, respectively, for a permeable sphere of minimum voidage (assuming the interstices are filled with the settling medium and that the solids fraction has a density of 2.2 g/cm$^3$). [Note that the Stokes' settling velocity of a permeable sphere can deviate significantly from that of a solid sphere with the same average density because of percolation through the pores (111). However, for a permeable particle composed of spherical units smaller than 150 Å, the permeability as calculated using the Ergun equation (112) is so small, that such deviations are negligible.] Thus, it can be concluded that particles produced by the method of Stöber et al. exist as solid spheres of amorphous silica.

Attempts to produce silica particles having different average diameters led to a verification of many of the results obtained earlier by Stöber et al. For example, for the TEOS/water/alcohol system, changing the mutual solvent from methanol to ethanol to n-propanol to n-butanol, under otherwise constant conditions, resulted in particles having mean diameters of 0.33, 0.38, 0.46 and 0.56 μm, respectively. Similarly, for the alkyl silicate/water/n-propanol system, a change in the alkyl group of the ortho-silicate gave the following average sizes: TMOS, 0.30 μm;
TEOS, 0.47 μm; and TBOS, 0.80 μm. Varying the initial water concentration in the TEOS/water/n-propanol reaction system yielded the curve shown as Fig. 3.4. Since the water-alcohol mixtures were always saturated with ammonia, increasing the water concentration also signified an increased ammonia content. Stöber et al. obtained a qualitatively similar relationship for the TEOS/water/ethanol system.

Of the three tetra-alkyl silicates tested, the most consistently uniform spheres were obtained by hydrolyzing tetra-ethyl orthosilicate. Thus, based on the experience gained in the present study, the recommended procedure for producing smaller monodisperse spheres is to react TEOS with water in one of the lower alcohols. For example, particles as small as 0.3 μm can be obtained by using methanol as the mutual solvent. Stöber et al. have suggested that even smaller particles, down to 0.05 μm, can be produced by hydrolyzing tetra-pentyl orthosilicate in ethanol.

The best method of producing larger particles is to use the TEOS/water/n-propanol system in a "seeding" procedure. In this method, a quantity of previously manufactured sol is introduced into the reaction bottle prior to the addition of further tetra-ethyl orthosilicate. These "foreign nuclei" act as growth sites which relieve the supersaturation of silicic acid that occurs as the hydrolysis proceeds. Thus, according to the nucleation and growth model developed earlier, the "seed" particles should continue to grow uniformly as long as further nucleation is prevented, i.e. if the concentration of Si(OH)₄ is maintained below C_{sat}. One method of satisfying this requirement is to continue to operate each seeding step in the batch
Figure 3.4. Effect of initial water concentration on particle size and percentage of perfect spheres produced by hydrolyzing TEOS in n-propanol. Bars represent maximum range of measured particle diameters.
mode, and arrange to have a sufficient number of seed particles present to adequately reduce the supersaturation at all stages of the reaction. However, because the Si(OH)$_4$ supersaturation goes through a high maximum near the beginning of the batch reaction, it was found that the required seed particle concentration was unduly high. Thus, the maximum change in particle size with each batch was rather small. To overcome this problem a continuous reagent replenishment method was devised. In this process, new TEOS was continuously added with a syringe pump to the pre-seeded reaction bottle. Thus, by controlling the concentration of TEOS in solution, the rate of production of new Si(OH)$_4$ molecules could be adjusted to suit the growth rate of the seed particles present. By using the continuous method, it was found that uniform spherical particles up to 2.0 μm could be produced in a single seeded experiment.

3.2.2.2 Introduction of Labelled Contaminants

It was felt desirable to have some flexibility in the means by which the particles were made radioactive. In the case of the silica spheres under consideration here, particle doping can be accomplished in one of two ways. The most expedient method is to incorporate a suitable radioactive nuclide into the particles as they are produced in the reaction bottle. In this case, a suitable nuclide should not only possess the prerequisite decay characteristics but should also be available in a form having a high specific
activity. The radionuclide, Co⁵⁸, is an obvious choice as a candidate material because of its half-life (71.3 days) and γ-energy (811 kev), and because it can be obtained in a carrier-free form, since it is the product of the neutron bombardment of Fe⁵⁸. In addition, cobalt was one of the contaminants successfully implanted in silica spheres by Flachsbart and Stöber (101).

A second method of doping the particles is to introduce into the growing spheres a suitable precursor nuclide which can be subsequently activated by irradiating the particles in a neutron flux. As well as eliminating many of the problems concerned with the handling of radioactive materials, this second technique has the additional advantage of offering a means of procuring identical radioactive and non-radioactive particles from a single batch (see Sect. 3.4.1). In this case, the precursor nuclide should have a large cross-section for neutron absorption. The nuclide, Sc⁴⁵, was chosen as the prime candidate for "precursor contamination" because it is the only naturally-occurring isotope of scandium, it has a relatively high neutron cross-section (25 barns), its neutron activation product, Sc⁶⁶, is reasonably long-lived (t₁/₂ = 83.8 days) and emits suitably energetic γ-radiation (Eγ = 889, 1120 kev), and finally because scandium forms a precipitable hydroxide compound in alkaline solutions. The development of a method for introducing comparatively gross amounts of cobalt (in a non-radioactive form, at present) and scandium into the silica particles is described below.

Solutions of cobaltous chloride (CoCl₂ • 6H₂O, reagent grade, MC&B) and scandium chloride (ScCl₃ • 6H₂O, 99.9% pure, Alfa Inorganics) were prepared by dissolving preweighed amounts of each chemical in 0.1 HCl and distilled water, respectively. The solution concentrations were adjusted in such a way that the addition of 0.5 ml. to a reaction bottle containing 75 ml.
n-propanol, 15 ml. water, and 3 ml. TEOS would produce silica particles having a final Co or Sc concentration ranging from 2 to 2000 ppm (µg/g. SiO₂).

As expected, attempts to obtain higher contaminant levels using the procedures developed by Flachsbart and Stöber met with little success. The injection of both the TEOS and the contaminant solution simultaneously into the reaction bottle resulted in the production of irregularly-shaped particles having a wide size distribution. Apparently, the presence of the contaminant at concentrations greater than its solubility limit at high pH results in the formation of additional nuclei and very likely disturbs the period of homogeneous silica nucleation.

A critical examination of the nucleation and growth model developed earlier suggests a more viable approach. According to the model, if the precipitable species is added to the reaction solution after a large number of nuclei have already been homogeneously generated, condensation of this species onto the existing nuclei should be preferred over the generation of new nuclei, as long as the concentration of the contaminant is not excessive. Thus, in subsequent experiments, the 0.5 ml. solutions containing the Co or Sc contaminants were injected into the reaction bottle after 100 seconds of reaction; i.e., when the contents of the bottle first appeared turbid. Under these conditions, it was found that the addition of solutions bearing enough contaminant to yield particles having at least 200 ppm Co or 2000 ppm Sc had no measurable effect on the sphericity or uniformity of the resultant particles. Furthermore, the presence of contaminants over a range of concentrations did not significantly affect the final average size of the spheres produced. For example, the cumulative size distribution curves as plotted on log-probability paper for two particle batches, contaminated respectively to 2 ppm
and 2000 ppm scandium, are shown in Fig. 3.5. As can be seen from the figure, both samples are normally distributed and have closely similar mean values and 95% confidence ranges.

To determine the uptake of contaminants into the particles, the product from each batch reaction was filtered, redispersed in pure n-propanol, filtered again, dried under the vacuum for ~48 hours, and then analyzed for its respective Co or Sc content. In some cases, the particles were re-suspended for 24 hours in acid (pH 4, HCl) or base (pH 10, NaOH) solution before washing (distilled water), filtering, drying, and analyzing. Cobalt concentrations were obtained through a commercial agency which used an atomic absorption technique. Scandium concentrations were determined by activation analysis using an A.E.C.L. Sherlock.II Neutron Activation Unit. Known amounts of scandium chloride mixed in with preweighed quantities of non-contaminated silica particles were used as calibration samples for the latter instrument. In all cases, including those samples leached with acid or alkaline solutions, the measured concentration of Co or Sc in the particles agreed with the value predicted from the amount injected into the reaction bottle, within the accuracy of the various measurements. Thus, it would appear that contaminant concentrations of at least 200 ppm Co and 2000 ppm Sc can be irreversibly incorporated into the matrix of the growing silica spheres.

3.2.2.3 Preparation of Disperse Silica Sol

One problem remaining to be solved was how to obtain a well-dispersed suspension of silica particles in water with little carry-over of contaminants from the production solution. The major contaminants residing in the solution at the end of the reaction are the mutual solvent alcohol, the
Figure 3.5. Log-probability plot of cumulative size distribution curves for silica particles contaminated to 2 and 2000 ppm Sc.
alcohol produced by the hydrolysis of the alkyl silicate, and ammonia. It is expected that there could also be trace amounts of chloride ion left over from the doping procedure, as well as dissolved silicon hydroxide.

The particles in the reaction bottle are already in a highly-disperse state. Thus, one way of meeting the stated objectives would be to devise a means of changing the suspension medium from a highly contaminated, essentially alcohol solution to pure water. The obvious method is simply to dialyze the production solution against pure water using a suitable membrane. However, because of the large volumes of solutions which would have to be handled and because of the long periods of time demanded by dialysis procedures, this approach was not pursued.

A second approach, which was followed up to some extent, is to remove the alcohol (i.e. n-propanol, ethanol, or methanol) by distillation, while continuously adding water. Since n-propanol and water form a minimum-boiling point mixture, enough water must be added initially to move the n-propanol concentration to the water-rich side of the azeotrope (0.433 mole fraction n-propanol). Because the solubility and dissolution rate of silica increase markedly with temperature (102), it was necessary to carry out the distillation under vacuum. Although the resulting hydrosol was suitably disperse, its conductivity was unacceptably high. To reduce the conductivity to acceptable levels, the suspension was then passed through a mixed bed (Amberlite MB-1 AR) ion exchange column. The desired decrease in conductivity was attained, but only at the cost of significant particle retention (20-25%) in the column even at high elutriation throughputs. Thus, because of the particle losses involved, and because of the general complexity of the method, the distillation transfer method was also abandoned. It should be
noted that neither of the transfer techniques, dialysis or distillation, could be used for the "precursor contamination" of silica particles, as a dried powder would be the only form acceptable for irradiation purposes.

Since the major contaminants are volatile, the most expedient method of achieving the desired hydrosol is simply to filter the particles, evaporate them to dryness, and then redisperse them in water. When this was first attempted, it was found that, no matter what efforts were applied, the final hydrosol was always far less disperse than the initial suspension in the reaction bottle. However, it was then discovered that washing the particles with n-propanol in order to remove non-volatile contaminants before drying appeared to make their subsequent dispersal much easier. Thus, a series of experiments were undertaken to find the washing technique which would lead to the optimal dispersion of the dried particles. A batch of particles produced by reacting 3 ml. TEOS with 15 ml. water in 75 ml. n-propanol was divided into nine separate lots. Each lot was filtered almost to dryness and the wet filter cake was placed in a water-cooled beaker containing the wash solution and a magnetic stirrer bar. The contents of the beaker were then simultaneously stirred and treated ultrasonically for 10 minutes. The ultrasonic action was provided by an Artek Systems Series 300 20 kHz generator with a 19 mm. dip-type probe. The wash solutions tested included methanol, n-propanol, n-butanol, distilled water, 0.002 N. HCl, 0.002 N. NaOH, and 0.2% tetra-methyl ammonium hydroxide (TMAH). The last solution was included on the basis of a suggestion by Iler (103), who has observed that pretreatment of silica particles with TMAH yields a sol which when dried to a powder redisperses readily in water. In some tests, the same wash solution was applied more than once. For each such treatment, the contents of the beaker were refiltered and the dispersion process repeated. The final product in
each case was filtered for the last time and then dried under vacuum for 48 hours.

A preweighed quantity of each test product was then dispersed in distilled water using the ultrasonic probe at 180 W. intensity. The dispersion process was followed with time by measuring the absorbance of the suspension at a constant wavelength of 400 nm. using a Unicam Model SP800B ultraviolet spectrophotometer. For a suspension of particles in the size range 0.4-0.7 μm, the absorbance measured at this wavelength was found to increase monotonically with increasing particle dispersity. After 20 min. of ultrasonic agitation, the distribution of single particles, doublets, triplets, etc. was determined by examining a sample of the suspension using a Wild-Heerbrug Model M20 oil-immersion microscope. The microscope samples were prepared by placing a droplet of the suspension onto a 25 x 75 mm. glass slide, covering the droplet with a 18 x 18 mm. cover glass, and then sealing the sandwiched suspension (to prevent evaporation) by applying clear nail lacquer around the edges of the cover glass. Presumably because the particles and the glass surfaces are similarly charged in water, the particles did not tend to settle out but instead remained suspended. A "cluster-size distribution" was determined by counting the number of clusters containing one, two, three, etc. particles in at least four randomly-chosen areas of the sample.

The results of these dispersion tests are shown in Fig. 3.6. The cluster-size distribution measurements are reported as the percentage of single particles present compared to the total number of clusters counted. Fig. 3.6 shows that consecutive washing in n-propanol or n-butanol improves the ease with which dried silica particles can be dispersed in water. Treatment with methanol or any aqueous solution has the reverse effect. The
Figure 3.6. Effect of wash pretreatment on particle dispersal. Increased absorbance corresponds to increased dispersal.
maximum state of dispersal obtained (as measured by the percentage of single spheres present) was in close agreement with the value obtained for the original production solution. Thus, two or three washings in n-propanol or n-butanol assure optimal dispersion. Marshall (92) has suggested that the maximum dispersion achievable by the use of ultrasonics is limited by a competing coagulation process which arises because of the large mechanical forces present. However, the equilibrium condition, which would be expected if the dispersal process were reversible, was not in evidence here. Apparently, under distilled water conditions, the highly-charged silica surfaces present too large an energy barrier towards one another to permit contact. Thus, for silica particles, the dispersion process may be considered essentially irreversible.

The reason why the alcohol pretreatment is so much more effective than any of the aqueous solutions in promoting dispersion is apparently a very simple one. The solubility of silica in water is quite significant [~0.1g./l at 25°C, pH = 7 (102)]. It is hypothesized that, as the water in the filter cake evaporates during drying, the dissolved silicic acid precipitates on the available surface area, thereby cementing together those particles in contact. Since, according to Iler (103), the solubility of concave silica surfaces is less than that of convex surfaces, these bridges tend to grow rather than dissolve upon subsequent redispersal. Thus, many particles remain chemically bound together after resuspension. As has been mentioned earlier (Sect. 2.1.1.4), silica surfaces strongly adsorb many layers of water. Consecutive washing of the particles in alcohol very likely promotes an increasing removal of these adsorbed water layers. Because the solubility of silica in alcohols is very small, a negligible amount of
precipitation takes place during the drying process. Thus, alcohol-treated silica particles can be dried to produce an easily dispersed powder.

This explanation is supported by additional experimental evidence. It was found that the ability to disperse water-washed particles is greatly improved by subsequently contacting them with n-propanol; whereas the reverse was the case for particles first washed in n-propanol and then in water. Also, a highly disperse suspension was obtained by ultrasonically treating a portion of still-wet water-washed filter cake. When the cake was dried, dispersion became much more difficult.

The conductivity of the suspensions obtained by dispersing pre-treated vacuum-dried particles in distilled water over the range of number concentrations to be used in the deposition experiments varied from 5 to 10 $\mu$mho/cm. These values are at the upper limit of what was considered desirable for streaming potential measurements and left little leeway for the effects of pH adjustment, possible additional contamination, etc. Using these conductivity data and simultaneous pH measurements, it was possible to estimate on the basis of ionization constants found in the literature, that the main contaminant leading to this undesirable conductivity was the $NH_4^+$ ion. Presumably, ammonia is strongly adsorbed to the silica surface during particle production and is not totally removed by vacuum drying alone. It was found that the addition of heat during the drying process greatly improved the desorption of ammonia. Thus, particles dried at 100°C for 48 hours in a Lab-line Instruments Duo-Vac vacuum oven yielded, upon dispersion, suspensions whose initial conductivities were in the range of 1-2 $\mu$mho/cm., values considered to be satisfactory for the purposes of the experiment. [Note that distilled water saturated with $CO_2$ under normal environmental conditions has a conductivity of 0.7 $\mu$mho/cm. (113, p. 328).]
Calculations of deposition rates based on the derived theory indicated that, for some experiments, it was desirable to use suspensions having particle mass concentrations near the solubility limit of silica in water. Thus, it was of some importance to determine if, at these low particle concentrations, the size of the particles changed significantly over the time allotted for experimentation. Although the rate of dissolution of silica has been measured in the past, e.g. (114), the reported values cannot be considered very reliable as the dissolution process is affected by many different factors including temperature of solution, degree of crystallinity, method of manufacture, and nature of solvent pretreatment. In addition, the dissolution rate should be related to the available surface area. As a rule-of-thumb, Iler (102) suggests that colloidal silica having a very high specific surface will require of the order of days to saturate pure water at room temperature, whereas massive silica may require months or years.

To test for the effects of dissolution, 50 mg. of freshly prepared silica particles were dispersed in 500 ml. of distilled water using ultrasonic agitation. The suspension was then placed in a stoppered glass flask and stirred magnetically for a period of 11 days. No detectable change in particle size, as determined from transmission electron micrographs, was found. In a second test, 4 L. of suspension containing 0.125 g./L. silica were circulated for 28 days in the deposition measurement loop (see Sect. 3.4.2.1) in order to simulate experimental conditions. Again, no apparent dissolution was observed. In addition, optical examination of samples of the suspension taken at various times throughout the test indicated that, under distilled water conditions, pumping and stirring operations in the loop caused no measurable particle degradation or coagulation.
3.2.3 Production of Co$^{58}$-labelled Silica Spheres

Because it appeared that replicable particles could be manufactured from batch to batch and because the production procedure lent itself to ease of handling, it was decided to tag the particles with Co$^{58}$ using the direct contamination method. In the course of experimentation, three batches of Co$^{58}$-labelled silica spheres were produced. Only the purest of reagents were used in the particle productions; the tetra-ethyl orthosilicate was redistilled within a day of its being used in each case. To test the viability of the reagents, a batch of non-radioactive cobalt-contaminated particles was produced first. The radioactive cobalt solutions (ICN Life Sciences) were supplied as CoCl$_2$ $\cdot$ 6H$_2$O dissolved in 0.5 N. HCl. The first two batches were produced using a solution initially containing 4.72 mCi Co$^{58}$/ml. (mass content unspecified), and enough was added to the reaction bottle (productions were about two months apart) to yield particles having a specific activity of $\sim$1.5 mCi Co$^{58}$/g. SiO$_2$. The third batch, manufactured using a solution initially containing 12.2 mCi Co$^{58}$/ml. was contaminated to a specific activity of $\sim$3mCi Co$^{58}$/g. SiO$_2$.

The general sequence of steps required for manufacturing, pretreating, and drying each batch of silica spheres is described below. This procedure, which is given partially as a means of summarizing the material presented in the previous section (3.1.2), results in the production of $\sim$1.6 g. of a dry, dispersible silica powder. The steps are:

i) 150 ml. n-propanol and 30 ml. water were measured into a magnetically-stirred I2-fluid ounce bottle maintained at 25.0 ± 0.1 °C in a constant temperature bath.

ii) ammonia was bubbled into the alcohol-water mixture until saturation conditions were achieved ($\sim$1 hour).

iii) 6 ml. tetra-ethyl orthosilicate were injected into the reaction bottle using a glass pipette.
iv) after 100 seconds duration, the appropriate amount of the radioactive (or non-radioactive) cobalt solutions was transferred to the bottle using a 2-ml. pipette (with 0.1-ml. graduations) joined to a 5-ml. glass syringe.

v) the bottle was tightly capped and the reaction was allowed to go to completion (~40 min.).

vi) the contents of the bottle were poured into a 250 ml. volumetric cylinder, and then about half of the production suspension was filtered under vacuum using a 90 mm. membrane filter (0.2 μm, Celotate) positioned in a 600 ml. fritted glass Buchner funnel.

vii) the still-wet filter cake was then transferred to a wide-mouth 16-fluid-ounce bottle containing 400 ml. of n-propanol.

viii) this bottle was placed in a constant temperature bath at 25 °C and its contents were redispersed by means of magnetic stirring and ultrasonic agitation. The probe extended into the suspension through a rubber gasket glued to the bottle's screw-on lid.

ix) after 15 minutes of dispersion, the contents of the wide-mouth bottle were again filtered under vacuum. The filter cake, in this case, was placed in a covered glass petri dish.

x) the second half of the production suspension was treated in an identical manner from step vi) on.

xi) the two petri dishes were then placed in the vacuum oven at 100 °C and dried for two days.

In the interests of radiological protection, apparatus containing radioactive particles was shielded at all times and, where possible, all handling operations were carried out using tongs and tweezers.

Transmission electron micrographs of the three radioactive particle batches are shown in Fig. 3.7. The results of their size distribution analyses are presented in Table 3.2 along with the data obtained for the non-radioactive particles produced in tandem with each radioactive batch.

Although all six batches were made using the same procedure, the resulting particles had a surprisingly wide divergency of size characteristics.
Figure 3.7. Co$^{58}$-contaminated silica particles produced for Series I (a), Series II (b), and Series III (c) experiments. Scale bars represent 1 $\mu$m.
Table 3.2
Size Distribution Results

<table>
<thead>
<tr>
<th>Series</th>
<th>Number Average Diameter (µm)</th>
<th>Smaller (%)</th>
<th>Larger (%)</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- radioactive</td>
<td></td>
<td></td>
<td></td>
<td>0.402 ± 0.010</td>
</tr>
<tr>
<td>- non-radioactive</td>
<td></td>
<td></td>
<td></td>
<td>0.457 ± 0.013</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>0.530 ± 0.041 (4%)</td>
<td>0.653 ± 0.011 (96%)</td>
<td>0.649 ± 0.027</td>
</tr>
<tr>
<td>- radioactive</td>
<td></td>
<td></td>
<td></td>
<td>0.582 ± 0.020</td>
</tr>
<tr>
<td>- non-radioactive</td>
<td></td>
<td></td>
<td></td>
<td>0.534 ± 0.019</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>0.395 ± 0.008 (6%)</td>
<td>0.613 ± 0.018 (94%)</td>
<td>0.600 ± 0.054</td>
</tr>
<tr>
<td>- radioactive</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- non-radioactive</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The variation in average size from batch to batch was greatest for the radioactive parties. In addition, the individual radioactive batches generally displayed a wider distribution of sizes (in fact, the last two series were clearly bi-modal) and in all cases were more difficult to disperse than their non-radioactive counterparts.

The unexpected differences in average diameter proved to be experimentally advantageous, as they introduced a reasonable variation of particle size into the deposition measurements. For example, a 0.649 µm particle is 4.2 times more massive than a 0.402 µm particle. However, the reasons for these differences are not easy to explain in view of the high replicability of results obtained earlier. It should be observed that the changes in average size of the non-radioactive particles followed the same trend (although not to the same extreme) as the radioactive spheres from series to series. Thus, the main cause of the size differences is probably the variation in the composition of the tetra-ethyl orthosilicate, which was redistilled prior to each series. The reason for the difference in size...
between the radioactive and non-radioactive particles of a given series is not known, particularly since the cobalt contaminants were not added until after the nucleation period was over. There is some evidence of secondary nucleation (smaller particles) in the case of the second and third batches of radioactive particles produced. However, additional nucleation should lead to smaller rather than larger average sizes.

The wider size distributions and lower ease of dispersal characterizing the radioactive particles is due either to the radioactivity itself or to the presence of other contaminants unknowingly introduced with the radioactive solution. There is some evidence that it is the latter. The radioactive particles of the first and second series were labelled to about the same specific activity by using approximately twice as much of the same cobalt solution for the second series as for the first. The second batch of particles was less uniform and more difficult to disperse than the first.

In view of these problems, it is recommended that, in the future, Sc$^{46}$-labelled particles produced by "precursor contamination" be used in the manufacture of experimental sols, especially when identical radioactive and non-radioactive spheres are required.

3.3 Test Sections

The test sections on which particle deposition is measured employ a parallel-plate geometry. As well as conforming to the requirements of the theoretical analysis, this arrangement allows the adjustment to a large ratio of deposition surface to suspension volume necessary for efficient counting. The desired degree of smoothness was obtained by constructing the test sections of plate glass. In order that the deposition surfaces might
exhibit a variety of double-layer potentials under conditions where the suspension remains stably dispersed, the test sections were coated with different plastics. Details of the construction and coating procedures are given below.

3.3.1 Construction

The test sections were constructed of two 254 x 140 mm. sheets of 7 mm. plate glass held apart by 254 x 14.3 x 0.79 mm. polyethylene spacers (see Fig. 3.8). The glass sheets and spacers are assembled in a special jig and then cemented together with an epoxide adhesive. Of the several adhesive resins recommended for binding glass, the best results were obtained using the epoxide Araldite 20AC OV (Industrial Formulators). Further improvements in the resin-glass bond strength were achieved by following the recommendations set forth by Martin (115). Before the adhesive was applied, the gluing surface was first roughened by grinding with 240x aluminum oxide powder, cleaned with chromic acid (conc. sulphuric acid saturated with sodium dichromate) at 50 °C, rinsed with distilled water, and then thoroughly dried for 4 hours in an oven at 230 °C. After the adhesive had set for 24 hours, the resin was cured by placing the test section in an oven at 100 °C for one hour. In this way, it was possible to produce test sections capable of being pressurized to 15 p.s.i. gauge and of withstanding harsh chemical treatment.

After heat-curing the resin, the test section was placed in a vertical holder. The ends of the test section were then ground on a grinding wheel using successively finer grades of aluminum oxide powder (finishing with 320 x) until a smooth surface was obtained. The smooth end surfaces
Figure 3.8. Parallel-plate test section.
were required to mate with soft rubber gaskets located in entrance and exit sections. The latter clamp together to hold the test section in place during the deposition experiments (see Sect. 3.4.2.1). Small (25.4 x 3.2 x 0.79 mm.) plastic pins fit into the slots shown in Fig. 3.8 and into mating slots milled into the entrance and exit sections to provide the necessary alignment.

After a thorough cleansing to remove any contaminants which may have entered during the grinding process, the internal dimensions of each test section were measured. The average length (L) and average width (W) were obtained using a travelling microscope. The average thickness of the gap between the two plates (2b) was calculated from the measured weight of mercury required to fill the test section almost to the top and from knowledge of the channel width and the height of the mercury meniscus, also determined with a travelling microscope. Surface tension effects prevented the complete filling of the test section. Repeated measurements on a single test section suggested that the value of average gap dimensions estimated using the mercury filling technique is accurate to within ±0.1%.

The glass surfaces were prepared for plastic coating by first cleaning each test section in chromic acid at 50 °C for 10 minutes. Then, to eliminate all traces of chromic acid remaining after the cleaning process, the test sections were continuously flushed with distilled water in an apparatus designed for this purpose. By monitoring the conductivity of the effluent with time for several test sections, it was found that, at a flush rate of 40 ml./min., complete removal could be guaranteed with a purge time of 48 hours.

The accidental introduction of trace amounts of chromic acid via poorly-flushed test sections in two early deposition experiments resulted in rapid coagulation of silica particles followed by random deposition around
the circulatory system. That chromic acid was the causative agent was demonstrated in two ways. In a small-scale loop set up to simulate the deposition-measuring apparatus, the addition of enough chromic acid to give similar changes in conductivity and pH as were measured in the earlier experiments yielded the same disastrous results. On the other hand, diligent flushing of each test section before installation eliminated the problem in the main loop. The reason why even trace amounts of this contaminant promote such large effects is not known.

It had been hoped that upon the completion of each deposition experiment, the "used" test section could be successfully cleaned and used again. However, all attempts at cleaning test sections bearing deposited radioactive particles using chemical agents such as chloroform, hot chromic acid, and 0.1 N NaOH failed to return the glass surfaces to their initial "clean" state. Thus, a new test section was prepared for each deposition experiment.

3.3.2 Coating

Over the range of chemical conditions which lead to a stable silica sol, glass will also present a highly negative charged surface. Thus, the deposition of stabilized silica particles onto a glass surface is expected to be minimal. To provide the double layer conditions which will yield measurable rates of particle deposition, it is therefore necessary to alter the surface characteristics of the glass test section. This is best accomplished by coating the glass surface with plastics which exhibit the required range of positive as well as negative surface potentials. Based on the deposition experiments of Marshall and Kitchener (16) and Hull and Kitchener (17), the following plastics were chosen: the anionic polymer polyvinyl formaldehyde (Formvar) and the cationic copolymer of 80% 2-vinyl pyridine and 20% styrene (2VP/S). Under neutral pH conditions, Formvar bears a
moderate negative charge whereas 2VP/S is slightly positive. Since both plastics become increasingly more negative with increasing alkalinity, a wide variety of surface potential combinations can be obtained merely by adjusting the pH of the suspension.

The polyvinyl formaldehyde used in the present experiments was supplied in the commercial form Formvar 15/95E (electron microscope grade, Monsanto). The co-polymer 2-vinyl pyridine/styrene, not available commercially, was prepared by solution polymerization following the procedure first described by Utsumi et al. (116). As supplied, both the 2-vinyl pyridine (b.p. 48-51 °C/12 mm., J.T. Baker) and styrene (b.p. 31-33 °C/8 mm., J.T. Baker) monomers contained higher boiling point inhibitors added to extend their shelf-life. Thus, as the first step in the preparation procedure, both monomers were purified by vacuum distillation in the fractionating column described earlier (Sect. 3.1.2.1). Using a clean glass syringe, 4 ml. methanol (reagent grade, Mallinkrodt), 4 ml. freshly distilled styrene and 15 ml. freshly distilled 2-vinyl pyridine were injected into a 100-ml. test tube. The test tube was equipped with a sealable screw cap and was tightly wrapped with aluminum foil to exclude light. Nitrogen gas, deoxygenated in a pyrogallol solution (5 g. pyrogallol, 50 g. KOH, and 100 ml. H₂O) and dried in a U-tube containing silica gel, was bubbled through the mixture via a glass capillary for one hour. At this point, 0.2 g. of benzoyl peroxide (m.p. 105-106 °C, MC&B) was added through a glass funnel to initiate the polymerization reaction. After a further six hours of N₂ bubbling, the viscosity of the solution had increased to the point where it was no longer possible to pass nitrogen through it. Hence, the glass capillary was removed from the solution and the test tube was tightly sealed and stored in a
dark location for two days at room temperature. At this stage, the polymer was a clear golden brown solid in the bottom of the test tube.

The glass test tube was carefully broken away from the polymer mass and the pellet of plastic remaining was dissolved in 250 ml. of chloroform (reagent grade, Mallinkrodt). The polymer was purified by reprecipitating it twice in petroleum ether. In each case, the polymer solution was placed in a separatory funnel and added dropwise to 1600 ml. of petroleum ether (reagent grade, Mallinkrodt) in a well-stirred 2000 ml. beaker. On contact with the petroleum ether, the polymer formed a white fibrous precipitate which could be continuously removed from the beaker using a glass rod. The final precipitate was washed in 400 ml. of fresh petroleum ether and then dried under vacuum for one day. Several such batches of 2VP/S copolymer were produced.

The test sections were coated with plastic in the apparatus shown in Fig. 3.9. The apparatus is a modified version of the equipment used by Revell and Agar (117) to prepare thin uniform films of plastic for electron microscope purposes. After all traces of residual chromic acid had been removed, the test sections were contacted with methanol for one hour and then dried under vacuum for an additional hour. It was expected that these two steps would assist in removing layers of adsorbed water and thereby improve the strength of the bond between the plastic film and the glass substrate. Each test section was placed in an aluminum holder. The holder was subsequently inserted into the 305 x 152 x 25 mm. stainless steel tank shown at the top of the photograph. A solution of plastic dissolved in chloroform was forced up into the tank containing the test section by pressurizing the glass storage tank with compressed air. The upper tank was filled until the level of the solution was about 1 cm. over the top of the test section.
Figure 3.9. Plastic coating apparatus.
The 3-way stopcock at the top of the storage tank was then opened to the atmosphere and the plastic solution was drained to the storage tank. By measuring the time taken for the liquid level to pass between two markings on a sight glass attached to the upper tank, a sensitive indication of any change in viscosity, and hence, plastic concentration of the solution was obtained. Because of the volatile nature of the solvent, chloroform make-up was frequently required to keep the plastic concentration constant. The test section was allowed to dry in situ (~5 min.) and then was stored under vacuum until required for a deposition experiment. After each coating, the apparatus (with the exception of the storage tank) was washed once with chloroform to remove any traces of plastic which might contaminate subsequent solutions or block the capillary tube.

According to Revell and Agar (117), the final film thickness attained is proportional to the concentration of plastic in the solution and is affected by the rates of draining and drying. Thus, in order to make the drainage rate approximately constant, the apparatus was designed such that the liquid head was much higher than the length of a test section. A 2 mm. capillary tube was chosen to give similar drainage rates to those used by Revell and Agar. Marshall (92) found that when the thickness of the films prepared by this "falling-level" method were less than ~100 Å, their coverage tended to be rather spotty; whereas, if it exceeded 300 Å, the films came away from the glass. He recommended an optimal thickness of 200 Å which he obtained on individual glass slides using a 0.5% (wt.) plastic solution. It was expected that these results would not be duplicated in a test section because its narrow cavity would greatly restrict the drying process. Thus, a series of coating experiments were undertaken to find the solution concentration which would yield a plastic film of optimal thickness and also to assess
the effect of the restricted volume of the test section on the uniformity of the film over its length.

The thickness of the coated films was measured by the multiple beam interference method developed by Tolansky (118). Because this method requires access to the coated surface, the test sections used in the experiments were assembled in the usual fashion but were held together by removable tape. After coating with plastic solutions containing 0.5, 1.0, and 2.0% Formvar, the test sections were dried under vacuum and then dismantled. A strip of plastic film was removed from both long edges of each glass plate to about 2 cm from the edge of the channel by dipping first one side and then the other in a trough of hot chromic acid for five minutes. Of several techniques investigated, etching in chromic acid was found to yield the sharpest edge on a Formvar film. After being rinsed with distilled water and allowed to dry, each plate was coated with a uniform reflecting layer of aluminum (~500 Å thick) by condensing the vapourized metal onto the surface in a vacuum chamber. Thickness measurements were then made as a function of length down the two film edges created by the etching procedure, using a Sloan Model M100 Angstrometer, a commercial instrument which operates on the principle of multiple beam interferometry. The aluminized glass plate was placed on the tiltable stage of the instrument. A silvered glass flat which forms part of the optical system of the Angstrometer was positioned upon the test section plate. The stage was then tilted in such a way as to create a wedge between the two reflecting surfaces that lay parallel with the film edge. When this system was illuminated from above by parallel monochromatic light (5890 Å, Na), multiple beam Fizeau fringes could be observed (with a microscope) running normal to the film edge. The step-change in elevation at the film edge appears in the pattern as a displacement of the fringes (see Fig. 3.10).
Figure 3.10 Interference microphotograph showing displacement of interference fringes due to step change in surface elevation.

\[ t = \frac{a}{b} \cdot \frac{\lambda}{2} \]
Since the distance between the fringes is proportional to half of the wavelength ($\lambda$) of the illuminating light, the thickness ($t$) of the film causing the displacement is calculated as $t = \frac{d}{b} \cdot \frac{\lambda}{2}$. The technique is accurate to $\pm 25$ Å.

The thickness of the films produced by the 0.5% and 1.0% solutions were exceedingly thin and in some places were not measurable. The 2.0% solution resulted in the film thicknesses plotted on Fig. 3.11 as a function of the distance from the top of the test section for the two edges bared by the etching procedure. The film produced by the 2.0% Formvar solution was not only reasonably uniform but had an average thickness of $205 \pm 39$ Å, which is very close to the value sought. Thus, all subsequent coatings were carried out using both Formvar and 2VP/S solutions containing 2.0% by weight of plastic. It was not possible, in fact, to measure the thickness of a 2VP/S-coated test section because the chromic acid etching solution tends to wet this film, producing an indistinct edge. However, Marshall (92) has shown that similar solution concentrations of a number of plastics (including the two used here) tended to give films of similar thickness. The fact that the fringes on both sides of the displacement zone in Fig. 3.10 lie parallel to one another suggests that the local surface anomalies on the plastic film (left-side) are no greater than on the glass itself, and both are less than 25-50 Å. Thus, the deposition surface may be considered smooth relative to the size of a particle.

3.4 Measurement of Particle Deposition

3.4.1 Introduction

The experimental apparatus was designed to fulfill two main purposes:
Figure 3.11: Thickness of Formvar film as a function of longitudinal distance 2 cm. from left (solid line) and right (dashed line) edge of test section.
i) to measure the rate of particle deposition from a flowing suspension onto the walls of a parallel-plate channel under the conditions specified by the derived theory.

ii) to measure separately the rate of release of deposited particles from the walls under the dynamic conditions where both deposition and release are occurring.

The first goal was satisfied by pumping a suspension of radioactive silica particles through the prepared test sections and monitoring the accumulation of material on the walls by using an externally-mounted scintillation counter. Ideally, in order to maintain constant suspension conditions, a once-through flow system should be employed. However, because of the time required to achieve measurable particle accumulation, especially at low deposition rates, a once-through system is not a practical choice. Thus, a circulatory loop was selected here. The particle depletion and contamination problems associated with circulating systems can be largely overcome by using some foresight in designing the loop and selecting the operating procedures.

The measurement of particle release is accomplished by using a second circulatory loop. Whereas the storage tank of the first loop contains suspended particles which are radioactively-tagged, the second contains inactive, but otherwise identical particles under the same concentration and chemistry conditions. The assumption which is the basis of all radiotracer work is made that the radioactive and non-radioactive particles behave identically in the process being studied. On the basis of this assumption, a release rate measurement may be made as follows. Consider that at time, \( t_0 \), the radioactively-tagged suspension is allowed to enter a test section which is being monitored by a counter. If, in fact, particles do release, then at any time after \( t_0 \) there will exist some probability that a deposited particle will transfer back into the suspension. Thus, as time passes, the
tagged particles will accumulate on the test section wall at a rate determined by the separate contributions of deposition and release. If at some time, \( t_1 \), the flow to the test section is changed from the tagged source to the untagged source under the same conditions of flow and temperature, the rates of deposition and release at that instant will be unchanged. However, because the concentration of suspended radioactive particles has been suddenly forced to zero, the rate-of-change of the activity of the particles on the surface at that moment in time is a measure of the particle release rate. At any time after \( t_1 \), the specific activity (mCi/g.) of the deposited material will suffer an unknown dilution by newly deposited nonradioactive particles. Hence, the release rate is found by extrapolating the first derivative of the release curve back to \( t_1 \). The deposition rate at \( t_1 \) can be easily found by subtracting the release rate from the accumulation rate measured at this time. By drawing from the radioactive source most of the time and making short, intermittent interruptions to obtain release measurements, curves of deposition rate and release rate can be constructed as a function of time. Because the wall is clean at the start of the experiment, the initial release rate (at time \( t_0 \)) is of course zero. The initial deposition rate is the slope of the accumulation curve at time \( t_0 \). Because it is this latter quantity which is required to test the derived theory, the major emphasis of the experimental work will be to determine initial deposition rates.

The double-loop apparatus designed to measure both deposition and release rates is described in the following section.
3.4.2 Apparatus

3.4.2.1 Double-Loop System

A cut-away drawing of the double loop system used for measuring particle deposition and release rates is shown in Fig. 3.12. A more detailed schematic of the apparatus giving all ancillary connections is shown in Fig. 3.13. The two loops were carefully constructed so as to be identical in every way. Wherever possible, components in contact with a suspension (either radioactive or non-radioactive) were fabricated from teflon. In a series of compatibility tests involving a variety of candidate construction materials, it was found that, over the range of chemistry conditions planned for the deposition experiments, silica particles showed the least tendency to deposit on this material. In addition, teflon is notably corrosion-resistant. Thus, both loops were constructed of 6.35 mm. (1/4 in.) I.D. teflon tubing (Chemplast Inc.) using fittings milled from solid teflon (Chemplast Inc.). All main loop valves were either diaphragm valves with teflon bodies and diaphragms (Valcor Engineering) or glass stopcocks with teflon plugs (Fisher Scientific).

The suspension storage tanks were fabricated from 254 mm. lengths of 165 mm. I.D. heavy-walled teflon tubing using 25.4 mm. thick teflon discs to form the bottoms. A conical depression was milled into the inside of each bottom plate to assure complete drainage through the centrally-located exit hole. Each tank was fitted with an air-tight plexiglass lid. The capacity of each tank was 4 litres of suspension. With this volume, changes in particle concentration due to deposition in the test section and on other loop components and due to flushing during the discontinuous counting procedure (Sect. 3.4.3.2) were usually kept to within less than 5% during a run.
Figure 3.12. Drawing of double loop system showing layout of major components and shielding.
Figure 3.13. Schematic diagram of double loop system.
Legend for Figs. 3.12 and 3.13

A. Radioactive suspension tank
B. Non-radioactive suspension tank
C. Entrance section
D. Test section
E. Exit section
F. Loop pump
G. Gas burette
H. Vent filter
I. Distilled water storage tank
J. Distilled water supply pump
K. Flush solution tank
L. Non-radioactive drain tank
M. Radioactive drain filter
N. Glove box sink
O. Pressure transducer
P. Distilled water syringe
Q. Constant temperature water bath
R. Lead shield
Particle make-up and chemicals required to adjust the electrolyte and pH conditions of the suspension were added through a port located in the plastic lid. The port was normally capped during a deposition experiment. To keep the particles in suspension, the contents of the tank were constantly stirred by means of a polyethylene stirrer rod with 44.5 mm. diameter blades. Each stirrer was driven by a 1/30 h.p. variable speed motor (Sargent-Welch). The stirrers were operated at ~60 rpm, a speed which is fast enough to assure complete suspension but does not promote significant coagulation. To provide pressure relief without admitting air-borne dust particles into the system, the tanks were vented through a 0.1 μm polycarbonate membrane filter (Nucleopore) retained in a 25 mm. in-line filter holder (Gelman).

The test section entrance and exit sections were designed to provide a smooth transition from tube to slot flow and from slot to tube flow, respectively. An exploded view of the entrance section is shown in Fig. 3.14. The exit section is identical to the entrance section except for the absence of the hole required for the two support pins in the latter. Both sections were formed from 2 sheets of 140 x 95 x 12.7 mm. teflon stock. Because silica particles do not tend to attach themselves to this material, the use of teflon in this capacity was expected to yield a homogeneous particle concentration at the test section inlet, one of the conditions assumed in the mathematical analysis. The transition region was carefully milled into the front plate. The slotted section was machined to a depth of 0.79 mm. and is long enough (50.8 mm.) to provide a fully-developed velocity profile at either end of the test section over the full range of laminar Reynolds numbers (119, p. 240). To assure proper test section alignment, the slots for the locating pins were milled to exactly the same depth. Holes were drilled in the back plate to admit or withdraw the suspension (6.35 mm., 1/4 in.) and acts as ports for
Figure 3.14. Test section entrance section.
sample withdrawal or pressure drop measurement (3.18 mm., 1/8 in.). A 63.5 x 3.18 x 0.25 mm. channel was milled 3.18 mm. from the edge nearest the test section to admit a bright platinum electrode of the same size. Two platinum wire leads which extended through undersize holes in the teflon plate were silver soldered 6.35 mm. from either end of the electrode. These electrodes, one in each of the entrance and exit sections, were used to measure the streaming potential of the test section (see Sect. 3.5.3.2.). The two halves of the entrance and exit sections were held together by 12 1/8-32 bolts which were countersunk to leave a flush outer surface. Once these sections had been assembled, a 2.38 x 1.19 mm. groove was milled entirely around and 2.38 mm. from the slot opening to accept a 1.59 mm. soft rubber O-ring. The O-rings, which seal each section to the ground glass and epoxy mating surfaces of the test sections, were formed by cutting the O-ring material to the correct length and joining the two ends (cut diagonally to increase the surface area) with silicone cement. The same cement was used to fix the O-ring in the groove.

The entrance and exit sections were supported in brass holders which could be raised or lowered along a track provided by an immobilized pair of 12.7 mm. dia. drill rods (see Fig. 3.15). The exit section holder was securely clamped to the guide rods and its position generally remained unchanged from experiment to experiment. The entrance section holder consisted of two components: a clamping bar which could be locked into position, and a movable unit which could be driven up and down the guide rods by means of a 19.1 mm. (3/4 in.) bolt which extended through the clamping bar. (The end of the bolt was secured to the movable part by a slip pin which allowed the bolt to rotate freely.) Thus, with the plastic alignment pin properly
Figure 3.15. Test section support stand showing arrangement of entrance and exit sections.
positioned in the test section and in the two end sections, the test section could be sealed into the loop simply by tightening the bolt in the clamping bar of the entrance section holder. Because it was not generally possible to grind the two ends of the test section perfectly parallel to one another, adequate sealing could only be attained by allowing the entrance section to "float" in its holder and by using a rounded pressure plate to apply the necessary force. The required freedom of movement was obtained by supporting the entrance section with 6.35 mm. steel pins in holes drilled 3.18 mm. oversize. Since ordinary teflon tubing is quite rigid, the inlet connection was constructed from a short length of 6.35 mm. (1/4 in.) I.D. flexible teflon tubing (Penntube Plastics) in order to accommodate the vertical movement of the entrance section.

Loop circulation was provided by a positive-displacement gear pump (Model 12-40-316, Micropump Corp.). This pump was chosen because it delivers a reasonably constant, non-pulsatile flow under varying head conditions and because it has a small internal volume. To minimize contamination problems when switching flow sources, it was considered desirable to make the volume of the common section of the two loops (i.e. test section, pump, and associated tubing) as small as possible. The pump body and shaft were constructed of 316 stainless steel; the gears were teflon. The pump was equipped with an internal by-pass which was adjusted to prevent overpressurizing the loop in the event of an erroneous valve closure. The driver gear of the pump was not directly connected to the motor but instead was propelled by means of a magnetic coupling. Thus, because the pump was completely sealed, it was virtually leak-proof and contamination-free. The pump was driven by a 1/12 h.p. d.c. electric motor (Century Electric Co.). The speed of the motor was controlled using a variable transformer-regulator (Ratiotrol Model 25B,
Boston Gear). Since the pump could be safely operated up to 10,000 r.p.m. whereas the maximum speed of the motor was 1750 r.p.m., the motor speed was geared up by a factor of 5:1 at the external shaft of the pump to provide a wider range of flows. The maximum flow rate attainable using this arrangement was 4.7 l/min. at 10 p.s.i. gauge.

The additional lines shown in Fig. 3.13 allowed for the draining and flushing of a test section prior to its removal at the end of an experimental run and for the filling of a fresh test section after its installation. They could also be used to flush out the suspension in the test section at any time during a run to permit a more sensitive measurement of particle deposition (if required) or to minimize cross-contamination when alternating from one suspension to another. To assist the exchange process, three 100-ml. gas burettes were provided for the three types of aqueous environments encountered; radioactive suspension, non-radioactive suspension, and flush solution. Their use will be discussed in more detail in the Procedures section (3.4.3). All three burettes were vented to the atmosphere through 0.1 μm filters.

The flush and fill solutions were stored in a 7.6 l. polyethylene carboy situated above the two loops. Thus, flushing and filling could be achieved by gravity feeding. The flush tank was filled with distilled and deionized water, stored in two 18.9 l. polyethylene carboys located at floor level, by means of a Jabsco Model 12310-0001 centrifugal pump. Solutions for adjusting the chemical make-up of the flush water were added through a port provided at the top of the flush tank. The distilled water storage tank and the flush tank were vented in common through a 0.1 μm filter.

Non-active solutions were drained to two 18.9 l. drain tanks. Solutions known to contain or suspected of containing radioactive particles
were filtered under vacuum using a 90 mm. membrane filter (0.2 μm Celotate) in a 600 ml. Buchner funnel with an air-tight lid.

All of the radioactive loop except the test section was enclosed by a lead wall (see Fig. 3.12). Since the volume of each test section was approximately 20 ml., only ~0.5% of the total activity in this loop (1.5 mCi maximum) was unshielded at any given time. The thickness of the lead shield has been designated on the basis of yielding a reasonable counting background in the vicinity of the test section and is far greater than safety considerations alone require. The shield was constructed of 203 x 102 x 50.8 mm. (8 x 4 x 2 in.) lead bricks stacked in a frame in a staggered pattern. As a further radiological precaution, the apparatus was completely contained in a wood and plexiglass glove box, the interior of which was kept at a negative pressure by drawing off air through an absolute (0.2 μm, Millipore) cartridge filter and ejecting it outside the building. The base of the glove box was made impervious to water and was deep enough to store indefinitely the total liquid volume of the two loops. Sealed into and flush with the base were two 102 mm. dia. x 102 mm. deep polyethylene sinks. One was connected to the non-active drain tank and the other to the active filter. These were used for disposing of samples of non-radioactive and radioactive suspensions, respectively. The sink connections also act to vent the filter and the drain tanks through the glove box. The active filter was contained within a 76.2 mm. thick lead well and covered with a 50.8 mm. lead lid.

3.4.2.2 Instrumentation

The concentration of radioactive particles deposited on the walls of the test section and in samples of the suspension was measured using a
scintillation detector and its associated electronics. A schematic drawing of the Ortec counting system is shown in Fig. 3.16. The Bicron scintillation detector consists of a hermetically-sealed 3 x 3 in. NaI(Tl) scintillation crystal and an in-line photomultiplier tube. The scintillator emits a flash of light when a photon of gamma radiation is absorbed. The photomultiplier tube detects the light flash and converts it to a voltage pulse whose amplitude is proportional to the energy of the incoming γ-ray. The signal from the detector undergoes two stages of amplification before being fed to an integral discriminator. The purpose of this instrument is to reject voltage pulses whose amplitude is smaller than the preset discriminator level, i.e. random pulses generated by low energy electrical noise. It was found that the best compromise between measurement sensitivity (counting rate) and measurement resolution (counts/background noise) for a Co$^{58}$ source was obtained with an amplifier gain of 24 and a discriminator level of 3.0. The voltage pulses accepted by the discriminator are counted in a six-decade scaler. The counting time is monitored by a timer. At the end of the preset counting time, a read-out control unit transfers the information accumulated in the scaler to a modified Teletype 33ASR Page Printer. The print-out control can be operated in a single-cycle or a recycle mode. In the latter mode, the control unit automatically resets the scaler and timer and initiates the next counting and printing cycle. The lag time between counts is 2.36 seconds.

To minimize background radiation levels, the detector was enclosed within a cylindrical counting chamber (Fig. 3.17) with 69.9 mm. thick lead walls. When measuring concentrations of deposited particles, one of two 50.8 mm. thick lead collimators was inserted into the front end of the counting chamber. These were designed to limit the area of the test section being
Figure 3.16. Schematic diagram of Ortec counting system.
Figure 3.17. Front view of double loop system showing counting stand and collimators. (Legend: A - counting stand, B - counting chamber, C - scintillation detector, D - entrance section, E - exit section, F - rectangular collimator, G - cylindrical collimator, H - blank collimator, I - plug for sample insertion hole, J - sample insertion hole.)
scanned by the detector. One collimator contained a 6.35 x 63.5 mm. slot and hence effectively scanned only a differential length of the test section. Using this rectangular collimator, deposition could be measured as a function of the distance from the channel inlet by raising or lowering the counting chamber in a specially-constructed counting stand. The approximately 200 lb: counting chamber was driven up and down by means of a worm gear linked to a manual crank. The position of the chamber could be determined from a centimetre scale attached to the stand. A second collimator, used when a more sensitive measurement was required, had a 63.5 mm. dia. cylindrical slot. When the cylindrical collimator was in place, measurements were usually taken only at the centre (longitudinally) of the test section. In order to translate an activity measurement into a wall concentration, it was necessary to calibrate the counting facility. Calibration curves were obtained for both collimators by measuring the radioactivity emanating from test sections with known surface concentrations of particles. Details of the wall concentration calibration procedure and the results obtained for the three different batches of radioactive particles are given in Appendix C, Sect. C.1.1.1.

To measure the concentration of radioactive particles in suspension, a blank collimator was inserted in the counting chamber and a 12-ml. counting bottle containing a 10-ml. sample of the suspension was positioned in front of the detector through an entry hole provided at the top of the chamber. A slot was milled into the blank collimator and a brass stopping plate was fixed in the slot to insure that the bottle was always counted in the same position. The sample bottle inserting hole was covered with a lead plug during sample and test section counting. Calibration curves for all three particle batches were obtained by counting 10-ml. aliquots of suspensions having predetermined particle concentrations. The procedures involved with,
147.

and the results obtained from, the suspension concentration calibration measurements are given in Appendix C, Sect. C.1.1.2.

The wheeled counting stand was mounted on two steel tracks running the width of the glove box. Thus, the counting chamber could be pushed to one side to allow the replacement of either test sections or collimators. When counting samples for suspension concentration, the stand was positioned away from the front of the test section in order to reduce background radiation. When counting deposited particles, the counting chamber could be locked into position at the exact centre-line of the test section by means of a locating pin which passed through a slot in the track into a mating hole in the counting stand.

The concentration of particles in the non-radioactive suspension was determined by measuring the absorbance at 400 nm. of a sample in a 4-cm. path-length optical glass absorption cell using a Unicam Model SP800B ultraviolet spectrophotometer. A calibration curve relating particle concentrations to absorbance measurements for the third particle batch only is given in Appendix C, Sect. C.1.2.

The flow-rate through the test section was determined by measuring the pressure drop between a teflon tee placed in the inlet line to the test section and the pressure port in the entrance section. The differential pressure was measured using a Datametrics pressure transducing system consisting of a Type 550 Barocel sensor, a Type 1015-S2 Auto Ranging signal conditioner and a Type 700 power supply. The analog signal from the signal conditioner was recorded continuously throughout each deposition run using a Hewlett-Packard Model 7101B strip chart recorder. In some experiments, a measurement of the change in pressure over the length of the test section was desired. It was therefore arranged that the two pressure lines mentioned
above, and an additional line connected to the pressure port in the exit section, could be switched through two glass and teflon 3-way stopcocks to achieve the desired combination (see Fig. 3.13). Access points were provided for flushing the pressure lines of air bubbles which could become entrapped during test section changes. Flushing was achieved using a glass syringe filled with distilled water. The procedures for calibrating flow against pressure drop are given in Appendix C, Sect. C.1.3, along with the resulting calibration curves. Because the transducer zero tended to drift unidirectionally with time, the flow calibration had to be repeated periodically.

The temperatures of the radioactive and non-radioactive suspensions were detected by thermistors sealed into the ends of glass probes, which extended into each tank through a fitting in its plexiglass lid. A similar thermistor probe detected the temperature of the water in the flush tank. The temperatures measured by the thermistors were monitored using a Yellow Springs Instrument Model 43 single channel Tele-thermometer. The contents of the two loop tanks were maintained at a predetermined temperature by circulating constant temperature water from a Colora Type K Ultra-thermostat through a coil of thin-walled teflon tubing installed in each tank. Because of the extreme temperature sensitivity of the Barocel pressure sensor, the bath water which was circulated in parallel through the two loop tanks also flowed through a specially-constructed brass housing which surrounded the transducer. The contents of the flush tank were maintained at the same temperature as the two suspensions by circulating water from a second Colora bath through a 316 stainless steel coil in the tank. The three tank thermistors and thermometer #2521A (15-35 °C, 0.1 °C divisions, used to measure temperatures of the electrophoresis bath and of conductivity and pH samples) were calibrated against a Hewlett-Packard Model 2801A quartz thermometer in a
large Colora Model NB thermostatted water bath. The actual versus observed
temperature readings for the four sensors are tabulated in Appendix C, Sect.
C.1.4.

The conductivities of samples of suspension and flush water were
measured with a Siebold conductivity meter Model LTA using a Siebold Type
LI probe. The conductivity meter was periodically calibrated against KCl
solutions of known concentration. The conductivity of KCl solutions at
given concentration and temperature conditions can be obtained from standard
reference sources (120). A calibration curve relating the concentration
of NaCl in solution to the measured conductivity is given in Appendix C,
Sect. C.1.5. This curve can be used to determine the NaCl content of the
solutions at higher electrolyte concentrations.

A Corning Model 101 digital electrometer with a Fisher combination
electrode was used to measure the pH of the solutions. The pH meter was
frequently calibrated against buffer solutions of known pH.

The zeta-potential of the particles was determined by electrophoresis.
The zeta-potential of the test sections was measured either by electro-osmosis
or streaming potential, depending on the conductivity of the suspension.
These techniques will be discussed separately in Sect. 3.5.

3.4.3 Procedures

Because radioactive decay is a random process, any activity measure-
ment has a certain degree of imprecision associated with it. This imprecision
is greatly compounded when the measured quantity does not differ signifi-
cantly from the background activity (see discussion in Appendix C, Sect.
C.2.1.4). The presence of the radioactive suspension in the test section
leads to a fairly high background activity. Thus, depending upon the initial particle deposition rate, accumulation measurements were made by operating the double-loop system in one of the following two modes:

i) continuous counting mode. In this mode, the counter is left to operate continuously as the suspension is pumped through the test section. This mode of operation was used when the initial rate of deposition was reasonably fast, i.e. when the negatively-charged particles deposited on a positively-charged 2VP/S-coated surface or on to a negatively-charged Formvar surface at high electrolyte concentrations.

ii) discontinuous counting mode. In this mode, the pump is periodically stopped and the radioactive suspension is flushed out of the test section before it is counted. At the end of the counting interval, the flush solution in the test section is displaced by the particle suspension and flow is resumed. This mode was used when slow deposition rates were encountered, e.g. deposition on a Formvar surface at low electrolyte concentrations.

The discontinuous method suffers from several disadvantages compared to the continuous method, especially when particle release occurs. A detailed description of the two modes of obtaining particle accumulation data as well as a discussion of their limitations is given in Sects. 3.4.3.1 and 3.4.3.2.

Since there is no suspension background present, particle release measurements can be made using the continuous counting mode. The procedures for measuring release rates are discussed in Sect. 3.4.3.3 along with their limitations.
To eliminate cross-contamination when, for example, release is being measured using the suspension of non-radioactive particles, the original suspension in the test section is first exchanged with flush water before introducing the second suspension. Thus, exchanges between suspension and flush solution in the common section of the double-loop system can occur many times during the course of a single experimental run particularly if particle accumulation is measured using the discontinuous method. Because of the mixing which inevitably takes place during the displacement process, the many exchanges act cumulatively to downgrade the suspensions. This downgrading can manifest itself in one of two ways. If, for example, it is felt desirable to maintain the concentration of particles in each suspension as constant as possible, the suspension-flush water exchanges result in a considerable loss of particles from the system. On the other hand, if the objective is to minimize particle losses, these exchanges lead to a considerable dilution of the suspensions. In order to find the exchange procedure which best compromises loss and dilution, the following experiments were carried out.

One of the loop tanks was filled with a 0.1 N. KCl solution and the flush tank with distilled water. After filling the installed test section with distilled water, the loop was broken at the exit of the common section. The loop tank exit valve was opened and the effluent from the common section was collected in 5-ml. lots. When all traces of flush water had been removed from the common section (as indicated by conductivity measurements), the loop valve was closed, the flush tank exit valve was opened and the collecting started anew. By measuring the conductivity of each 5-ml. sample, it was possible to estimate the cumulative amounts of both distilled water (flush
water) and KCl solution (suspension) in the effluent as a function of the total throughput for each of the two types of exchanges.

On the basis of these results, the following optimal exchange procedures were devised. When exchanging flush water in the test section with a suspension, the first 70 ml. of solution from the common section was displaced to the active filter or the inactive drain. A 100 ml. "flush" burette was provided to assist in this operation. The loop pump could then be turned on. When exchanging suspension for flush water, the first 70 ml. was displaced to the suspension tank, via the appropriate 100 ml. "suspension" burette provided for this purpose. To remove all traces of suspension from the common section for counting purposes or to prevent cross-contamination, an additional 200 ml. was flushed to the active drain filter or to the inactive drain tank. The maximum change in concentration of either suspension resulting from a two-step exchange cycle carried out as described above was about 0.5%.

Three series of deposition measurements were carried out corresponding to the three batches of radioactive particles whose production was described earlier (Sect. 3.2.3). At the start of each series, approximately 1/3 of the particle batch was added to 400 ml. of freshly distilled and deionized (Calgon mixed-bed cartridge deionizer) water in a wide-mouth 16-oz. bottle. The contents of the water-cooled bottle were dispersed by simultaneous magnetic stirring and ultrasonic agitation. The progress of the dispersion process was followed by measuring the change with time of the cluster-size distribution using the Wild microscope. When an adequate degree of dispersion (>95% single spheres) had been obtained, the suspension was added through the entry port of the radioactive tank by means of a glass funnel. Another 3600 ml. of distilled and deionized water was added to
dilute the particle suspension to the desired starting concentration. Only in the last series of runs was a non-radioactive suspension made up in a similar manner and placed in the inactive tank.

The remaining two-thirds of each particle batch was used for calibration and make-up purposes. In fact, the lack of sufficient particles to restore the suspension concentration to a predetermined level was the signal to end a given series. In this manner, it was possible to complete 12-20 separate deposition runs for each batch of particles.

Between the experiments of a given series, the suspension in each tank was stirred continuously. At the end of each series, the radioactive suspension was drained to the active filter. The non-radioactive suspension was emptied to the inactive drain tank and discarded. Both loops were then decontaminated by filling their tanks with 0.1 N NaOH solution and circulating it for several hours. After a second application of NaOH solution, the double-loop system was flushed continuously until no further change in the conductivity (or radioactivity) of the effluent was observed.

3.4.3.1 Accumulation Measurements - Continuous Mode

In the procedure to be described below, it will be assumed, for the sake of completeness, that both loop tanks are filled with their respective particle suspensions.

At the start of each experiment, the two constant temperature baths were switched on to bring the contents of the two loop tanks and the flush tank up to the operating temperature. At the same time, all of the measuring instruments including the counting system, the pressure-transducing system, the electrometer (Sect. 3.5.3.2), the two recorders, the pH and
conductivity meters, and the electrophoresis water bath (Sect. 3.5.2) were also turned on to allow a sufficient warm-up period before any readings were taken. While the instrumentation and the various tank solutions were warming up, the radioactive and non-radioactive suspensions to be used as make-up were prepared by ultrasonically dispersing preweighed quantities of particles in measured amounts of distilled and deionized water. The approximate make-up requirements for any given experimental run could usually be estimated on the basis of the experience gained in the previous run.

A freshly coated and dried test section was installed in the system. It was found that the test section could be completely filled with flush water and that all traces of air could be eliminated from the system by adhering to the following sequence of steps (given with reference to Fig. 3.13):

i) Vent valve 9 was opened.

ii) By opening the flush return valve 10, the common section could be filled with flush water from bottom to top. The filling, which was carried out very slowly, was stopped whenever the flush water level reached a pressure port to allow any air trapped within the pressure lines to be flushed towards the common section. Pressure line flushing was carried out using a glass syringe filled with distilled water.

iii) When the flush water level reached the vent line, value 10 was closed.

iv) Flush valve 5 was opened.

v) By quickly opening and then closing valves 9, 3, 4, 17 and 18, any bubbles of air which may have been present in their respective lines were flush out.

With valve 10 reopened, the loop pump was then switched on to circulate flush water through the test section. The circulation of flush water provided a means of exposing the existence of air bubbles in the system (if
present, these invariably became lodged in the test section), and also of testing the reliability of the seal between the test section and the entrance and exit sections before introducing the radioactive suspension to these parts. It also assisted in adjusting the temperature of the common section components to the operating value and in mixing the contents of the flush tank.

Samples of the suspensions in the two loop tanks were withdrawn using the tank sample lines (valves 15 and 16) for conductivity, pH, and particle concentration measurements. When withdrawing suspension samples, at least 40 ml. was flushed through the lines (and poured back into the appropriate tank) before the sample (~20 ml. in a 100 ml. volumetric cylinder cut down to hold 30 ml.) was taken. A sample of the flush water for conductivity and pH measurement was similarly withdrawn through the entrance section sample line (valve 17). Conductivity and pH measurements were made by placing the conductivity probe and the pH electrode directly into the sample. Readings from the conductivity meter were taken at the two dial temperatures which bracketed the actual temperature of the sample (measured with thermometer #2521A), and the final conductivity value was estimated by a linear interpolation. The pH measurements were also temperature corrected. The concentration of particles in the radioactive suspension was determined by pipetting 10 ml. of the sample to a precounted 12 ml. bottle, placing the bottle in the shielded counting chamber and counting it again. The one-minute background and sample counts, considered long enough to obtain a measurement precision (95% confidence) of less than 1%, were usually repeated twice. The concentration of radioactive particles was calculated from the measured activities by subtracting the background from the sample count, correcting for decay, and using the appropriate calibration curve given in
Appendix C, Sect. C.1.1.2. A sample calculation is shown in Appendix C, Sect. C.2.1.1. The concentration of particles in the non-radioactive suspension was found by pipetting 10 ml. of the sample to a 4-cm. path-length absorption cell and measuring its absorbance at 400 nm. against a reference cell containing distilled water. The calibration curve relating the non-radioactive suspension concentration to the measured absorbance is given in Appendix C, Sect. C.1.2.

On the basis of the measured particle concentrations, the two suspensions were adjusted to the same predetermined concentration level by injecting calculated volumes of dispersed make-up particles through the ports provided, using glass syringes. In some experiments, make-up particles were added to the radioactive suspension at various times throughout the run. On these occasions, the make-up suspension was stored in a 100-ml. capped test tube positioned in the cavity between the active tank and its lead shielding wall. After adding the particles, the pH and electrolyte concentrations of the two suspensions and the flush solution were adjusted to the same predetermined values. Changes in pH were affected by adding either NaOH (0.1 N. Certified ACS, Fisher) or HCl (0.1 N. Certified ACS, Fisher) to the solutions by means of syringes. The electrolyte concentration as determined by conductivity measurements (see calibration curve, Appendix C, Sect. C.1.5) was increased by adding preweighed quantities of NaCl (reagent grade, Fisher) to the solutions.

Once all solutions had been adjusted, the background radiation emanating from the newly-installed test section was measured in the following manner. The rectangular collimator was inserted in the counting chamber and the counting stand was locked into position in front of the test section. With the detector removed from the counting chamber, the upper edge of the
test section was aligned with a line scribed across the centre of the inside surface of the collimator. Thus, the height of the inlet to the test section \((x = 0)\) could be obtained by noting the location of the pointer attached to the chamber on the centimetre scale fixed to the stand. With the detector reinstalled and the preferred collimator in place, the counting chamber was then lowered to the desired longitudinal distance as indicated by the pointer. All accumulation measurements made using the continuous counting mode were obtained at \(x = 12.5\) cm. The discontinuous mode of operation, discussed in the next section, offered a more practical method of measuring accumulation as a function of longitudinal distance. With the chamber in position, the test section background was counted twice for 10 minutes, the time of day being recorded in each case to permit the calculation of the decay correction.

After counting the test section background, a final sample of the radioactive suspension was removed for particle concentration, conductivity, and pH measurements. The portion of the sample contained in the capped counting bottle was saved for particle \(\zeta\)-potential measurement by electrophoresis, and at higher electrolyte concentrations for an ex-situ wall \(\zeta\)-potential measurement by electro-osmosis. It was these values of the various parameters which were used in estimating the theoretical initial deposition rate (i.e. at \(t = 0\)).

The flow of flush water through the test section was then stopped. The pressure transducer was adjusted to zero and the pump-motor potentiometer was set to give the desired flow rate. The flush water in the common section was exchanged for the radioactive particle suspension as follows (referring again to Fig. 3.13):
i) Valves 6 and 10 were closed.

ii) Valves 1 and 3 were opened.

iii) The drain valve 6 was opened and enough suspension was displaced by gravity into the common section to fill the flush water burette to 70 ml.

iv) Valve 6 was closed and valve 7 opened.

At this point, the pump, the counting system (recycle mode), and a stopwatch were all started simultaneously. The time of day was recorded for later use in calculating decay corrections. In the continuous mode, the flow of suspension and test section counting were maintained throughout the run. A shorter counting period (eg. 2 minutes) was usually employed initially in order to capture the initial accumulation curve in more detail. When the accumulation rate slowed noticeably, a longer (eg. 10 minutes) counting period was used. Periodically, the counter was taken out of action for short periods of time to allow a measurement of the concentration of particles in the radioactive suspension. In some runs, make-up particles were added to the suspension tank on the basis of these measurements. In those experiments where the suspension medium was essentially distilled water, streaming potential measurements were made at various times throughout the run by briefly (~5 sec.) stopping the flow (see Sect. 3.5.3.2.). The initial wall ζ-potential corresponding to the initial deposition rate was found by extrapolating the wall ζ-potential versus time curve (as obtained from the streaming potential measurements) back to t = 0. Soon after the start of the run, the level of solution in the flush burette was returned to the zero mark by opening valve 13 and draining the contents to the active drain filter. Also, at this time, the electrophoresis and electro-osmosis (when required) measurements were carried out (see Sects. 3.5.2 and 3.5.3.1, respectively).
The duration of runs made using the continuous mode of operation varied between two and eight hours. At the end of each run, the pump was stopped and the suspension remaining in the common section was exchanged for flush water using the following procedure:

i) Valve 3 was closed and the 3-way stopcock 1 was set to connect the suspension return line to the active burette.

ii) Valve 5 was opened and enough flush water was displaced by gravity into the common section to fill the active burette to 70 ml. The flush water flow-rate was always less than the pump circulation rate.

iii) Valve 7 was closed.

iv) Valve 6 was opened and an additional 200 ml. of flush water was displaced into the common section by twice filling and draining the flush burette. Valve 6 was then closed.

v) The 3-way stopcock 1 was set to connect the active burette to the suspension tank and the contents of the burette were drained to the zero mark. The 3-way stopcock 1 was then set to connect the tank with the suspension return line.

With all suspended radioactive particles now having been flushed from the common section, the test section was counted (usually twice). In some experiments, an attempt was made to measure particle release at this point (see Sect. 3.4.3.3). If such a measurement was not carried out, the flush valve 5 was closed, the vent valve 4 was opened, and the test section was drained to the active filter by closing valve 1 and opening valves 6 and 13. The used test section was then removed and replaced with a clean one. With the counting chamber back into position a new background count was measured. A sample of the radioactive suspension was then removed and a final measurement of suspension concentration, pH, and conductivity was made.
Surface concentrations of deposited particles were calculated from the measured radioactivity data in the following manner. First, all counts were corrected for decay. Then, the activity due to deposited particles was evaluated by subtracting the counts due to the suspension and the background from the continuously measured counts. Both the suspension concentration and the background changed to some extent during the course of a run. However, it was generally only possible to estimate the value of these two parameters at the beginning and at the end of each experiment. Thus, in order to provide a realistic assessment of these two contributions to the overall count, it was assumed, as a first approximation, that both changed linearly with time (see discussion in Appendix C, Sect. C.2.1.3). The net activity due to deposited particles was then converted to a surface concentration by making use of the appropriate calibration curve (Appendix C, Sect. C.1.1.1). A first- or second-order polynomial was fitted to an appropriately chosen number of initial data points on the accumulation curve. The initial deposition rate was then found as the first derivative of this fitted relationship at \( t = 0 \). A sample calculation demonstrating the conversion of activities obtained using the continuous mode first to an accumulation curve and thence to an initial deposition rate is given in Appendix C, Sect. C.2.1.3.

Some of the limitations imposed by the continuous counting method thus described arise from the fact that the measurements are obtained using a circulating loop. For example, in order to conserve particles, the radioactive suspension is exchanged into the test section before the pump is turned on and then is exchanged out again after the flow has stopped. Thus, there exists a finite time at either end of the experiments when there are suspended particles present in the test section under conditions (flow, concentration) which are highly different from the desired operating conditions.
However, since the time consumed by these "end effects" is rather small (10-15 sec./exchange) compared to the duration of a run (2-8 hours), their effect on the overall accumulation curve is probably insignificant. Another by-product of the use of a circulating system is that the concentration of suspended particles, a parameter which influences the rate of deposition, changes with time. However, these changes were not very large; usually less than 5% over the extent of any given run. Furthermore, other changes were simultaneously taking place which were expected to have a far more important affect on the deposition rate (e.g., changes in the deposition environment due to the accumulation of particles on the surface). Thus, it was anticipated that even moderate variations in the suspension concentration would not significantly influence the measured accumulation curve. In any event, the primary objective of these accumulation measurements was to obtain an accurate evaluation of the deposition rate at t = 0, a time when the concentration of the suspension was explicitly known.

The flow stoppages required for streaming potential measurements impose further limitations on the method. However, since the total outage time resulting from these measurements never amounted to more than a minute in any given run, it was assumed that their effect could be neglected.

One problem which had not been anticipated was the increase in the background activity which occurred with time. This increase, it was eventually discovered, was due primarily to the accumulation of particles within the entrance and exit sections. Although it had been demonstrated earlier that silica particles did not tend to deposit on smooth teflon surfaces (and, in fact, no significant deposits were observed on other teflon components, e.g. tanks, tubing), the radiation emanating from the end sections continued to increase with every run in a given series. The probable
explanation for this phenomenon is that the milled surfaces of the entrance and exit sections are not microscopically smooth. Thus, it is conceivable that deposition on these surfaces was being promoted by a mechanical trapping mechanism. If particle deposition was, in fact, taking place in the entrance section, then the theoretical condition calling for a homogeneous suspended particle concentration at the test section inlet was not being met.

The approximate method used in estimating the change with time of the overall background activity can also be criticized. However, because the changes in suspension concentration and in the background (especially at \( x = 12.5 \text{ cm.} \) were usually small, the overall accumulation curves were not greatly influenced no matter what particular functional relationships were chosen to represent the changing suspension and background activities. In fact, it is the initial deposition rate which is most sensitive to this choice. The use of a linear relationship to describe the time-dependency of the overall background activities results in a maximum change of only about 4% in the corrected compared to the uncorrected initial deposition rate (calculated by assuming that the overall background remains constant during the run).

3.4.3.2 Accumulation Measurements - Discontinuous Mode

The discontinuous mode of making particle accumulation measurements was identical to the continuous mode except that at intervals throughout the experiment, the flow was stopped and the suspension was flushed out of the test section before the latter was counted. Thus, all of the preparatory arrangements and the exchange procedures outlined in the previous section also apply here. In fact, the counting system was invariably in operation during those periods when the suspension was being circulated through the
test section, in the event that the continuously-measured counts might yield a more detailed description of the accumulation curve.

Thus, at a prechosen time after the start of the run, the pump was switched off, and the suspension in the common section was exchanged for flush water. After flushing an additional 200 ml. through the common section in order to remove all traces of suspension, the test section was counted, usually for 10 minutes. At the end of the first count, the test section was flushed with another 100 ml. of flush water and counted a second time. If there were any discrepancies between the two measurements, the flushing and counting procedure was repeated until the activity measured was (statistically) constant. A sample for suspension concentration measurement was usually withdrawn at this time. In some cases, particle make-up was added to the active tank in accordance with the measured value.

In several experiments, where the deposition rate was, in fact, fast enough that the accumulation data could be obtained using the continuous mode, the discontinuous method was applied in order to measure deposited particle concentrations as a function of longitudinal distance as well as time. Once the test section had been flushed of suspension, the counting chamber was either raised or lowered to the required position prior to making each distance-dependent count. Only the rectangular (differential length) collimator was used for these measurements. Because the background activities (obtained at the start and finish of each experimental run) were also distance-dependent, they too had to be measured at each longitudinal location.

Prior to restarting the circulatory flow, the pressure transducer was rezeroed. Then, after all of the activity measurements had been completed, the flush water in the common section was exchanged for the
radioactive particle suspension and the loop pump was switched on. Circulation was continued until the next discontinuous counting period.

The surface concentrations of deposited particles were calculated from the radioactivity measurements in the following manner. First, all counts were corrected for decay. By subtracting the background activity from the discontinuously measured counts, the contribution due solely to deposited particles was determined. As in the case of the continuous mode, it was again necessary to assume that the background radioactivity varied linearly with time during the course of the run. The net count rate was then converted to a local surface concentration of particles by employing the appropriate calibration curve (Appendix C, Sect. C.1.1.1). The initial deposition rate was determined by one of two methods. Usually, the accumulation data were fitted to a second-order polynomial. The initial deposition rate in these cases was given by the first derivative of the fitted relationship at \( t = 0 \). In other experiments the deposition rate was so low that such a formal procedure was not warranted by the poor precision of the data. In these cases, the initial deposition rate was determined as the slope (at \( t = 0 \)) of the line which by inspection seemed to best represent the available data points. A sample calculation for an accumulation experiment carried out using the discontinuous mode is presented in Appendix C, Sect. C.2.1.2.

The discontinuous method shares all of the limitations listed for the continuous mode. Some of these are magnified by virtue of repetition in the discontinuous mode. For example, the concentration of particles in suspension decreases even more significantly during each run because of the dilution which occurs with each two-step exchange cycle. It is this loss of particles from the system which determines the upper bound on the number of discontinuous activity measurements which can be made over the course of a
single experiment. To conserve particles, between four and eight determinations were made, the usual number being six. As a result of this lack of detail, it was difficult to accurately assess the initial deposition rate in some experiments. The total time spent in making exchanges in the discontinuous mode is also much greater than in the continuous method. However, because the number of exchanges was never large (<16), the total exchange time (<4 min.) could still be considered negligible compared to the actual run time (6-8 hr.).

In addition, use of the discontinuous method creates a number of other possible shortcomings. First, the removal of all traces of particles in suspension must be assured before any measurement of deposited particle concentration takes place. The thoroughness of the displacement procedure was checked by repeating the flushing and counting steps a number of times. Secondly, when carrying out the flushing process, care must be taken not to disturb the particle deposit. Thus, rather than risking the possibility of large pressure transients created by switching the loop pump on and off, flush water flows were achieved by hydrostatic pressure differences. The flush water flow rate was always less than the experimental circulating flow rate. In addition, attempts were made to match the chemistry conditions (pH and electrolyte concentration) of the flush water to that of the suspension. Such matching was generally possible except at the lowest electrolyte concentrations (essentially distilled water) where the specific ion content of the suspension was not known. However, even under these circumstances, the pH condition of the various solutions was adjusted to the same value.

The occurrence of particle release further reduces the accuracy of the discontinuous measurement technique. If release by diffusion is
performing a role in the accumulation process, deposited particles would continue to transfer from the test section surface into the flush water during the counting period. Thus, it is conceivable that a significant change in the concentration of deposited particles could take place during each period, especially when it is lengthened to accommodate repeated flush and count procedures or distance-dependent surface concentration measurements. Such changes would alter the accumulation curve and hence given an erroneous value for the initial deposition rate. This problem can be minimized by ensuring that the overall counting time is only a small fraction of the actual running time. Of course, if release does not occur, the problem automatically vanishes.

Estimating the changing background activity without specific knowledge of its variation with time may also lead to large inaccuracies, especially for those experiments where deposition is measured as a function of longitudinal distance. Radioactive particles which have deposited in the entrance and exit sections contribute quite heavily to the activities measured near the ends of the test section. Not only does this large background lead to a substantial statistical error in these measurements, but also the change in the background during the course of a run was generally quite significant compared to the change in activity due to deposition in the test section itself. Thus, if the background changed in some more complex way, the assumption of a linear variation could lead to serious inaccuracies. The only foreseeable way of overcoming this problem would be to remeasure the background during each counting interval by temporarily removing the test section from the loop. However, because such a procedure would greatly increase the chances of altering the deposit (especially if the test section was drained before removal), its practicality seems somewhat doubtful. Thus,
since accumulation results obtained in the vicinity of the test section extremities could only be viewed with some skepticism, measurements of particle deposition as a function of longitudinal distance were generally not pursued.

3.4.3.3 Release Measurements

In an early series of experiments carried out to assess the performance of the double-loop system, several attempts were made to measure release by passing flush water through test sections on which considerable particle deposition had already occurred. The activities emanating from the test sections showed no change even over periods as long as 24 hours, indicating that no release had taken place. Thus, rather than complicate procedures unnecessarily, release rate measurements were generally carried out only after the accumulation curve had been completed. The objective of these experiments, therefore, was primarily to determine whether or not release took place under the particular conditions of each run. If measurable release did occur, the run could be repeated following the more rigorous approach described in the introductory section 3.4.1.

In order to shed some light upon the specific mechanism by which deposited particles were removed from the test section wall, three different types of release measurements were undertaken:

i) release into stagnant flush water,

ii) release into flowing flush water,

iii) release into flowing non-radioactive suspension.

Generally, each accumulation run was followed by some kind of release measurement. In some cases, two or even all three types were attempted on the same
contaminated test section. The use of the non-radioactive suspension was restricted to the last series of runs. All release rate measurements were made at the longitudinal centre of a test section (x = 12.5 cm.). A more detailed description of the procedures involved in the three types of measurements is given below.

After the completion of the accumulation experiment, all traces of radioactive suspension were flushed out of the test section. Regardless of the type of release experiment planned for it, the test section was then counted. To measure release into stagnant flush water, this solution was simply allowed to stand in the test section for a specified period of time. The test section was then flushed with at least 200 ml. of fresh flush water and counted again.

In the second type of release measurement, valve (10) was opened and the pump was switched on to circulate flush water from the flush tank through the test section and back to the flush tank. At the same time, a stopwatch and the counting system operating in the recycle mode were also turned on. Using the pressure drop readings as a guide, the pump speed controller was adjusted to yield a flush water flow rate which was identical to the suspension flow rate employed during the accumulation measurement. After the passage of a specified interval of time, the pump and the counting system were turned off. In the event that the flush water had become contaminated with particles removed from the test section or other components of the common section, the solution was usually drained and replaced prior to the next accumulation experiment.

Before measuring release using the flowing non-radioactive suspension, a sample of this suspension was taken for pH, conductivity, and particle concentration (absorbance) determinations. Any significant differences
between these parameters and those measured for the radioactive suspension were then adjusted. To determine the contamination level, the activity of a 10-ml. aliquot was also measured. The contents of the capped counting bottle were saved for subsequent electrokinetic determinations. The flush water in the common section was then exchanged for the non-radioactive suspension following a procedure similar to the one previously described for displacing flush water with the radioactive suspension (see Sect. 3.4.3.1). After valves 4 and 8 had been opened, the pump, stopwatch, and counting system (in recycle mode) were started simultaneously. The suspension flow-rate was adjusted to the value which had been used during the accumulation part of the experiment. The activity of the test section was measured continuously until a specified time had elapsed. At this point, the pump and the counting system were switched off. The non-radioactive suspension in the common section was then exchanged for fresh flush water (procedure is similar to exchange of radioactive suspension with flush water described in Sect. 3.4.3.1). The test section was flushed with an additional 200 ml. of flush water and then counted. A final sample of the non-radioactive suspension was taken for pH, conductivity, absorbance, and activity measurements.

After the release rate measurement(s) had been completed, the test section was drained and removed from the system. A clean test section was then positioned between the entrance and exit sections and the final background activity was counted.

The calculation of the variation in surface particle concentrations from the activities measured in the different release experiments is very straightforward. In each case, once all counts had been corrected for decay, the net contribution to the total activity made by the particles remaining on the wall was determined by subtracting the background activity from the
gross counts. Since the background activity at the start of the release experiment could not be measured, it was assumed to remain constant over the whole interval at the value measured at the end. Thus, this same value was used as the final background activity for the accumulation part of the run. Each net count rate was converted to a particle concentration using the appropriate calibration curve (Appendix C, Sect. C.2.1.1). In those cases where the measured concentration of radioactive particles decreased with time, the release rate was estimated as the slope of the straight line which best fit the initial data points of the release curve. Since these calculations are rather similar to those already performed for the accumulation measurements, a sample calculation has not been included.

As might be expected, the procedures for measuring particle release share many limitations in common with the methods used for obtaining accumulation data. For example, it is necessary to account for discrepancies which could occur because of the time spent in exchanging solutions, because of declining particle concentrations in the case of the non-radioactive suspension, and because of chemically ill-matched solutions. However, because these have already been discussed in detail in the previous two sections, they will not be further belaboured here.

In addition, the release procedures can lead to the creation of at least two new problems. First, if particles which have deposited in the entrance or exit sections are also released during the measurement, the background activity will no longer remain constant. This difficulty is minimized by making the measurement at the test section centre, the position where the recorded activities are least influenced by occurrences in the end sections. Secondly, again because circulating systems are involved, the release of deposited particles into a flowing solution gradually increases the contamination
level of that system. However, the internal volume of the common section components is small (-60 ml.) compared to the volume of either the flush water system (8.9 l.) or the non-radioactive suspension loop (4.0 l.). Thus, if only release from the test section surface was involved, the increase in background due to contamination would be insignificant considering the dilution factors involved. However, it is conceivable that gross amounts of contamination could be released into the flowing solution from other surfaces in the common section (e.g. end sections, pump). In this case, the extra background could rise to levels which seriously affect the validity of the measurements. This problem was dealt with by keeping a close account of the change in activity of the two solutions during each release experiment. In addition, when measuring release into the flowing non-radioactive suspension, the final concentration of radioactive particles in the test section was found by flushing all traces of the suspension from the common section with a fresh flush solution.

3.5 Measurement of Zeta Potential

3.5.1 Introduction

The calculation of the electrical double layer interaction energy between a suspended particle and the test section surface requires knowledge of the Stern potentials (ψδ) of the two surfaces (see Sect. 2.1.1.1). Unfortunately, a direct measurement of the ψδ is not possible. However, it is possible to experimentally determine the zeta potential (ζ) of each surface by exploiting any of the four electrokinetic effects.

These effects arise when there is a bulk relative motion between the charged solid and solution phases. For example the application of an
external electric field can induce movement between the two phases. Thus, if the solution is stationary and the particles move towards one of the electrodes, the phenomenon is termed "electrophoresis." If the solid surface is restrained such that the solution itself moves, electro-osmosis results. On the other hand, mechanically initiated motion gives rise to an induced electric field and a transport of electricity. Thus, particles sedimenting in a stagnant solution generate a "sedimentation potential" whereas the forced convection of solution through a stationary channel induces a "streaming potential." The electrokinetic or "zeta" potential is the potential difference between the plane of slip and the bulk solution when relative motion occurs. Theoretical expressions relating the zeta potential to the measured electrokinetic effect have been reasonably well established for all of the electrokinetic phenomena (121,21).

How does the measured zeta potential compare to the Stern potential? Another way of formulating this question is to ask how closely does the hydrodynamic slip-plane \((\zeta\)-plane\)) coincide with the outer Helmholtz plane \((\psi_\delta\)-plane\)) of the Stern layer? [It should be noted that the OHP and slip-plane concepts are only convenient abstractions of the physical reality. The outer Helmholtz plane of the double layer is the plane beyond which the charge distribution obeys Poisson-Boltzmann statistics. Any deviations from ideality such as finite ion volume and specific adsorption effects are assigned to the Stern layer. However, in reality, the double layer becomes progressively more ideal with increasing distance from the surface. Similarly, the concept of a slip-plane tacitly presupposes the existence of a fluid whose viscosity is infinite near the surface and jumps to the bulk value at the plane of slip. It would be more realistic to treat the viscosity as a continuous function which decreases gradually with distance from the surface. However,
since years of accumulated experience have shown that both models work well in practice, these concepts will be preserved here.] The Stern layer is acknowledged to be at most only a few angstroms thick. The position of the slipping plane is much more elusive. It is generally considered to lie beyond the OHP and thus in the diffuse region, for at least two reasons. First, the interaction of polar solvent molecules such as water with the high electric field \( \alpha \frac{\partial \psi}{\partial h} \) in the vicinity of the surface is expected to promote a boundary layer of structured water with an anomalously high viscosity (122). Accounting for this higher viscosity layer by means of the simple slip-plane model has the effect of moving the slip-plane further out into the solution. Secondly, all solid surfaces are microscopically rough (123). During shear, the moving liquid will not penetrate the depressions but instead will tend to glide across them. Thus, again, the effective slipping-plane will be moved away from the surface. Eversole and Boardman (124) have estimated that the distance between the interface and the slip-plane for glass- or ceramic-water systems varies between 8 and 63 Å. Overbeek (121, p. 229) criticizes the latter value as being unrealistically high. In a separate study, Hunter and Alexander (125) used the Eversole and Boardman technique and located the slipping plane at 10 Å from the kaolinite surfaces. Thus, for reasonably smooth surfaces, it appears probable that the slip-plane is located approximately 10 Å from the surface, whereas the OHP is some fraction of this distance.

Since the OHP, by definition, forms one boundary of the diffuse layer, the potential across this layer falls monotonically from a value \( \psi_\delta \) at the OHP to zero in the bulk solution. Thus, although changes in \( \zeta \) reflect changes in \( \psi_\delta \), the magnitude of the zeta potential is always less than that of the Stern potential. However, at very low electrolyte concentrations,
the double layer thickness greatly exceeds the distance between the OHP and the shear plane, and $\zeta$ approaches $\psi_0$. In the present study, the value of $1/\kappa$ varied from 18 to 1350 Å and was generally greater than 100 Å. Thus, it will be assumed here that $\psi_0 = \zeta$. This assumption is commonly made in the application of the DLVO theory in studies of colloid stability (e.g. 39,40). In fact, although they estimated $\zeta$ and $\psi_0$ separately, Hunter and Alexander (125) found that their kaolinite coagulation results could be more reasonably interpreted by replacing $\psi_0$ by $\zeta$ in their calculations. Recently, Lyklema (126) used the results of stability studies on a sodium iodide sol to obtain independent estimates of $\psi_0$ and demonstrated that in each case, the OHP potential coincided with the zeta potential (measured by electrophoresis) within experimental error.

In the present experiment, the zeta potential of the particles was determined by micro-electrophoresis (Sect. 3.5.2) whereas that of the wall was obtained by electro-osmosis (Sect. 3.5.3.1) or by means of a streaming potential technique (Sect. 3.5.3.2), depending on the conductivity of the suspension.

### 3.5.2 Particle Zeta Potential - Electrophoresis

The zeta potential of the particles was determined from mobility measurements obtained using a Rank Bros. Mark II micro-electrophoresis apparatus. The apparatus consists essentially of a transparent cell containing a sample of the particle suspension, a system of electrodes for applying a potential gradient within the suspension, and a microscope for observing the resulting motion of the particles. The average electrophoretic mobility ($\mu$m/sec.)/(volt/cm.) is obtained by measuring the time taken for a number of
individual particles to cover a given distance (as determined by a calibrated grid in the microscope eyepiece) in a known potential gradient. The mobility can then be converted into a zeta potential using the appropriate theoretical relationship. The theory and experimental technique of micro-electrophoresis have been reviewed by Brinton and Lauffer (127), Shaw (128) and more recently, by Dukhin and Derjaguin (122). Details of the experimental apparatus and procedures as well as the theoretical methods used in the present study are presented below.

The cells used in micro-electrophoresis studies are usually constructed of optical glass and are rectangular or circular in cross-section. Although the Rank Bros. instrument was designed to accommodate both types of cells, a single rectangular cell (approximately 0.1 x 1.0 cm. in cross-section and 7 cm. in length) was employed for most mobility measurements. For particles having an average diameter of approximately 0.5 μm the manufacturers recommend the use of the thin-walled cylindrical cell over the rectangular or "flat" cell because the superior heat transfer qualities of the former mean fewer problems from convective currents, and because its smaller cross-sectional area results in lower current densities at the electrode surfaces and hence less likelihood of degassing and polarization. However, initial experimentation with the cylindrical cell revealed that, under the concentration conditions planned for the deposition experiments, significant sedimentation to the bottom surface of the cell (axis horizontal) occurred during the time required to obtain the necessary number of mobility measurements. The accumulated material disturbs the electro-osmotic velocity distribution (see discussion below) and hence, results in measurement errors. This difficulty can be overcome by using a rectangular cell whose longer cross-sectional side is vertical. In this case, sedimenting particles fall onto an electro-osmotically
unimportant surface and thus do not significantly influence the measurement which is taken at the plane mid-way between the top and the bottom of the cell. In addition, it was found that the plastic coating required by the electro-osmosis measurements (Sect. 3.5.3.1) could be applied more easily to the rectangular cell than to the cylindrical one.

During the measurement, the cell is clamped within a constant temperature bath. The temperature of the bath water was maintained at 25.0 ± 0.2 °C, equivalent to the operating temperature of the deposition runs. A sample of the suspension was transferred to the cell from a sample bottle using a clean glass syringe. The capacity of the cell was approximately 5 ml.

Once the sample was in position, electrodes sealed into standard-taper glass fittings were placed in mating electrode compartments at either end of the cell. The electrodes were used to apply a d.c. potential gradient along the length of the cell. The glass fittings served to seal the ends of the cell in order to prevent evaporation and, hence, troublesome convective currents within the cell. Each electrode was constructed of a 13 x 20 x .013 mm. sheet of bright platinum rolled into a cylinder. The platinum electrodes were occasionally "reblacked" in a solution of 3% platinum chloride containing ~0.025% lead acetate (Yellow Springs Instrument Co.). After each electrophoresis measurement the blacked electrodes were thoroughly washed with distilled water and stored in more distilled water until required for the next measurements.

Direct illumination, provided by a 12V, 100-watt quartz iodine lamp, is used for the flat cell. The light beam can be focused at any position within the cell by means of a low power darkground condenser. In
order to reduce convection effects, the beam is passed through a heat filter prior to entering the cell.

The movement of the particles within the cell was observed with a microscope employing a 20x objective and 10x eyepiece. The microscope was attached to a micrometer stage and hence could be focussed at any position along the line normal to, and passing through the centre of, the large face of the cell across its entire smaller width. To register the mobility of the particles, the eyepiece contains a graticule with a square grid. The graticule was calibrated against a "stage micrometer" (see Appendix C, Sect. C.1.5.4) and was found to have an average grid spacing of 63.93 ± 0.05 μm.

The potential gradient was applied using a d.c. supply which is stabilized against load and mains voltage variations. The overall voltage drop between the two electrodes was read from a voltmeter. An ammeter for measuring the current through the cell was also supplied. Both the voltmeter and ammeter were recalibrated prior to use (Appendix C, Sects. C.1.5.1 and C.1.5.2, respectively). In order to determine the potential gradient from the measured voltage drop, it was necessary to establish an effective inter-electrode distance for each cell. If $R$ is the resistance between the two electrodes when the cell is filled with a solution of known conductivity, $λ$, and $A$ is the cross-sectional area of the cell at the plane of viewing, the inter-electrode distance, $λ$, is given by $λ = RAλA$. The procedures used for measuring these quantities are given in Appendix C, Sect. C.1.5.5. The effective inter-electrode distance for the rectangular cell used in the present study was found to be 7.68 cm.

When a potential difference is applied to the cell, both the particles (electrophoresis) and the solution (electro-osmosis) are set into motion. A correct interpretation of the electrophoretic results requires
knowledge of the liquid motion. When the double layer thickness, \(1/\kappa\), is small compared to the half-thickness of the cell, \(b\), the electro-osmosis manifests itself as a constant velocity flow at the four walls of the channel. Since the cell is closed, this electro-osmotic movement generates a difference in pressure between the extremities of the cell. As a consequence of this pressure difference, a return flow down the centre of the channel ensues. Thus, there exists within the cell cross-section a locus of streamlines where the fluid velocity is zero. The location of these "stationary levels" can be determined from the solution of the equation of hydrodynamic motion describing the steady-state flow in the channel. Starting from the no-slip solution given by Cornish (129), the velocity distribution due to electro-osmosis in a closed rectangular cell is derived in Appendix B, Sect. B.1. These results show that for a rectangular cell of half-width \(a\) and half-thickness \(b\), if \(a/b > 2\) and for measurements taken at the centre of the cell width, the stationary levels are symmetric about the mid-plane of the channel and are located at

\[
y/b = \pm \left( \frac{1}{3} + \frac{128}{\pi^8} \frac{b}{a} \right)^{1/2}
\]

[3.2]

where \(y\) is the distance from the mid-plane. Eq. [3.2] has also been derived by Komagata (130). For the cell used in the present experiments, \(a = 0.494\) cm., \(b = 0.0545\) cm. (see Appendix C, Sect. C.1.5.5), and hence \(y/b = \pm 0.616\).

The true electrophoretic velocities of the particles are measured with the microscope focussed at the two stationary levels. The stationary levels were located by moving the microscope focus a distance of 0.384 \(b\) and 1.616 \(b\) from the front inside face of the cell. Once the microscope
was correctly positioned, a potential difference was applied, and the electrophoretic velocity was determined by measuring the individual times taken for a number of particles to traverse a prechosen number of grid spaces of the eyepiece graticule. To eliminate polarization effects, each particle was timed over the same distance in both directions. The necessary field reversal was attained by means of a simple switching circuit provided with the instrument. Random errors due to Brownian motion and depth-of-field effects were minimized by measuring the velocity of at least 10 different particles. In some experiments, 20 separate determinations were made. The same number of measurements were taken at both stationary levels to assure that their positions had been properly located. The measured velocities were converted to an average mobility by dividing by the applied potential gradient.

In order to correctly interpret the experimental mobility in terms of a \( \zeta \)-potential, an understanding of the various effects which play a part in electrophoresis is required. Almost immediately after the application of the d.c. field to the suspension in the cell, each particle is accelerated to a constant velocity parallel to the direction of the field. At this steady-state condition, there are thought to be four balanced forces acting on the particle. First, and most importantly, there is a force exerted by the electric field on the particle charge. Thus, for example, a negatively-charged particle will always migrate towards the positive electrode. Secondly, there is a viscous retarding force which opposes the migratory motion of the particle. For a solid sphere which is large compared to the molecules of the liquid, this retarding force is given by Stokes' law.

The two remaining forces are due to the presence of electrolyte ions in the solution. The d.c. field exerts a net force on the excess ions in the diffuse layer which is transferred to the molecules of the solvent.
Since the excess charge is opposite in sign to the charge on the particle, the resulting electro-osmotic flow causes an additional retarding force. This effect is called "electrophoretic retardation." Because of the relative motion between the charged particle and its ionic atmosphere and because a finite time is required to re-establish an equilibrium double layer, the charge centre of the diffuse layer always lags behind the centre of the particle. The coulombic attraction between the separated charge centres results in another force, usually a retarding one, called the "relaxation effect." Generally, the latter two forces are complicated functions of several physical parameters of the colloid system, such as the zeta potential, the particle size, the thickness of the double layer, and the valence and mobility of the specific ions in the solution.

The theory of electrophoresis has historically evolved around the problem of correctly interpreting the role played by retardation and relaxation effects. The history of this evolution has recently been reviewed by Overbeek and Wiersema (131). Major landmarks in the development of a comprehensive theory of electrophoresis may be found in the works of Smoluchowski (132), Hückel (133), Henry (134), Overbeek (135), Booth (136), and Wiersema et al. (137).

The theory of Wiersema et al. is probably the most inclusive theory available as it not only accounts for the effects of retardation, relaxation, and surface conductance, but it also can be used for \( \zeta \)-potentials as high as 150 mv. However it still suffers from a few shortcomings. It assumes that the particle (and the adjacent layer of liquid which moves with it) is a non-conducting rigid sphere and that the physical properties of the fluid retain their bulk values up to the slip plane. Furthermore, this analysis presupposes that the distribution of ions in the diffuse layer is represented by the
Gouy-Chapman model (see Sect. 2.1.1.1). Wiersema et al. simultaneously solve the Poisson equation which governs the distribution of electrical potential, the Navier-Stokes' equation which describes the fluid motion, and the transport equations which control the movement of the individual ions in the solution. The solution is obtained by the method of successive approximations using an electronic computer. Their results are given in tabulated form in terms of dimensionless variables.

Wiersema et al. have used these results to establish the range of validity of the various approximate analytical treatments. Their analysis indicates that many of the mobility results encountered in the present study cannot be correctly interpreted by any of the existing analytical solutions. Hence, all mobility results obtained here were converted to $\zeta$-potentials using the theoretical computations of Wiersema et al. A sample calculation demonstrating this procedure is shown in Appendix C, Sect. C.2.2.2. Aside from the measured mobility, the technique requires knowledge of the double layer thickness, and hence, the concentration of the various ions in the solution. At higher electrolyte concentrations where the predominant ionic species are Na$^+$ and Cl$^-$, these latter data may be determined from conductivity measurements (see Appendix C, Sect. 1.1.5). However, under conditions where the electrolyte is essentially distilled water, it was necessary to estimate the specific ion concentrations from the available pH and conductivity measurements (see sample calculation in Appendix C, Sect. C.2.2.1). In general, this procedure leads to a range of $1/\kappa$ values (depending on the specific ions assumed to be present) and hence widens the 95% confidence bounds placed on the $\zeta$-potential determination.

One interesting feature of the Wiersema et al. model is that in the range $5 \leq \kappa a \leq 50$ ($a =$ particle radius), it predicts a maximum in the
electrophoretic mobility versus $\zeta$-potential curve. This implies that for a fixed value of $\kappa a$ in this range, the mobility cannot exceed a certain maximum value no matter how large the zeta potential becomes. In the present study, a few cases were observed where the experimental mobility exceeded the maximum predicted from the theory. Similar discrepancies have been reported by others (138, 139, 140). In these cases, a $\zeta$-potential cannot be calculated but usually can be inferred by interpolation between data taken at higher and lower values of $\kappa a$. These discrepancies indicate that even this very comprehensive numerical theory does not give a fully accurate description of electrophoretic behaviour.

3.5.3 **Test Section Zeta Potential**

3.5.3.1 **Electro-osmosis**

The streaming potential technique is the preferred method of measuring the zeta potential of the test section surface for two reasons. First, the measurement is obtained in situ. In addition, the average wall $\zeta$-potential can be monitored continuously as particle deposition proceeds. However, for a given value of the $\zeta$-potential, the measured response (streaming potential) is inversely proportional to the conductivity of the suspension. For this reason, it was only possible to obtain accurate measurements for solution conductivities $\leq 20 \mu$mho/cm. Thus, at higher electrolyte concentrations, the $\zeta$-potential of the plastic lining the test section walls was measured ex situ in a similarly-coated rectangular electrophoresis cell.

Prior to coating, the cell was cleaned in a manner similar to the treatment given to each test section. First, the cell was immersed for 10 minutes in hot chromic acid, a procedure which was found to be very effective in removing the plastic film used in the previous measurement. After thorough
flushing with distilled water, the cell was soaked for an additional hour in a distilled water bath to remove all traces of the cleaning agent. To improve the adherence of the plastic to the glass surface, the cell was immersed in methanol for one hour and then dried under vacuum for another 60 minutes. The cell was coated, while being supported vertically in the coating apparatus described in Sect. 3.3.2, following the same procedure as was used to apply a plastic film to a test section. The cell and its associated test section were coated consecutively using the same plastic solution. It was not possible to disassemble the cell in order to measure the uniformity of the coated film. However, since the half-thickness of both the cell and the test sections were approximately the same, it seemed reasonable to assume that the coating results would also be similar. After coating, the cell was allowed to dry in place for about 5 minutes and then was stored under vacuum until required for the next zeta-potential determination.

The wall and particle \( \zeta \)-potentials are obtained simultaneously in the coated cell. The wall \( \zeta \)-potential is responsible for the electro-osmotic flow which occurs when a potential gradient is applied along the axis of the cell. Thus, if the electro-osmotic velocity is determinable at any location in the rectangular cell, the wall \( \zeta \)-potential can be estimated from the equation of electro-osmotic motion derived in Appendix B, Sect. B.1. However, the movement of the liquid cannot be measured directly. But, if the liquid contains suspended particles, the measurement of the apparent electrophoretic velocity at one other position besides the stationary level allows an estimation of the electro-osmotic velocity at this position. The centre of the channel is chosen as the second position because the gradient of the apparent velocity profile is zero and hence, the depth-of-field errors minimal at this location. Thus, when a simultaneous electro-osmotic measurement was required,
at least 10 particles were timed at the centre of the channel as well as at the stationary levels. For a cell with \( a/b \geq 2 \), the wall \( \zeta \)-potential, \( \zeta_W \), was determined using the relationship (see Appendix B, Sect. B.1)

\[
\zeta_W = \frac{8\pi\mu}{e\varepsilon} \left( \frac{1 - \frac{192b}{\pi^2a}}{1 + \frac{384b}{\pi^2a}} \right) \left( v_E - v_0 \right)
\]  

[3.3]

where \( v_E \) is the true electrophoretic velocity (measured at the stationary level), \( v_0 \) is the apparent velocity at the mid-plane, \( \mu \) the solution viscosity, \( \varepsilon \) the solution dielectric constant, and \( X \) the applied potential gradient.

This combined electrophoretic-electro-osmotic technique has been used before (92,130) with cells of rectangular cross-section, but it is not usually appreciated that even when \( a/b \gg 1 \), the electro-osmotic velocity distribution at the centre of the cell width can differ quite significantly from that obtained in a true parallel-plate channel. The ratio, \( \frac{(1 - \frac{192b}{\pi^2a})}{(1 + \frac{384b}{\pi^2a})} \), is, in fact, the correction factor to the parallel-plate expression for \( \zeta_W \) which accounts for the influence of a finite half-width when estimating wall \( \zeta \)-potentials using this technique. Table B.1 (Appendix B) demonstrates that appreciable errors in the calculated \( \zeta \)-potential can result if this correction factor is ignored for rectangular cells with \( a/b \leq 50 \).

In the present experiment, \( a = 0.494 \text{ cm.}, b = 0.0545 \text{ cm.} \), and hence \( \frac{(1 - \frac{192b}{\pi^2a})}{(1 + \frac{384b}{\pi^2a})} = 0.818 \).

For the range of chemistry conditions studied in the deposition experiments, the magnitude of the wall \( \zeta \)-potential is always considerably less than that of the particle. Thus, because electro-osmosis is always a weak effect, the measured values of \( v_E \) and \( v_0 \) never differ significantly from
from one another. As a result, the uncertainties associated with the individual measurements of $v_E$ and $v_0$ are greatly magnified in the calculation of $\zeta_w$. A discussion of the precision of the electrophoresis and electro-osmosis measurements is given in Appendix C, Sect. C.2.2.3.

### 3.5.3.2 Streaming Potential

At low electrolyte concentrations, the $\zeta$-potential of the test section walls was determined by means of a streaming potential technique. This technique is an obvious choice for the present experiments, since, during each deposition run, the particle suspension is being pumped in laminar flow through a narrow test section. The liquid stream carries with it the excess ions in the diffuse part of the wall double layer giving rise to a steady electric current (the "streaming current") along the surface of the test section. The transport of ions by this convective current generally leads to the accumulation of charges of opposite sign at the ends of the test section and consequently, to the appearance of a potential difference along the test section length. This electric field, in turn, gives rise to an electromigration current of ions which is usually directed oppositely to the streaming current.

If the flow path forms an open circuit such that there exists no alternate electrical pathway between the two ends of the test section, the induced potential difference continues to increase until the conduction current exactly balances the convection current. The steady-state potential difference which results in no net current is called the "streaming potential." Expressions relating the channel $\zeta$-potential to the measured streaming potential have been derived for a number of flow geometries. For laminar flow in a parallel-plate channel under conditions where the double layer
thickness is small compared to the half-thickness of the channel, \( b \), where
the solution dielectric constant, \( \varepsilon \), and viscosity, \( \mu \), remain at their bulk values up to the plane of slip, and where surface conductance is negligible, Smoluchowski (141) has shown that

\[
\zeta_w = \frac{8\pi b^3 W \lambda}{3cL} \frac{\Delta E_{str}}{Q}
\]  

[3.4]

In Eq. [3.4], \( W \) and \( L \) are the width and length, respectively, of the test section, \( \lambda \) is the conductance of the bulk suspension, \( \Delta E_{str} \) is the measured streaming potential, and \( Q \) is the suspension flow-rate.

The circulation loop in which the deposition experiments are carried out, however, forms a closed electrical circuit. Thus, although the streaming current in the test section remains the same as for an open circuit, the potential difference induced at the ends of the channel can now be dissipated by conduction through both the test section and the parallel pathway created by the rest of the flow loop. In addition, because all other surfaces in contact with the suspension medium are also electrified, the circulating flow gives rise to streaming currents in each flow segment which makes up the loop. These streaming currents also induce potential differences which further affect the distribution of potential around the circulation system. As a result of these two effects, at steady state in a closed circuit, there is generally a net current flow which must be the same in all segments of the system. If a net flow of current exists, the potential difference measured across the test section will not be equal to the streaming potential.

Although an analysis of the various potential differences induced in a closed flow system is certainly more complicated than in an open one, the complexity is reduced considerably under the present circumstances where
the circulation loop is essentially constructed of only two materials. The
test section has a coated plastic surface and almost all other loop components
are teflon. A theory of the measurement of \(\zeta\)-potentials in complex closed
systems constructed of only two materials is given in Appendix B, Sect. B.2.
The theory shows that a correct determination of the test section \(\zeta\)-potential
in such a system requires two independent potential difference measurements.
If \(\Delta E_t\) is the potential difference measured across the test section, and \(\Delta E_a\)
is a second potential difference measured across a larger portion of the loop
including the test section, then, under the same simplifying conditions used
in the derivation of Eq. [3.4], the test section zeta potential is now given by

\[
\zeta_w = \frac{8nb^3W\lambda}{3eL} \frac{\Delta E_t}{Q} + 4\pi b^2\lambda \frac{\Delta E_t}{Q} + \Sigma_1 \frac{\Delta E_t}{Q} + 4\pi b^2\lambda \Sigma_2 \frac{\Delta E_a}{Q} \]

[3.5]

where \(\Sigma_1\) and \(\Sigma_2\) are systemic constants which depend only on the geometries
of the various flow elements (excluding the test section) of the circulation
loop. The constants, \(\Sigma_1\) and \(\Sigma_2\), must be determined empirically before Eq.
[3.5] can be employed.

The potential difference across the test section, \(\Delta E_t\), was measured
by means of the two bright platinum electrodes installed in the entrance and
exit sections as near as possible to the surfaces which mate with the two
ends of the test section (see Fig. 3.14). A second pair of bright platinum
electrodes, used to measure \(\Delta E_a\), were located in the teflon fittings which
connect the inlet and outlet tubing segments to the entrance and exit sections,
respectively. All electrodes were mounted flush with the surface of the flow
segment so as not to impede the flow of suspension. Bright platinum electrodes
were chosen over their more reversible counterparts because they can be
installed permanently, require little attention, and do not significantly
contaminate the system. Bull (142) has shown that polarization effects with bright platinum electrodes are negligible provided the current drawn from the system is very small. Since a minimal current drain is also required for accurate potential difference determinations, $\Delta E_t$ and $\Delta E_a$ were measured using a Keithley Model 640 Vibrating-Capacitor electrometer with an input resistance of $10^{16}$ ohms. A simple switching arrangement permitted readings from both electrode pairs within quick succession. The measured potentials were recorded continuously by means of an Esterline-Angus Model S-601-S strip chart recorder.

Many of the experimental problems associated with streaming potential measurements have recently been reviewed by Ball and Furstenau (143). These authors suggest that the major source of error in streaming potential measurements is caused by the existence of asymmetric electrode potentials which persist even under conditions of zero flow. These extraneous potentials which are particularly common when polarizable electrodes are used, vary with time in an unpredictable manner. Various methods for eliminating asymmetry effects in potential difference measurements have been devised. Horn and Onoda (144) utilized an R-C circuit in their measuring system to directly null out all background potentials. Korpi and deBruyn (145) incorporated a recorder in their system to aid in the measurement of the instantaneous voltage changes which occur during flow initiation and termination. Somasundaran and Agar (146) have argued that since the asymmetric potentials vary relatively slowly with time, the instantaneous change in voltage initiated by a step change in flow conditions is the true streaming potential.

In the present investigation, the method of Korpi and deBruyn was adapted to the measurement of $\Delta E_t$ and $\Delta E_a$. The measuring technique was very simple. While the suspension was being pumped through the test section at a
known flow rate (as determined by the pressure drop measurement), the electrometer was switched to record the potential difference across the test section. The pump was stopped for a period of about 5 seconds and then turned on again. The recorded change in potential difference at the moment of flow termination was taken as the "true" value of $\Delta E_t$ for the given flow rate. The electrometer was then switched to the second set of electrodes and the flow termination procedure repeated to obtain the true value of $\Delta E_a$.

It is shown in Appendix B, Sect. B.2, that if either $\Delta E_t$ or $\Delta E_a$ is plotted as a function of the flow-rate $Q$, the data should be represented by a straight line passing through the origin. Thus, one method of checking to see if the asymmetry potentials are being correctly accounted for is to measure the $\Delta E_t$ and $\Delta E_a$ generated at a number of flow rates and determine whether the results obey the expected relationships. It was found that the $E$ versus $Q$ curves obtained for a wide range of test section $\zeta$-potentials all followed the expected behaviour (see, for example, Figure 3.18).

The systemic constants, $\Sigma_1$ and $\Sigma_2$, can be evaluated empirically by measuring $\Delta E_t$ and $\Delta E_a$ under condition where the wall $\zeta$-potential has already been determined by an independent method. The two different $\zeta$-potential conditions required to evaluate the two parameters were obtained by using an uncoated test section and another coated with the cationic copolymer 2-vinyl pyridine/styrene. The $\zeta$-potential in each case was determined independently by measuring $\Delta E_t$ in an open flow circuit formed by pumping the solution used to generate the streaming currents from one
loop tank to the other. It is easily demonstrated that for a once-through system, since there is no alternate electrical pathway between the two tanks, the conduction current must exactly balance the convection current in each flow segment of the system. Hence, the potential measured across the test section is the true streaming potential and Eq. [3.4] can be used to evaluate $\zeta_w$.

Thus, experiments designed to evaluate $\Sigma_1$ and $\Sigma_2$ using first an uncoated and then a 2VP/S-coated test section were carried out in the following manner. The active tank was filled with distilled water (of known conductivity). With this solution circulating through the active tank, both $\Delta E_t$ and $\Delta E_a$ were measured as a function of $Q$ using the flow interruption technique. The measurements of $\Delta E_t$ ($= \Delta E_{str}$) were then repeated with the solution being pumped from the active tank to the non-active tank. Because of the differences in head created between the two tanks during the latter measurements, it was necessary to simultaneously manipulate stopcock 2 (see Fig. 3.13) and switch off the pump in order to achieve a true no-flow condition. This procedure resulted in a noisy electrometer signal and hence, to a decline in the precision of the open circuit measurements. The $\Delta E_a$ readings were also quite noisy, presumably because of the turbulent flow in the vicinity of these electrodes.

A comparison of the $\Delta E_t$ values measured in a closed circuit (single tank) and an open circuit (two tanks) as a function of $Q$ for an uncoated (glass) test section is shown in Fig. 3.18. Similar results were obtained for a 2VP/S-coated test section. These data show that within the accuracy of the various measurements, the potential differences generated
Figure 3.18. Comparison of $\Delta E_t$ values measured in a closed circuit (one tank) and an open circuit (two tanks) as a function of flow rate $Q$ for an uncoated (glass) test section.
across a parallel-plate test section by an open and a closed streaming flow are nearly identical. At first, this result seemed rather surprising, especially since the close circuit analysis predicts that there should be some difference between the two types of measured potentials. However, a closer examination of the theory indicates the probable cause of this measured agreement. It can be shown (see Appendix B, Sect. B.2) that for a closed flow system, the potential difference generated across the test section is related to the \( \zeta \)-potential of the test section material, \( \zeta_w \), and that of the loop material, \( \zeta_a \), by

\[
\Delta E_t = \frac{\varepsilon Q}{\lambda \left( 1 + \frac{2bW}{L} \sigma_1 \right)} \left[ \frac{3}{4\pi b^2} \sigma_1 \zeta_w + \sigma_2 \zeta_a \right]
\]  

[3.6]

where \( \sigma_1 \) and \( \sigma_2 \) are constants which depend only on the geometries of the various flow elements (excluding the test section) which make up the flow circuit. In Eq. [3.6], the term \( 2bW\sigma_1/L \) is, in fact, the ratio of the electrical resistance of the rest of the system in series to the resistance across the test section. Thus, because of the relatively long length of small cross-sectional tubing which form the bulk of the present flow system, \( 2bW\sigma_1/L \gg 1 \). In addition, because of the comparatively high surface area-to-volume ratio of the test section and the large fluid velocities created
near its walls, it can be demonstrated that in the present system, $3\sigma_1/4\mu b^2 \gg \sigma_2$. Thus, as long as $|\zeta_w| \geq |\zeta_a|$, it can be seen from a comparison of Eq. [3.6] with Eq. [3.4] that $\Delta E_t = \Delta E_{str}$. In the present experiments, the magnitude of $\zeta_w$ at the start of each deposition run generally exceeded 25 mv. Although measured values for the $\zeta$-potential of teflon under distilled water conditions could not be obtained from the literature, it is expected that $\zeta_a$ is small. Thus, it is assumed in all of the subsequent analyses that $\Delta E_t = \Delta E_{str}$ and hence, that $\zeta_w$ may be calculated from Eq. [3.4]. It should be noted that during the course of some of the deposition runs the $\zeta_w$ estimated from Eq. [3.4] approached very close to zero. Under these circumstances, it is expected that errors caused by a failure to account for the second term in Eq. [3.6] could be quite substantial. However, since it is only the initial value of $\zeta_w$ that is required to validate the theory, no attempt was made to accommodate this shortcoming.

Ideally, according to Ball and Furstenau (143), streaming potentials should always be taken for a number of different flow-rates (including reverse flows) and the slope of the $\Delta E_{str}$ versus $Q$ curve used in the $\zeta$-potential calculation. Such a procedure is not practical in the course of a deposition run, where it is desirable to maintain the suspension flow-rate as constant as possible. Thus, each value of $\zeta_w$ obtained using the streaming potential technique is based on individual measurements of $\Delta E_t$ recorded at various times throughout the run by momentarily (~5 sec.) stopping the suspension flow. The precision of $\zeta_w$ values obtained in this manner is estimated to be ±2 mv (95% confidence) for suspensions having a conductivity of less than 10 umho/cm. The wall $\zeta$-potential at $t = 0$ was obtained by extrapolation.

In several runs, overlapping measurements of the initial wall $\zeta$-potential were made using both the ex-situ electro-osmosis and in-situ streaming
potential techniques. In almost every case the in-situ measurement gave a lower value of \( \xi_w \) than the ex-situ measurement; the ratio of the former to the latter was generally in the range of 0.5-0.6. The probable cause for this discrepancy is that the influence of surface conductance has not been accounted for in the streaming potential analysis. It has often been observed that surface conductance effects can become quite important in solutions of low bulk conductivity as in the case of the present streaming potential measurements. When surface conductance is included in the analysis, it can easily be shown that Eq. [3.4] must be amended to

\[
\Delta E_{\text{str}} = \frac{3eLQ\xi_w}{8\pi b^2 W \left( \lambda + \frac{\lambda_s}{b} \right)}
\]

[3.7]

where \( \lambda_s \) is the surface conductance (ohm\(^{-1}\)). Eq. [3.7] shows that the effect of surface conductance is to reduce the electrical resistance across the test section and hence, to reduce the magnitude of the streaming potential generated. Thus, failure to account for surface conductance can give an erroneously low value of the calculated zeta potential.

Surface conductance effects are best dealt with by measuring the apparent conductivity \( (\lambda' = \lambda + \lambda_s/b) \) across the test section in tandem with each streaming potential determination and using \( \lambda' \) in place of \( \lambda \) in Eq. [3.4]. However, for polarizable electrodes, such measurements must be carried out with a high frequency alternating current bridge. Such an instrument was not available for measuring the high resistances (6-30 Mohm) encountered here.

When the surface conductance is due only to the presence of an excess concentration of ions in the diffuse part of the electrical double layer, it is possible to estimate \( \lambda_s \) from the measured \( \xi \)-potential.
Bikerman (147) considered the effects of ion migration and electro-osmosis (due to the generated potential gradient) on the charge transfer in a diffuse layer adjacent to an ideally flat surface and obtained

$$\lambda_s = \left[ \frac{e^{-RT/L}}{2\pi F^2} \right]^{1/2} \left[ e^{rac{1}{2}e_0 \zeta w/2kT} - 1 \right] \left( L_+ + \frac{eRT}{2\pi \mu} \right)$$

$$+ \left[ e^{-e_0 \zeta w/2kT} - 1 \right] \left( L_- + \frac{eRT}{2\pi \mu} \right)$$  \[3.8\]

where $R$ is the gas constant, $F$ is the Faraday, $c$ is the electrolyte concentration (moles/cm$^3$), $e_0$ is the charge of an electron, $k$ is the Boltzmann constant, and $L_+$ and $L_-$ are the average mobilities (cm$^3$/sec-mole) of the cations and anions, respectively. Since $\lambda_s$ is a function of $\zeta_w$, the value of the latter cannot be calculated explicitly from Eq. [3.7] but instead must be obtained by an implicit trial-and-error method. Accounting for the contribution of $\lambda_s$ by means of Bikerman's formula has the desired effect of increasing the value of $\zeta_w$, but, in general, the change is very small and never exceeds 5%.

The above evidence, however, does not necessarily discount the importance of surface conductance in the present streaming potential measurements. Measured values of $\lambda_s$ generally exceed those estimated by Eq. [3.8], in some cases by one or two orders of magnitude (121). This additional conductance is usually attributed to the presence of excess ions in the region between the electrokinetic slip-plane and the Outer Helmholtz Plane of the Stern layer, to the possibility of surface diffusion of adsorbed ions in the Stern layer, and to such extraneous conduction effects as might occur, for example, if the walls were constructed of a semi-conductor. In the
present experiments, it is highly possible that highly-conductive contaminants left in cracks between the plate glass and the spacers following the test section cleaning process could also be providing an extraneous conduction pathway. Evidence that such material is present despite extensive flushing is demonstrated by the fact that conductivity of the suspensions increased measurably during the course of each deposition run.

Thus, wall ζ-potentials obtained by the streaming potential technique are probably somewhat less than the actual Stern potentials. To improve the measuring technique, consideration should be given to improving the design of the test section and to building or procuring an a.c. bridge circuit capable of measuring very low apparent conductivities.
Chapter 4

RESULTS AND DISCUSSION

4.1 Introduction

The experimental results have been tabulated in their entirety in Appendix C, Sect. C.3. As well as a record of the particle accumulation and release measurements, the tables contain a listing of all other parameters relevant to each experimental run including the test section length, width, and half-thickness, the suspension flow rate, the suspension concentration, the counterion concentration, the solution pH, and the various measured zeta potentials.

The dimensionless particle deposition rate, \( J_D(\gamma) \), given by Eq. [2.91], can be rewritten in a slightly different form as

\[
J_D(\gamma) = \frac{1}{\Gamma(4/3)(9\gamma/2)^{1/3}} + \frac{1}{K} \tag{4.1}
\]

Eq. [4.1] shows that the overall (dimensionless) resistance to particle deposition is the sum of two separate resistances acting in series: a mass-transfer resistance \( [\Gamma(4/3)(9\gamma/2)^{1/3}] \) due to the convective-diffusion transport of particles from the bulk suspension to the wall region and a surface reaction resistance \( (1/K) \) due to the various physical interaction forces affecting the particle motion in the wall region. It was found that, for the
accumulation of negatively-charged silica particles onto positively-charged plastic substrates, the deposition process was mass-transfer controlled. On the other hand, for negative particles and negative channel walls, the process was surface reaction controlled. Furthermore, although the rate of accumulation declined with increasing surface coverage for all experimental runs, the mechanism for this decline also appeared to be a function of the sign of the charge on the channel wall. Thus, it is convenient to discuss the accumulation results in two separate sections depending on whether the deposition substrate is initially positively-charged (Sect. 4.3.1) or negatively-charged (Sect. 4.3.2). Since knowledge of particle release rates is vital to interpreting the effect of surface coverage on the accumulation process in all cases, the results of the release measurements will be discussed first (Sect. 4.2).

4.2 Particle Release

The objective of the present experiments was to shed some light on the time-dependent nature of the particle accumulation process, which, except at $t = 0$, involves the two competing processes of deposition and release. For this reason, all release rates were measured at conditions representative of those under which the particles were originally deposited on the wall. It is hypothesized that, under the conditions of the present study, particle release can only take place via the following three mechanisms:

i) diffusion,

ii) shear-aided diffusion,

iii) erosion.
Three types of release measurements were undertaken (see Sect. 3.4.3.3) to establish the importance of each of these mechanisms to the overall release process.

Because of the existence of Born repulsion and possible steric exclusion forces at very small separations between the particle and the wall (see Sect. 2.1.4), the primary minimum of the interaction potential energy curve can never be infinitely deep. Thus, there is a finite probability that a deposited particle could diffuse out of the energy well and back into the medium. To determine if diffusion from the surface occurs, release measurements using a stagnant solution having the same electrolyte properties as the deposition medium were carried out. It should be noted that measurements of diffusion release yield information about the depth of the primary energy minimum and, as a consequence, about the balance of forces operating at small distances of approach. Such quantitative data have heretofore been unavailable.

In turbulent flows, where the distribution of fluid shear over the channel walls is in a random state of flux, it has been suggested (148) that local shear rates may at times be sufficiently high to dislodge previously deposited particles. In laminar flows, however, the local shear rate on the walls of the channel remains constant with time. Thus, a particle which has managed to attach itself to a wall in the presence of this steady shear is not likely to be further disturbed by the flow on its own. However, the lift force created by the fluid shear (Sect. 2.1.4) contributes to the balance of forces acting on a particle at the wall. It therefore affects the shape of the interaction energy curve and, as a result, the rate at which the particle may diffuse from the wall. Because there are indications that the lift force always acts to pull particles away from the wall, this
mechanism is termed "shear-aided diffusion." To determine the importance of this mechanism, measurements of release into a flowing solution were carried out. In this case, both the flow rate and the electrolyte properties of the solution were adjusted to those of the deposition medium.

It is conceivable that when a suspended particle collides with one already attached to the wall, it could impart enough kinetic energy to dislodge it from the surface. This third possible release mechanism, termed "erosion" release, occurs therefore only under the dynamic conditions when deposition is also taking place. Erosion release was measured by monitoring the change in activity emanating from the channel wall as a suspension of non-radioactive particles was pumped through the test section. In this case, the concentration of suspended particles as well as the electrolyte and flow conditions were made the same as for the radioactive suspension used in the deposition measurements. To determine the separate contributions of each of these mechanisms to the overall release rate, it is, of course, necessary to perform all three types of measurements on each deposit.

The results of the various measurements of particle release are very simple to report. In almost all cases representing a wide variety of fluid flow, particle size, and double layer conditions, no measurable re-entrainment of particles occurred no matter what type of release experiment was performed. Figure 4.1 shows, for example, the complete accumulation curves obtained for runs III-5 (positively-charged 2VP/S substrate) and III-6 (negatively-charged Formvar substrate). In both cases, the accumulation measurements using the radioactive particle suspension were continued for six hours. At this time, the radioactive suspension in the test section was exchanged for a solution with similar electrolyte properties, and a
Figure 4.1. Complete accumulation curves for runs III-5 (positively-charged 2VP/S substrate) and III-6 (negatively-charged Formvar substrate) showing release measurements. \(R_2\)-flowing solution. \(R_3\)-flowing suspension.
release measurement of the second type (R\textsubscript{2}-flowing solution) was carried out. In run III-5, after an additional hour, the solution was replaced by a non-radioactive suspension, and a release measurement of the third type (R\textsubscript{3}-flowing suspension) was performed. In both cases, even though the activity of the test sections was monitored for a period equivalent to twice the time taken for the accumulation measurements, no observable change in the concentration of deposited particles took place. The only exceptions to this general trend occurred in runs III-3 and III-8, where a flow of flush solution through the test section brought about a statistically significant decline in the wall concentration with time. However, in both cases, the measured release rates were very small and, in fact, were negligible in comparison with the initial deposition rates observed for these two runs.

The apparent absence of particle release was not a surprising outcome. For example, the prospect of erosion release seemed very unlikely for two reasons. First, the kinetic energy of such fine particles moving close to the channel walls is extremely small, only \(-0.001 \text{kT}\) for the flow conditions employed here. Secondly, because of the highly charged double layers surrounding each sphere, collisions between particles will not be elastic. Rather, most, if not all, of the kinetic energy of the suspended particle will be absorbed by the double-layer interaction itself.

Also, the fact that the primary potential energy minimum is apparently far too deep to permit significant diffusion from the walls even in the presence of fluid shear, is in accord with results obtained for other types of measurements. For example, the spontaneous redispersion of coagulated particles is very uncommon; in fact, coagulated sols are often referred to as "irreversible" or "irresoluble" (149).
In adhesion studies, it is frequently found that the force required to remove a spherical particle from a flat surface greatly exceeds that predicted from the Hamaker equation, assuming reasonable values for the Hamaker constant and the minimum separation distance. To explain this discrepancy, it has been postulated (63) that the attractive forces cause both surfaces to deform slightly on approach such that the actual area of intimate contact is greatly increased. The amount of deformation is a function of the hardness of the materials involved. For the relatively soft plastic substrates used in the present study, a significant degree of accommodation might be expected. As a result, the overall attraction energy at the primary minimum is probably far greater than the theory of rigid body interactions would predict.

For the range of conditions investigated here, it can be concluded that particle deposition is an essentially irreversible process. Thus, release plays only a negligible role in determining the time-dependent shape of the measured accumulation curves. Furthermore, the absence of particle release alleviates many of the potential problems associated with the accumulation measurements obtained using the discontinuous mode of operation (Sect. 3.4.3.2). The excellent reproducibility between accumulation results measured using both the continuous and discontinuous mode (see Sect. 4.3.1.2) testifies to this fact.

Although diffusion release is negligible under the present circumstances, there may still exist conditions, particularly for other pairs of materials, which favour reversibility. Since increased diffusion from the surface implies a reduction in the depth of the primary potential energy minimum, any combination of the following factors could promote a higher rate of release:
i) weak van der Waals attraction, eg. small system Hamaker constant, hard, smooth particles and substrate;

ii) strong electrical double layer repulsion, eg. high concentration of potential determining ions, low concentration of indifferent electrolyte;

iii) large minimum distance of separation, eg. exclusion due to steric repulsion;

iv) large lift and drag forces, eg. high fluid shear rate, large particle size.

For example, Visser (65) has shown that increasing the solution pH or decreasing the concentration of neutral electrolyte (both being factors which enhanced double layer repulsion in his experiments) greatly reduces the force required to remove adhering spherical polystyrene particles from a cellulose substrate. In this case, a very high shear rate created in the narrow gap between two concentric cylinders provided the force needed to dislodge the particles.

4.3 Particle Deposition

4.3.1 Positively-Charged Substrates

4.3.1.1 Initial Deposition Rates

As was discussed earlier, the theory of particle deposition developed in Sect. 2.2.1 cannot strictly be applied to the case where particles of one sign deposit on an oppositely charged substrate. Double layer, van der Waals, and hydrodynamic interaction forces can be lumped into a boundary condition on the convective-diffusion equation only if the overall interaction energy has a repulsive maximum greater than 5 kT. This condition is not fulfilled when the interaction involves oppositely charged surfaces.
However, in their study of particle transport to a rotating disc, Hull and Kitchener (17) have demonstrated that, under distilled-water conditions, the deposition of negatively charged (-70 mv.) polystyrene spheres (0.308 μm dia.) onto a positively charged (+72 mv.) plastic substrate is mass-transfer controlled. They found that, for the range of surface coverages studied (≤0.004), particle accumulation was linear with time and, under a variety of fluid convection and suspension concentration conditions, their measured accumulations were generally slightly smaller than, but in a close agreement with, those predicted by the theory of mass transfer to a rotating disc developed by Levich (19). The Levich theory assumes that the disc surface acts as an infinite sink to depositing particles and hence, ignores surface interaction effects. Recently, Dabrós and Czarnecki (150) have shown that the Levich theory must be corrected to account for the finite size of macroscopic particles when their dimensions are no longer negligible compared to the thickness of the concentration boundary layer which exists at the surface of the rotating disc. A correction of the calculations of Hull and Kitchener demonstrates that, even in the worst case (highest rotational speed), this interception effect only increases the deviation between theory and experiment by about 6%. Thus, the conclusion reached by the latter authors remains unaltered, i.e. deposition in the absence of a potential energy barrier is essentially mass-transfer controlled. They reason that, since the interaction potential energy is everywhere attractive, an increase in the deposition kinetics over the diffusion-controlled rate might be expected. However, because the interaction energy is confined to such small distances of separation between the particle and wall, its influence is negligible, and hence, the process is mass-transfer controlled.
Thus, it is of interest to see how well the initial deposition rates obtained in the present study for the negative particle, positive wall case conform to the assumption of mass-transfer control. Complete mass transfer control implies that the second term in the denominator of Eq. [4.1] is zero, i.e. that \( K = \infty \). In this case, the dimensionless deposition rate \( J_D \) is given by

\[
J_D = \left(\frac{2}{9\gamma}\right)^{1/3} \Gamma(4/3) \tag{4.2}
\]

and hence, its corresponding dimensional form, \( J'_D \), by

\[
J'_D = \frac{D_\infty}{b} \frac{C_0}{J_D} = 0.6163 \left(\frac{Q}{Wx}\right)^{1/3} \left(\frac{D_\infty}{b}\right)^{2/3} C_0 \tag{4.3}
\]

where the experimental parameters \( Q, W, x, b, \) and \( C_0 \) have all been defined earlier (Sects. 2.2.1 and 3.5.3.2) and the bulk particle diffusivity, \( D_\infty \), is estimated using Eqs. [2.17] and [2.14].

Figure 4.2 shows the variation of the concentration of deposited particles, \( C_w \), with time for Run II-2. [Note that for this and all other plots of the wall concentration, the 95% confidence limits on \( C_w \) lie within the boundaries of the symbol denoting each experimental point unless otherwise indicated by the usual bars.] In Run II-2, the suspension medium was essentially distilled water (counterion conc. = \( 6.8 \times 10^{-6} \) moles/\( \ell \)) and the zeta potential of the silica particles was \(-75 \) mv., while that of the 2VP/S-coated test section, as determined by a streaming potential measurement, was \(+15 \) mv. The experimental initial deposition rate, \( J'_{D, \text{expt}} \), determined by fitting a straight line passing through the origin to the first 6 points
Figure 4.2. Deposition onto a positive 2VP/S substrate. Run II-2.
in Fig. 4.2 (dashed line), was found to be $7.87 \times 10^2$ particles/cm$^2$-sec. By substituting the relevant experimental parameters into Eq. [4.3], the theoretical initial deposition rate was estimated as $7.22 \times 10^2$ particles/cm$^2$-sec. The theoretical accumulation curve, constructed by assuming that the initial deposition rate remains constant with time, is plotted as a dash-dot line on Fig. 4.2. The close agreement between experiment and theory suggests that, at least for this case, the measured data are well represented by assuming that the deposition process is mass-transfer controlled.

How do the other results obtained with a positively charged substrate compare with the mass-transfer controlled theory? A comparison of $J_{D,\text{expt}}^\prime$ (measured) with $J_{D,\text{theory}}^\prime$ (predicted from Eq. [4.3]) for all cases where the channel is initially positively charged is presented in Table 4.1. It can be seen from the table that, in many cases, the agreement between theory and experiment is very good. But there are also a few exceptions where the measured rate is either significantly larger or significantly smaller than the value predicted by the theory. On closer inspection, Table 4.1 reveals that these larger discrepancies cannot be attributed entirely to experimental error, as they correlate quite well with at least one of the measured experimental parameters, namely, the double layer thickness. For example, Fig. 4.3 illustrates the deposition results obtained in runs III-1, -4, and -5, the only series of experiments in which the double layer thickness was changed in a systematic manner. A decrease in the double layer thickness was obtained by progressively increasing the NaCl concentration of the suspending solution while maintaining constant pH conditions. It can be seen that, although the deposition conditions remained otherwise reasonably constant,
Table 4.1
Initial Deposition Rates - Attractive Double Layer Interactions

<table>
<thead>
<tr>
<th>Run</th>
<th>Coating</th>
<th>1/κ (μm)</th>
<th>ζ_p (mv)</th>
<th>ζ_w* (mv)</th>
<th>x (cm)</th>
<th>Q (cm³/sec)</th>
<th>J_D^expt (particles/cm²-sec)</th>
<th>J_D^theory (particles/cm²-sec)</th>
<th>J_D^expt / J_D^theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1</td>
<td>2VP/S</td>
<td>.1358</td>
<td>-95</td>
<td>+26</td>
<td>12.5</td>
<td>12.7</td>
<td>2.64 x 10⁶</td>
<td>2.06 x 10⁴</td>
<td>1.28</td>
</tr>
<tr>
<td>I-2</td>
<td>2VP/S</td>
<td>.1020</td>
<td>-96</td>
<td>+25</td>
<td>12.5</td>
<td>12.0</td>
<td>1.73 x 10⁶</td>
<td>1.91 x 10⁴</td>
<td>0.90</td>
</tr>
<tr>
<td>I-3</td>
<td>2VP/S</td>
<td>.0944</td>
<td>-71</td>
<td>+28</td>
<td>5.0</td>
<td>12.4</td>
<td>2.76 x 10⁴</td>
<td>2.59 x 10⁴</td>
<td>1.06</td>
</tr>
<tr>
<td>I-3</td>
<td>2VP/S</td>
<td>.0944</td>
<td>-71</td>
<td>+28</td>
<td>10.0</td>
<td>12.4</td>
<td>2.29 x 10⁴</td>
<td>2.06 x 10⁴</td>
<td>1.11</td>
</tr>
<tr>
<td>I-3</td>
<td>2VP/S</td>
<td>.0944</td>
<td>-71</td>
<td>+28</td>
<td>12.5</td>
<td>12.4</td>
<td>2.31 x 10⁴</td>
<td>1.91 x 10⁴</td>
<td>1.21</td>
</tr>
<tr>
<td>I-3</td>
<td>2VP/S</td>
<td>.0944</td>
<td>-71</td>
<td>+28</td>
<td>15.0</td>
<td>12.4</td>
<td>1.78 x 10⁴</td>
<td>1.80 x 10⁴</td>
<td>0.99</td>
</tr>
<tr>
<td>I-3</td>
<td>2VP/S</td>
<td>.0944</td>
<td>-71</td>
<td>+28</td>
<td>20.0</td>
<td>12.4</td>
<td>1.50 x 10⁴</td>
<td>1.63 x 10⁴</td>
<td>0.92</td>
</tr>
<tr>
<td>I-4</td>
<td>2VP/S</td>
<td>.0753</td>
<td>-64</td>
<td>-4**</td>
<td>12.5</td>
<td>8.3</td>
<td>1.79 x 10⁴</td>
<td>1.71 x 10⁴</td>
<td>1.05</td>
</tr>
<tr>
<td>I-6</td>
<td>2VP/S</td>
<td>.0437</td>
<td>-98</td>
<td>+3**</td>
<td>12.5</td>
<td>15.4</td>
<td>2.09 x 10⁴</td>
<td>2.11 x 10⁴</td>
<td>0.99</td>
</tr>
<tr>
<td>II-1</td>
<td>2VP/S</td>
<td>.1283</td>
<td>-75</td>
<td>+27</td>
<td>12.5</td>
<td>13.1</td>
<td>1.056 x 10³</td>
<td>7.56 x 10²</td>
<td>1.40</td>
</tr>
<tr>
<td>II-2</td>
<td>2VP/S</td>
<td>.1171</td>
<td>-75</td>
<td>+15</td>
<td>12.5</td>
<td>13.0</td>
<td>7.87 x 10²</td>
<td>7.22 x 10²</td>
<td>1.09</td>
</tr>
<tr>
<td>II-3</td>
<td>2VP/S</td>
<td>.0030</td>
<td>-63</td>
<td>+5*</td>
<td>12.5</td>
<td>12.9</td>
<td>2.29 x 10²</td>
<td>2.27 x 10²</td>
<td>0.90</td>
</tr>
<tr>
<td>II-4</td>
<td>2VP/S</td>
<td>.1303</td>
<td>-68</td>
<td>+28*</td>
<td>12.5</td>
<td>4.2</td>
<td>6.01 x 10²</td>
<td>5.41 x 10²</td>
<td>1.46</td>
</tr>
<tr>
<td>II-5</td>
<td>2VP/S</td>
<td>.0726</td>
<td>-62</td>
<td>+60*</td>
<td>12.5</td>
<td>8.6</td>
<td>6.19 x 10²</td>
<td>7.71 x 10²</td>
<td>0.80</td>
</tr>
<tr>
<td>II-6</td>
<td>2VP/S</td>
<td>.0729</td>
<td>-68</td>
<td>+69*</td>
<td>12.5</td>
<td>12.9</td>
<td>6.63 x 10²</td>
<td>8.54 x 10²</td>
<td>0.78</td>
</tr>
<tr>
<td>II-7</td>
<td>2VP/S</td>
<td>.0738</td>
<td>-68</td>
<td>+37</td>
<td>12.5</td>
<td>16.6</td>
<td>6.62 x 10²</td>
<td>7.43 x 10²</td>
<td>0.89</td>
</tr>
<tr>
<td>II-8</td>
<td>2VP/S</td>
<td>.0705</td>
<td>-67</td>
<td>+54*</td>
<td>12.5</td>
<td>12.6</td>
<td>3.02 x 10³</td>
<td>3.71 x 10³</td>
<td>2.86</td>
</tr>
<tr>
<td>II-10</td>
<td>2VP/S</td>
<td>.1189</td>
<td>-75</td>
<td>+27</td>
<td>12.5</td>
<td>12.6</td>
<td>1.062 x 10⁴</td>
<td>3.71 x 10³</td>
<td>2.86</td>
</tr>
<tr>
<td>II-12</td>
<td>FORMV</td>
<td>.1014</td>
<td>-73</td>
<td>+0.3**</td>
<td>12.5</td>
<td>12.5</td>
<td>3.22 x 10³</td>
<td>3.35 x 10³</td>
<td>0.96</td>
</tr>
</tbody>
</table>

* ζ_w-values obtained by electro-osmotic technique; otherwise the streaming potential measurement was used.

** These low ζ_w-values are somewhat suspect, esp. negative value obtained in Run I-4.

*** Measured mobility of particles used in Run III-1 too high to allow ζ_p calculation by W.L.O. method. ζ_p = -99 mv. assumed.
Figure 4.3. Effect of double layer thickness on deposition onto a positive 2VP/S substrate. Run III-1: \( \kappa a = 6.5 \), run III-4: \( \kappa a = 17.9 \), run III-5: \( \kappa a = 54.8 \). Bars represent error limits of all points in a given series.
decreasing the thickness of the double layer markedly reduced the initial deposition rate. For these three experiments, the ratio of $\frac{J_D^{\text{expt}}}{J_D^{\text{theory}}}$ declined progressively from 0.90 to 0.75 to 0.49 as $\kappa a$ increased from 6.5 to 17.9 to 54.8, respectively. A similar result was obtained in runs II-2 and -3 where increasing $\kappa a$ from 2.8 to 107 caused a dramatic decline in the ratio $\frac{J_D^{\text{expt}}}{J_D^{\text{theory}}}$ from 1.09 to 0.31. In a few other cases, notably runs I-1, II-1, II-4, and II-10, the initial deposition rate is much higher than the theoretical prediction. These four runs all correspond to the preparation of a new suspension in distilled water, i.e. when the counterion concentration is lowest and hence, the double layer thickness greatest. Why does the thickness of the double layer have such a pronounced effect on the deposition rate under conditions when it might be expected that the process is mass-transfer controlled?

To understand this phenomenon, it is necessary to re-examine the arguments used by Hull and Kitchener. The mass transfer theories of Leveque for a parallel-plate channel and Levich for a rotating disc both assume that the potential energy of interaction is everywhere zero except at the limit where the particle and collector are in contact. Here, the potential energy is assumed to be infinitely attractive such that a particle which diffuses to the collector surface is irreversibly removed from the suspension. In addition to excluding a more realistic description of the interaction energy curve, these theories also ignore the influence of viscous interaction as a sphere approaches a plane surface. Assume for the moment that the Leveque-Levich description of the interaction energy profile is the correct one. Thus, if the viscous interaction force is now accounted for, it will result in a very significant resistance to particle deposition because the Stokes'
law correction factor $\alpha(=a/h$ for $h/a << 1)$ assumes very large values at small separation distances.

Clearly, the role of the attractive van der Waals and, in this case, attractive double layer interaction forces is to counteract the viscous interaction, making it easier for particles to diffuse to the collector surface. To determine how much of a counterbalancing effect these two attractive forces have in the present problem, it is necessary to solve the complete mass transfer equation [2.20] which treats convective-diffusion in a field of force. Because the various forces involved contribute many non-linear terms to this second-order differential equation, the solution very likely must be obtained by numerical methods. For lack of time, such a solution was not attempted here. However, recently, Dabrós et al. (151) have obtained a numerical solution to the related rotating disc problem when only viscous interaction and London-van der Waals forces are operative. They found that for small particles ($0.1 < a < 0.5 \, \mu\text{m}$) where interception effects are not important and for Hamaker constants in the range applicable to aqueous solutions, the predicted deposition rates were always significantly less than the Levich rates. Thus, for a disc rotating in an aqueous suspension, because the van der Waals forces are never strong enough to completely counteract the effects of the viscous interaction, there is a net resistance to particle deposition at the disc surface.

It is strongly suspected that the same situation exists in the case of particle transfer in a parallel-plate channel. Although the proof requires a numerical solution, it will be assumed for now that the combined effect of viscous and van der Waals interactions leads to a net resistance to deposition at the channel wall. It then becomes possible to speculate about the role played by attractive double layer forces in the overall deposition process.
It is expected that, as the importance of the double layer attraction is increased (i.e. by increasing the magnitudes of $\zeta_p$, $\zeta_w$, or $1/\kappa$), the influence of the viscous interaction will be further counteracted. Thus, the net repulsion associated with the wall region will decrease (and, in fact, could become a net attraction) resulting in higher deposition rates. This is exactly the trend observed in Fig. 4.3, where an increase in the double layer thickness (accompanied by a related increase in the magnitude of the zeta potentials) causes an observable increase in the initial deposition rate.

Although the other runs (with the exception of II-3) using a positive substrate were carried out over a rather limited range of double layer conditions (i.e. solutions were all essentially distilled water), they yield a fairly wide variation of $J^i_D/ J^i_{D,expt}$ ratios. It is of interest to determine whether this scatter can be explained in terms of the combined effect of the various interaction forces or if it is due only to experimental error. In the absence of a numerical solution to the combined transport equation, this question is best answered by examining to what degree the results correlate with a suitably chosen parameter which successfully accounts for all of the particle-wall interactions.

One such correlating parameter is the dimensionless surface reaction rate constant, $K$, which is obtained from Eq. [2.38] and the definition of $K$ (Sect. 2.2.2) as

$$K = \frac{K_i b}{D_{oo}} = \frac{b}{\int_0^\delta \left[ \alpha e^{\psi/kT} - 1 \right] dh} \quad [4.4]$$

In Eq. [4.4], $\delta$ is the distance of separation at which the integral becomes insensitive to further changes in $h$. An additional restriction on $\delta$ is that
its value must be small compared to the thickness of the concentration boundary layer. As was discussed in Sect. 2.2.1, it can be shown that for attractive double layer interactions, the integral in Eq. [4.4] does not converge even as $\delta \to \infty$ mainly because of the behaviour of $\alpha$ at large $h$. Thus, it is not possible to obtain a valid $K$-value in the present situation.

However, since Eq. [4.4] does account for all factors of interest, a pseudo-$K$-value, $K_\delta$, obtained by integrating this expression to a finite limit $\delta$, was chosen instead as a possible correlating parameter. In each numerical integration, $\delta$ was arbitrarily assigned a value of 5 $\mu$m., a distance which is large compared to the range of the dominant interaction forces but is still small compared to the thickness of the concentration boundary layer, for the various deposition conditions encountered in the present investigation.

Rather than compare the $J_D^{expt}/J_D^{theory}$ ratios with the $K_\delta$ predictions directly, it is of greater interest to see if the latter values correlate with a second pseudo-$K$-value, $K^{expt}$, obtained using Eq. [4.1] as

$$K^{expt} = \frac{(2/9\gamma)^{1/3}}{(2/9\gamma)^{1/3} - \Gamma(4/3)J_D^{expt}}$$

[4.5]

where the dimensionless experimental deposition rate, $J_D^{expt} = (bJ_D^{expt})/D_{\infty}C_0)$. Furthermore, since both $K_\delta$ and $K^{expt}$ are discontinuous functions, it is easier to plot their reciprocals, $1/K_\delta$ and $1/K^{expt}$, respectively. The dimensionless pseudo-resistances, $1/K_\delta$ and $1/K^{expt}$, obtained for all runs in which the substrate was initially positively-charged, are compared in Fig. 4.4. The bars illustrate the range of $1/K^{expt}$ that might be expected if there were a 10% error in the measured deposition rates. Negative values of $1/K_\delta$ and $1/K^{expt}$ represented cases where the expected or measured deposition rate is greater than the $J_D^{theory}$ value predicted by Eq. [4.3].
Figure 4.4. Plot of predicted pseudo-resistance, $1/K_8$, against measured pseudo-resistance, $1/K_{\text{expt}}$. Bars represent 10% error in measured deposition rates.
Even though there is quite a large scatter in the results, Fig. 4.4 demonstrates that there is a definite correlation between the experimentally-determined psuedo-K-values and those predicted by limiting the wall region to approximately 10 particle diameters. Not only do both quantities tend to increase in magnitude together, but there is also a reasonable correspondence between positive and negative values. In other words, where the $K_\delta$-value predicts an enhanced deposition rate, the $K_{\text{expt}}$-value demonstrates that this is indeed the case. [Of course, if the limit $\delta$ is greatly increased or decreased, all of the $K_\delta$'s become positive or negative, respectively, and the latter correspondence disappears. However, the choice of limiting $\delta$ to just outside the region where the interaction forces predominate but still within the concentration boundary layer seems a reasonable one in the present circumstances.] The correlation observed in Fig. 4.4 suggests that the primary cause of the variation in the measured deposition rates compared to the purely mass-transfer controlled values is the influence of the interaction forces. Of secondary importance are experimental errors. In fact, the scatter in the correlation depicted on Fig. 4.4 is probably a good indicator of the magnitude of the error in experimentation. It would therefore appear that at least the rather stringent mass-transfer requirements imposed by the theory are being met reasonably well in the present experimental setup. What error there is can be attributed to such factors as variations in particle size, incompletely dispersed suspensions, deposition in the entrance section (see Sect. 3.4.3.1), and uncertainties in the various measurements and in the treatment of the data.

Another interesting feature of Fig. 4.4 is that the values of $|1/K_\delta|$ are almost always less than the experimentally determined values of
In other words, the surface interactions play a much stronger role in determining the overall deposition rates than would appear theoretically possible. For example, in several runs, notably II-1, -4, and -10, enhancements in deposition of more than 40% over the mass-transfer controlled rates were obtained. In all three cases, the theory suggests that the double layer and van der Waals forces predominate over the viscous interaction force, resulting in a net attraction at the channel wall. However, even if this net attraction were very large, if the interaction region were confined to small distances from the wall relative to the concentration boundary layer (as is required by the present theory), very little enhancement would be expected. The rather large increases actually obtained suggest that this requirement is also not being met under the present experimental conditions.

It is possible to obtain an estimate of the thickness of the concentration boundary layer if it is assumed that the deposition process can be represented by Eq. [4.1]. In general, because of the interactions at the wall, the concentration of suspended particles in the vicinity of the wall will have some non-zero value \( C_s \). Thus, the thickness, \( \delta_C = \delta_C(x) \), of the concentration boundary layer may be defined as the distance from the wall where

\[
\frac{C - C_s}{C_0 - C_s} = 0.99 \tag{4.6}
\]

By dividing the numerator and denominator by \( C_0 \), Eq. [4.6] may be rewritten as
\[
\frac{C/C_0 - C_s/C_0}{1 - C_s/C_0} = 0.99 \tag{4.7}
\]

The entrance-region solution for \(C/C_0\) is given by Eq. [2.90]. At the wall, \(h = 0, \ C = C_s\) and Eq. [2.90] becomes

\[
\frac{C_s}{C_0} = \frac{1}{K\left(\frac{2}{9\gamma}\right)^{1/3}} \frac{0.893 + \frac{1}{K\left(\frac{2}{9\gamma}\right)^{1/3}}}{0.893 + \frac{1}{K\left(\frac{2}{9\gamma}\right)^{1/3}}} \tag{4.8}
\]

Substitution of Eq. [2.90] and [4.8] into [4.7] yields

\[
\frac{1}{\left(\frac{2}{9\gamma}\right)^{1/3}} \frac{\frac{\delta_c}{b} e^{-u^3} du + \frac{1}{K\left(\frac{2}{9\gamma}\right)^{1/3}}}{0.893 + \frac{1}{K\left(\frac{2}{9\gamma}\right)^{1/3}}} - \frac{\frac{1}{K\left(\frac{2}{9\gamma}\right)^{1/3}}}{0.893 + \frac{1}{K\left(\frac{2}{9\gamma}\right)^{1/3}}} = 0.99
\]

or

\[
\int_0^{\left(\frac{2}{9\gamma}\right)^{1/3}} \frac{\delta_c}{b} e^{-u^3} du = 0.8841 \tag{4.9}
\]

Using the tables of the function \(\int_0^X e^{-u^3} du\) given by Abramowitz (78), Eq. [4.9] can be integrated to yield

\[
\frac{\delta_c}{b} = \frac{1}{K\left(\frac{2}{9\gamma}\right)^{1/3}} = 1.405
\]

or
\[ \delta_c = \frac{1.405 b}{(2/9y)^{1/3}} \]  

[4.10]

Since \( y = (4 D_\infty Wx)/(3Qb) \), Eq. [4.10] may be rewritten in dimensional terms as

\[ \delta_c = 2.553 \left( \frac{D_\infty b^2 Wx}{Q} \right)^{1/3} \]  

[4.11]

Equations [4.10] and [4.11] demonstrate that the thickness of the concentration boundary layer is completely independent of the value chosen for the reaction rate constant \( K \). Thus, the same expressions are obtained for the purely diffusion-controlled case where \( C_s = 0 \).

When the appropriate values were substituted into Eq. [4.11], it was found that the concentration boundary layer thicknesses encountered at the position of measurement in the present experiments ranged from 11.6 to 18.4 \( \mu \)m. Of course, as is suggested by Eq. [4.11], these were thinnest at the highest flow rates, smallest longitudinal distances, and for the largest particle sizes. If the thickness had been defined differently, e.g. as \( (C-C_s)/(C_0-C_s) = 0.90 \), the resulting \( \delta_c \)-values would have been approximately 70% of those obtained above.

The viscous interaction is significant at several particle diameters from the wall. At one particle diameter, \( \alpha = 1.569 \), and at ten particle diameters, \( \alpha \) is still 1.057 (Eq. [2.16]). It can be shown that for the sphere-plate system, the double layer interaction begins to influence the viscous interaction at a distance of \( h \sim 10/\kappa \) from the wall, i.e. up to \( \sim 3 \) particle diameters under the present experimental conditions. The range of the van der Waals interaction is of the order of one particle diameter. Thus, it is clear that the surface interactions in many cases extend much
further into the developing concentration profile than is allowed for by
the uncoupled mass transfer theory.

When the dimensions of the wall region are no longer insignificant
compared to the thickness of the concentration boundary layer, the influence
of the surface interactions on the overall deposition process is greatly
magnified. Under the less favourable mass-transfer conditions which promote
a thicker boundary layer, a closer agreement between the measured results and
those predicted from the purely diffusion-controlled Leveque theory might be
expected. The present results await a numerical solution to the complete
mass-transfer equation [2.20] which has no restrictions regarding the range
or magnitude of the interaction energy field.

4.3.1.2 Deposition with Time

The effect of surface coverage on particle deposition onto a posi-
tively charged substrate is considered in this section. The surface coverage
\( \theta \) is defined as the fractional area covered by deposited particles of radius
a assuming that each particle occupies an area equal to \( 4a^2 \). Complete
coverage, i.e. \( \theta = 1 \), therefore corresponds to the formation of a close-
packed monolayer of particles having a square array. If \( C_w \) is the surface
concentration in particles/cm\(^2\), then \( \theta \) is given by

\[
\theta = 4a^2 C_w
\]  

[4.12]

In the only comparable experimental study of particle deposition,
Hull and Kitchener (17) found that, for the range of surface coverages in-
vestigated (\( \theta \leq 0.004 \)), the accumulation of negatively charged polystyrene
spheres (\( a = 0.154 \, \mu m \)) onto a positively charged 2VP/S-coated disc was linear
with time. For the same range of surface coverages in the present study, it was found that the deposition of negatively charged silica spheres (a = 0.201, 0.300, 0.324 \mu m) onto positively charged channel walls behaved similarly. However, at higher surface coverages, the present results show that the rate at which the particles accumulate on the wall no longer maintains its initial value but begins to decrease with time. For example, in Figs. 4.2 and 4.3, the accumulation rate begins to deviate from the initial deposition rate at \( \theta = 0.013 \) and \( \theta \approx 0.007 \), respectively.

Since the major objective of the present experimental investigation was to test the theory developed in Sect. 2.2, only enough data were gathered in most runs to accurately establish initial deposition rates. However, in a few runs (notably I-1, -2, -3, -4, -6, II-9, -12, and III-1), deposition was allowed to continue until the rate of accumulation had decreased almost to zero. On the basis of the latter experiments (and by careful consideration of some of the former runs), it can be demonstrated that the relationship between particle accumulation and surface coverage is not a simple one, but in fact is influenced by a variety of experimental parameters. These effects are discussed below.

As far as it is known, the present experimental results represent the only hard data available concerning the effect of surface coverage on particle deposition in a well-defined system. Thus, it is of some interest to compare these results with predictions obtained using two recent models (152,153), both of which explicitly account for the influence of surface coverage. Because these models represent only the initial step in the understanding of a complex problem, they deal with the effect of surface coverage in a rather simplistic manner and hence cannot be expected to yield results which are in exact quantitative agreement with those obtained experimentally.
However, the basic assumptions underlying each model are quite different and in many ways contradictory. Thus, it is hoped that a comparison of the two models, particularly in their ability to account for the influences of the various experimental parameters, will indicate which one is the more relevant, and hence the more worthwhile to pursue. Suggestions are made as to the possible changes which could be incorporated to improve the reliability of both models. However, because the present investigation is mainly concerned with initial rates, extensive reworking of the models is not carried out here.

The accumulation-time curves for those runs continued until an almost constant wall concentration was attained all shared two rather distinctive features. First, the overall shape of the curve was almost identical in each case. This shape, which is illustrated in Fig. 4.5 for run 1-2, may be characterized in the following manner. Initially, the accumulation of particles on the wall is linear with time. At a certain point, there is a sudden sharp decline in the accumulation rate. This is followed by a long period of slower accumulation during which the accumulation rate steadily decreases. For the operating periods selected in the present investigation (maximum 8.4 hrs.), a true asymptotic condition (zero accumulation rate) was never reached.

The other interesting feature of these accumulation-time curves is that the maximum surface coverages attained were remarkably low. Because it was necessary to operate each run under conditions where the suspension was stable, it was expected that a suspended particle would show little inclination towards adhering to a previously deposited particle. Consequently, surface coverages exceeding the formation of a complete monolayer were not anticipated and coverages of $\theta < 1$ seemed more likely. The maximum coverages
Figure 4.5. Measured changes in wall concentration and wall $\zeta$-potential for deposition onto a positive 2VP/S substrate. Run I-2.
obtained for those experiments in which the wall concentration approached an approximately asymptotic value fell in the range $0.007 < \theta < 0.080$. It must be kept in mind that a true asymptote was never reached in any experiment and hence it is quite conceivable that the wall concentrations could continue to grow well beyond the coverages indicated above. However, the fact that the accumulation rates were so grossly decreased below their initial values at such low surface coverages seems somewhat remarkable.

The effect of surface coverage on particle accumulation is a function of many different experimental parameters. The influence of some variables is quite clear. However, because the parameter range was not very wide and because most runs were simply not continued long enough, the suggested role played by other variables must, until further experimentation is completed, be considered still tentative.

Perhaps the clearest trend indicated by the results is that of the influence of the double layer thickness. The complete accumulation-time curves for runs III-1, -4, and -5 in which $1/\kappa$ decreased from 0.0459 to 0.0168 to 0.0055 $\mu$m, respectively, have been plotted as Fig. 4.6. As was discussed earlier (Sect. 4.3.1.1), Fig. 4.6 shows that as the concentration of indifferent electrolyte (NaCl) increases, the initial deposition rate declines quite markedly. However, as $1/\kappa$ decreases in this range, the accumulation rate is less affected by surface coverage and a higher surface concentration is attained.

A similar relationship can be seen in the case of the fluid flow rate. Figure 4.7 is a plot of the accumulation results obtained in runs II-5, -6, and -7 where, under otherwise reasonably constant conditions, the flow of suspension through each test section was increased from 8.6 to 12.9 to 16.6 cm$^3$/sec., respectively. As predicted, the initial deposition rates
Figure 4.6. Effect of double layer thickness on deposition onto a positive 2VP/S substrate. Run III-1: $\kappa a = 6.5$, run III-4: $\kappa a = 17.9$, run III-5: $\kappa a = 54.8$. 

Figure 4.7. Effect of suspension flow rate on deposition onto a positive 2VP/S substrate. Run II-5: 8.6 cm³/sec, run II-6: 12.9 cm³/sec, run II-7: 16.6 cm³/sec.
increase in correspondence with the increasing flow rate. However, increasing the flow also appears to increase the effect of surface coverage on the accumulation rate. Although a stronger case for this conclusion could have been made had all three runs been continued longer, the results obtained in run II-6 were replicated almost exactly in run II-8 (see Fig. 4.8).

The proposed role played by other variables must be considered even more tentative. A comparison between accumulation curves is made much easier if instead of plotting the particle concentration, $C_w$, against the time, $t$, the dimensionless surface coverage, $\theta = 4a^2C_w$, is plotted against a dimensionless time, $\tilde{t} = 4a^2J_{D_{\text{expt}}}^{'} t$, where $J_{D_{\text{expt}}}^{'}$ is the experimentally measured initial deposition flux. The accumulation results of several selected runs have been plotted in this form on Fig. 4.8. This figure illustrates the usefulness of the plotting scheme. As long as the accumulation rate maintains its initial value, $J_{D_{\text{expt}}}^{'}$, the accumulation results follow the line $\theta = \tilde{t}$. Any deviation of $\theta$ from the line is a measure of how much the accumulation rate is being affected by the surface coverage.

The accumulation curves in Fig. 4.8 have been grouped according to similarities in the various experimental parameters. For example, runs I-1 and I-2 are essentially replicates obtained under very similar experimental conditions. In fact, the only difference between the two curves is the method by which they were measured. The accumulation results for run I-1 were obtained using the discontinuous mode of operation whereas those of run I-2 were measured continuously. Similar reproducibility was achieved in runs II-6 and II-8, the former using the continuous method and the latter using the discontinuous one. This agreement between pairs of curves demonstrates that, despite its greater possibility for error, the discontinuous
Figure 4.8. Surface coverage versus dimensionless time. Runs are grouped according to similarities in operating conditions.
method yields almost exactly the same results as the continuous mode of operation.

Curves II-1, -2, and -10 illustrate an additional advantage of the use of the θ - t plot. Although all three runs were obtained under otherwise similar conditions, the concentration of particles in the new suspension prepared for run II-10 was much higher than in runs II-1 and II-2. Consequently, the initial deposition rate in run II-10 was approximately ten times greater than in either of the other two runs. However, the θ - t curves for all three runs are closely grouped together. This correspondence demonstrates that for constant conditions of double layer thickness, particle and wall zeta potential, flow, and particle size, the effect of surface coverage on particle accumulation can thus be reproduced fairly reliably in a manner independent of the initial deposition rate.

Except for the size of particles used, the experimental conditions in runs II-1, -2, and -10 were approximately the same as those in runs I-1 and I-2. The diameter of the particles employed in the series I experiments was 0.402 μm compared to 0.649 μm in series II. Thus, on the basis of these five runs, it appears that the influence of surface coverage is a function of particle size; more specifically, the larger the particle size, the greater the influence of surface coverage on the accumulation rate.

Runs II-1, -2, -10, -6, and -8 were obtained under similar conditions of flow and ζ-potential using the same size of particles. However, the 1/κ values could be generally arranged into two distinct groups: runs II-1 (1/κ = 0.1283 μm), II-2 (0.1171), II-10 (0.1189) and runs II-6 (0.0729), II-8 (0.0705). Thus, there is indication here that, at least in the range 0.07 < 1/κ < 0.13 μm, decreasing the thickness of the double layer increases the effect of surface coverage on the rate of particle accumulation. A similar
trend could be observed in the series I results for the same range of $1/\kappa$-values. However, because chemistry conditions were less rigidly controlled, this conclusion is less certain in the case of the latter series.

This finding is exactly the reverse of what was observed earlier for runs III-1, -4, and -5 (see Fig. 4.6). However, in the latter case, the $1/\kappa$-values were 0.0459, 0.0168, and 0.0055 μm., respectively, and hence represent a range which does not overlap with either the series I or the series II experiments. Is it possible that the double layer thickness affects the time-dependency of the accumulation process in two competing ways, with the overall influence having a maximum in the range $0.05 < 1/\kappa < 0.07$ μm? This possibility is discussed below.

The final piece of information which can be gleaned from Fig. 4.8 concerns runs II-9 and II-12. Run II-9 was obtained under similar conditions of double layer thickness, particle $\zeta$-potential, and flow as were runs II-6 and II-8, while run II-12 had these conditions in common with runs II-1, -2, and -10. However, in both runs II-9 and II-12, the deposition substrate was Formvar and the solution pH was such that the initial wall $\zeta$-potential was very close to zero. Thus, it would appear that the magnitude of the wall (and probably the particle) zeta potential affects the accumulation process.

As is shown below, by making appropriate conjectural changes in the two models of surface-coverage-dependent accumulation, it becomes possible to explain many of the trends observed above. However, before getting into the details of and the proposed alterations for the models, it is first useful to deal with some general considerations which affect the modelling process.

First, it must be emphasized that the decline in the accumulation rate with increasing surface coverage is not due to the release of deposited
particles from the surface. It is possible to imagine that the accumulation process is a reversible one, with the rate of release increasing as the build-up of particles on the wall increases, until a steady-state condition is reached, signifying equality of the rates of deposition and release. Such a process would result in accumulation curves very similar in appearance to those observed here, namely, curves characterized by an asymptotic approach to a wall concentration which corresponds to some fraction of the maximum conceivable surface coverage.

Reversible accumulation models have been widely used (89,154) to explain the asymptotic growth curves frequently encountered in studies of the particulate fouling of heat exchangers. However, in the latter studies the fouling films are generally composed of many layers of particles, and fluid flows are almost invariably in the turbulent regime. Both are factors which could lead to particle release. In the present investigation, where the flow is laminar and the maximum possible coverage appears to be less than one monolayer of particles, it has been demonstrated (Sect. 4.2) that the accumulation process is essentially irreversible. Thus, the characteristic shape of the accumulation curves can only be explained in terms of a declining deposition rate. This is one of the assumptions implicit in both models of surface coverage to be discussed below.

Why does the deposition rate decrease with time? As the channel wall becomes covered with particles, the deposition environment at the wall is altered. Presumably, because the particles are highly-negatively charged, they influence the positively charged substrate in such a way that the rate of deposition is reduced. The precise mechanism by which the newly deposited particles affect the deposition rate is in fact the main issue on which the two models diverge. It should be noted that a change in the local deposition
rate results in a modification of the local distribution of suspended particles. As a consequence, the deposition rate at any given longitudinal position in the channel is not only affected by changes in the local environment but is also influenced by all changes which occur upstream of that location. The incorporation of time-dependency into the process of particle deposition in channel flows leads to a rather complex mathematical problem wherein the integrated effects of all upstream disturbances as well as those which occur locally must be accounted for. To simplify the problem and also to comply with another major premise of the two available models, it will be assumed in the following discussion that all changes occur simultaneously over the entire deposition surface of the channel. As a result, only a consideration of the local changes is necessary.

There is some justification for the use of this assumption in the present circumstance. All results were obtained under conditions where the concentration boundary layer was developing at every position along the channel length. As a result, the maximum differences in initial deposition rate as a function of channel length are obtained when Leveque's solution, Eq. [4.3], applies. An inspection of Eq. [4.3] reveals that the mass-transfer controlled initial deposition rates are not a strong function of longitudinal distance \( J_D^* \propto x^{-1/3} \). With time, because the upstream regions receive more deposition than their downstream counterparts, it might be expected that the upstream deposition rates would decline more rapidly than those downstream. As a net result, the accumulation curves obtained at all positions in the channel should not be significantly different from one another. This hypothesis is corroborated by Fig. 4.9, which is a plot of the accumulation results measured at four different longitudinal distances in run I-3. Figure 4.9 demonstrates that the concentration of deposited particles measured at
Figure 4.9. Effect of longitudinal distance on deposition onto a positive 2VP/S substrate. Run I-3.
any given time does not vary markedly with distance and, in fact, for the reasons mentioned above, appears to be converging to the same asymptotic coverage. [Some licence was admittedly taken in drawing the curves in Fig. 4.9. However, for reasons given in some detail in Sect. 3.4.3.2, the distance-dependent accumulation measurements were not considered to be very accurate.]

The first model, due to Wnek et al., was devised to predict the effect of surface coverage on the rate of particle deposition onto spherical filter collectors (153) and onto a rotating disc (155). The basic premise of this model is that the deposition of each particle alters the average charge density of the entire surface by a fixed amount such that, when the surface is completely covered with particles \( \theta = 1 \), a new plane surface is created which has the same charge density as the particles. Thus, because the charge density and the \( \zeta \)-potential (Stern potential) are intimately related, the deposition of negatively charged particles onto a positively charged substrate effectively decreases the \( \zeta \)-potential of the substrate. With sufficient deposition, the substrate \( \zeta \)-potential becomes negative. This gives rise to a repulsive potential energy barrier and hence, a reduced rate of deposition.

For both geometries considered, Wnek et al. assumed that the overall deposition process could be represented by the same model used in the present study, i.e. convective-diffusion in the bulk with a first-order reaction at the collector surface. Thus, while the wall \( \zeta \)-potential remains positive, deposition should be approximately mass-transfer controlled and the initial portion of the accumulation curve should be nearly linear with time. Once the wall \( \zeta \)-potential becomes negative, because the resulting K-value is generally very sensitive to changes in \( \zeta_w \), a sharp drop-off in the rate of deposition might be expected. Furthermore, because at \( \theta = 1 \) the
deposition surface would have the same high charge density as the suspended particles, it would be expected that these changes in deposition rate would occur when $\theta < 1$.

Thus, the model of Wnek et al. provides a good qualitative explanation for the characteristic shape of the accumulation curves obtained in the present investigation (see, for example, Fig. 4.5). This qualitative picture is strongly supported by the wall $\zeta$-potential measurements obtained for run I-2, which have also been plotted on Fig. 4.5 as a function of time. As predicted by the model, $\zeta_w$ decreases with time and eventually assumes negative values. Furthermore, the $\zeta_w$ curve is almost the mirror-image of the accumulation curve, demonstrating the same steep rate-of-change initially followed by a much slower approach to an approximately asymptotic value.

The fact that the deposition rate begins to decline markedly before $\zeta_w$ reaches zero may be explained on two counts. First, the measured $\zeta_w$ is the average value for the entire surface of the test section and is therefore not necessarily an accurate representation of the local (average) $\zeta$-potential at the position where the accumulation curve was measured. In addition, for the reasons mentioned in Sect. 3.5.3.2, $\zeta$-potentials measured in the region $\zeta_w \sim 0$ by the streaming potential technique must be viewed with some skepticism.

In order to test the ability of the model to predict quantitative behaviour, it is first necessary to carry out some mathematical development. A charge balance over a local area of the wall surface gives

$$\frac{d \sigma_w}{dt} = \hat{q}_p J_D$$  \hspace{1cm} [4.13]
where \( \sigma_w \) is the surface charge density (coulombs/cm²) of the wall, \( \hat{q}_p \) is the effective charge (coulombs) of a depositing particle, and \( J_D^t \) is the dimensional instantaneous deposition rate (particles/cm²-sec.). In the model of Wnek et al., the effective particle charge \( \hat{q}_p \) is such that when the wall is covered by a monolayer of deposited particles (i.e. \( \theta = 1 \)) a new surface is formed having the same charge density as the suspended particles. Thus,

\[
\hat{q}_p = 4a^2\left[\sigma_p^0 - \sigma_w^0\right] \tag{4.14}
\]

where \( a \) is the particle radius and \( \sigma_p^0 \) and \( \sigma_w^0 \) are the initial charge densities of the particle and wall, respectively. [In fact, in the analysis of Wnek et al., the effective particle charge is given by \( \hat{q}_p = 4a^2\left[\sigma_p^0 - \sigma_w^0(1 - e^{-2\kappa a})\right] \). The authors suggest that the last term in this expression must be included to account for the influence that the underlying wall might have on the charge density of the new pseudo-surface located at a distance of one particle diameter from the wall, i.e. they suggest that at \( \theta = 1 \), the final surface charge density would be equivalent to \( \sigma_p^0 + \sigma_w^0 e^{-2\kappa a} \). However, it seems unlikely that the wall surface potential would fall off according to the usual relationship (i.e. as \( e^{-\kappa h} \)) when the wall is covered with solid particles. Thus, this additional term was neglected in the present analysis. In any event, since \( \kappa a \) is always greater than unity in the present experiments, \( e^{-2\kappa a} \ll 1 \), and hence little error is incurred in Eq. [4.14] by neglecting this term.]

The surface charge and the \( \zeta \)-potential for a flat surface are related approximately by

\[
\sigma_w = \frac{\varepsilon \kappa \zeta_w}{4\pi} \tag{4.15}
\]
and for a spherical particle, approximately by

\[ \sigma_p = \frac{\varepsilon (1 + \kappa a) \zeta_p}{4\pi a} \]  

where \( \varepsilon \) is the solution dielectric constant as before (20). If Eqs. [4.14], [4.15], and [4.16] are substituted into Eq. [4.13], the following equation relating the change in the wall \( \zeta \)-potential with time is obtained:

\[ \frac{d \zeta_w}{dt} = 4a^2 \left[ \frac{(1 + \kappa a)}{\kappa a} \zeta^0_p - \zeta^0_w \right] J_D' \]  

The wall concentration \( C_w \) at any given time may be obtained from the differential equation

\[ \frac{d C_w}{dt} = J_D' \]  

Since \( J_D' = J_D'(\zeta_w) \), Eqs. [4.17] and [4.18] constitute a system of two first-order differential equations which must be solved simultaneously to obtain \( \zeta_w \) and \( C_w \) as functions of the independent variable \( t \). This system of equations is subject to the initial conditions \( \zeta_w = \zeta_w^0 \) and \( C_w = 0 \) when \( t = 0 \).

Because the relationship between \( J_D' \) and \( \zeta_w \) is generally rather complicated, the system of equations can only be solved numerically using, for example, Runge-Kutta methods. For relatively large potential barriers (\( \phi_{\text{max}} \geq 5 \, \text{kT} \)), \( J_D' \) is related to \( \zeta_w \) through Eqs. [4.1] and [4.5]. However, as was pointed out in the previous section, there is as yet no solution for \( J_D' \) when \( \phi_{\text{max}} < 5 \, \text{kT} \) and particularly when the double layer interaction is attractive. In their numerical calculations, Wnek et al. circumvent this problem by assuming that \( J_D' \) remains constant at the mass-transfer controlled rate until a finite energy barrier appears (i.e. soon after \( \zeta_w \) changes sign).
From this point onwards, a value of $J_D^i$ can be estimated by carrying out an approximate integration for the $K$-value.

On the basis of these assumptions, it becomes necessary to examine only the initial part of the accumulation curve in order to obtain a comparison between predicted and experimental results. Therefore, it is assumed in the following analysis that $J_D^i$ remains approximately constant until such time as $\zeta_w = 0$. Thus, in the interval $\zeta_w^0 \geq \zeta_w \geq 0$, Eqs. [4.17] and [4.18] can be integrated immediately to yield

$$C_w = J_D^i t \quad \text{[4.19]}$$

and

$$\zeta_w = \zeta_w^0 + 4a^2 \left[ \left( 1 + \kappa a \right) \frac{\zeta_w^0}{\kappa a} - \zeta_p^0 \right] J_D^i t, \quad \text{[4.20]}$$

respectively. By substituting Eq. [4.19] into [4.20] and recognizing that $\theta = 4a^2 C_w$, the following relationship between $\zeta_w$ and $\theta$ is obtained:

$$\zeta_w = \zeta_w^0 + \left[ \left( 1 + \kappa a \right) \frac{\zeta_w^0}{\kappa a} - \zeta_p^0 \right] \theta \quad \text{[4.21]}$$

Thus, the concentration of deposited particles should increase approximately linearly with time at least until $\zeta_w = 0$, i.e. when the surface coverage reaches

$$\theta_0 = \left[ 1 - \frac{(1 + \kappa a) \zeta_p^0}{\kappa a \zeta_w^0} \right]^{-1} \quad \text{[4.22]}$$

For run 1-2 (Fig. 4.5), for example, where $\kappa a = 1.97$, $\zeta_p^0 = -96 \text{ mv}$ and $\zeta_w^0 = +25 \text{ mv}$, Eq. [4.22] predicts that significant deviations from the initial rate of deposition should not occur until $\theta_0 = 0.147$. In fact, as
can be seen from Fig. 4.5, such deviations begin to occur at a much smaller surface coverage, namely about 0.050. With the exception of those few runs (I-4, I-6, II-9, and II-12) where $\zeta^0_w \sim 0$, a similar discrepancy between theoretical and measured results was obtained for all other experiments, i.e. the surface coverage at which the deposition rate began to fall dramatically was always significantly less than predicted by Eq. [4.22]. When $\zeta^0_w$ becomes small, Eq. [4.22] predicts that under otherwise constant conditions, $\theta_0$ should also become small. This is precisely the trend which was observed earlier in Fig. 4.8 for runs II-9 and II-12.

Thus, although the model of Wnek et al. correctly predicts the shape of the accumulation curves [see for example the calculated curves in reference (155)] and the observed influence of the wall $\zeta$-potential, it does not yield a good quantitative agreement with the experimental results. Furthermore, it does not provide a satisfactory interpretation of the other observed trends. For example, Eq. [4.22] predicts that as the double layer thickness ($1/\kappa$) is decreased, $\theta_0$ should decrease. This is in fact the trend observed in runs III-1, -4, and -5 (Fig. 4.6). However, because $\kappa a \gg 1$ in these experiments and because $\theta_0$ is very insensitive to changes of $1/\kappa$ in this range, the equation is not capable of predicting the rather substantial effects which were actually observed. For larger double layer thicknesses, where Eq. [4.22] becomes much more sensitive to $1/\kappa$ changes, the theory predicts the opposite trend to that which was actually observed. Eq. [4.22] predicts that $\theta_0$ increases with increasing particle size, a direct contrast to the observed trend. In addition, the Wnek model suggests that the effect of surface coverage on the deposition process should be independent of the fluid flow rate, whereas experimentally it appears (Fig. 4.7) that increasing the velocity increases the effect.
An improvement in the model could possibly be attained by providing a more realistic interpretation of the discharging effect of each depositing particle. For example the measured average wall \( \zeta \)-potentials in Fig. 4.5 suggest that the local values of \( \zeta_w \) fall much faster than predicted by the present model. Thus, the effective particle charge \( \hat{q}_p \) must be greater than that predicted by Eq. [4.14]. If it is assumed that \( \hat{q}_p \) is an arbitrary constant, Eqs. [4.13] and [4.18] can be re-integrated with the usual constraints to give

\[
\theta_0 = \frac{-a^2 \varepsilon \kappa \zeta_0^0}{\pi \hat{q}_p}
\]  

[4.23]

Thus an increase in \( \hat{q}_p \) causes \( \theta_0 \) to become smaller, which brings the prediction more in line with the actual measured results. For example, for run 1-2 (Fig. 4.5), Eq. [4.14] gives \( \hat{q}_p = -1.857 \times 10^{-16} \) coulombs. If it is assumed that the average rate of deposition on the surface is given by the measured value at \( x = 12.5 \text{ cm} \) (probably slightly low), then the effective particle charge which would yield the initial rate of change of the \( \zeta_w \) curve observed in Fig. 4.5 can be estimated as \( \hat{q}_p = -4.302 \times 10^{-16} \) coulombs. When this latter value is substituted into Eq. [4.23], a much more realistic estimate of \( \theta_0 \), namely 0.063, is obtained.

Thus, it is tempting to use the measured changes in \( \zeta_w \) to predict the influence of surface coverage on the deposition rate. However, aside from the uncertainties in estimating average deposition rates and in the \( \zeta_w \) values themselves, such a method is after all only an empirical one. A model which requires \( J_D' \) to be dependent on the local average \( \zeta_w \) should be capable of predicting both parameters.
It is possible to imagine how the deposition of individual particles could have a larger effect on the local wall ζ-potential than is suggested by Eq. [4.17]. Consider the changes in the average potential of an arbitrary area of the channel wall caused by the deposition of a single particle into this area as they might appear to an observer situated directly above the surface. Initially, the surface would have an average ζ-potential of ζ₀.

After the particle had deposited, there would exist a circular zone of area πa² where ζₚ = ζ₀, surrounded by a region (whose radial dimension is proportional to 1/κ) where ζₚ gradually changes spatially from ζ₀ to ζ₀. Thus, assuming that the distribution of ζₚ in the latter region is known and that ζₚ → ζ₀ within the limits of the boundaries of the arbitrarily chosen area, it becomes possible to estimate the change in the average potential of this area due to the deposition of a single particle. The total change in surface charge required to affect this change in average potential is the new effective particle charge ̂qₚ. By making different assumptions regarding the distribution of potential at distances beyond the particle radius, several alternative representations of ̂qₚ were derived. These generally tended to increase ̂qₚ and increase the sensitivity of the predicted results towards changes in 1/κ (in line with the trend observed in Fig. 4.6). However, these improvements were not very substantial. In addition, it is rather difficult to imagine how the model could be modified to correctly predict the other observed trends.

It is believed that the approach taken by the model of Wnek et al. is fundamentally incorrect. The model assumes that the deposition of particles onto a surface which is taken to be initially homogeneous does not change the homogeneous character of the surface. All that is changed is the value of the assumed homogeneous charge on the surface. However, because the
deposited particles are identical in size with those in suspension, considering how the surface now appears to a suspended particle, deposition in fact leads to a very heterogeneous surface, not only in terms of energy but also in terms of geometry. It is believed that only by accounting for heterogeneities of energy and geometry will a satisfactory explanation of the observed phenomena be obtained. A new model is required which takes these heterogeneities into account.

The second model was developed by Ruckenstein et al. (153) to explain the coverage-dependent rate of cell deposition through a stagnant fluid onto a horizontal plane by sedimentation and diffusion when there is a repulsive double layer interaction present. This model is a first attempt to account for the heterogeneity introduced by the deposition of particles onto a surface. It is based on the simple assumption that the rate of deposition on the bare surface does not change with time but, because of coverage, the surface area available for deposition decreases and hence, the overall deposition rate decreases with time. In fact, the model of Ruckenstein et al. was generalized to include the possibility of further deposition, at a second characteristic rate, onto previously deposited particles. Thus, in their case, the overall deposition rate was the surface area average of the two characteristic rates. In the present case the high charge density on the particles precludes the possibility of further deposition.

If it is assumed that each deposited particle occupies an area of $4a^2$ (i.e. a complete monolayer corresponds to $\theta = 1$ as before), then the differential equation describing the variation of the surface concentration $C_w$ with time is given by
\[
\frac{d C_w}{dt} = (1 - 4a^2 C_w) J_D'
\]  \[\text{[4.24]}\]

subject to the initial condition \(C_w = 0\) at \(t = 0\). In this model, \(J_D'\) is the initial dimensional deposition rate, i.e., the deposition rate onto the bare surface. Eq. [4.24] can be integrated immediately to yield

\[
C_w = \frac{1}{4a^2} \left[ 1 - e^{-4a^2 J_D' t} \right]
\]
or

\[
\theta = 1 - e^{-4a^2 J_D' t}
\]  \[\text{[4.25]}\]

since \(\theta = 4a^2 C_w\). This model, as proposed by Ruckenstein et al., predicts that the surface coverage should asymptotically approach \(\theta = 1\) with time, a result which is apparently not borne out by the present experimental evidence.

How can the model be improved? First it should be recognized that, because of the finite thickness of the electrical double layer surrounding each sphere, there is a certain minimum distance of separation below which two particles cannot approach each other. Thus, each particle has an effective radius of influence \(a_e\) which is larger than the particle radius \(a\). If \(a\) is replaced by \(a_e\) in Eq. [4.24], re-integration now gives

\[
\theta = \left( \frac{a}{a_e} \right)^2 \left[ 1 - e^{-4a^2 J_D' t} \right]
\]  \[\text{[4.26]}\]

Thus, since \(a_e/a > 1\), the asymptotic surface coverage must always be less than unity. Furthermore, because the ratio \(a_e/a\) increases with increasing double layer thickness, Eq. [4.26] predicts that the maximum coverage attained should decrease with increasing \(1/\kappa\). This was the trend observed earlier in Fig. 4.6.
In order to obtain a quantitative comparison between Eq. [4.26] and the measured results, it is necessary to establish a method for estimating \( a_e \). Let us assume that \( 2(a_e - a) \) is the distance of separation between two particles at which the overall interaction energy is equal to \( kT \), the average thermal energy of the particles. In fact, because there is a finite probability that one particle could approach to within any distance of a second particle, \( a_e \) may have a distribution of values. However, the characterization of \( a_e \) given above seems a reasonable choice for the average value of this distribution. The double layer interaction energy of two spheres at separations large compared to the double layer thickness may be found by applying the linear superposition approximation (see Sect 2.1.1.1). For two equal spheres of surface potential \( \zeta_p \) embedded in an infinite medium, Bell et al. (28) obtained the following expression for the double layer interaction energy:

\[
\phi_{edL} = \frac{\varepsilon \zeta_{pe}^2 a^2 e^{-2\kappa(r-a)}}{2r}
\]

where \( 2(r-a) \) is the separation distance and \( \zeta_{pe} \) is the effective surface potential of the spheres. The latter is defined as the surface potential which would correspond to the actual potential distribution at large \( \kappa(r-a) \) if the linearized Poisson-Boltzmann equation were to apply at all distances \( (r-a) \) from the particle surface. Because, for \( \zeta_p \geq 25 \text{ mv} \), the potential versus distance relationship is much stronger than the exponential one obtained by linearizing the P.-B. equation, \( \zeta_{pe} \) is always less than \( \zeta_p \). Numerical values for \( \zeta_{pe} \) as a function of \( \zeta_p \) and \( \kappa a \) have been tabulated by Loeb et al. (156). The potential distribution between two spheres situated on a wall will be distorted by the presence of this additional plane surface. Thus,
Eq. [4.27] very likely overestimates the double layer interaction energy between two negatively charged spheres on a positively charged wall. For \( \kappa a \gg 1 \), this deviation is expected to be minimal. The retarded London-van der Waals interaction energy \( \phi_{vdw} \) between two identical spheres is also given by Clayfield et al. (36). This equation, which is similar in form to Eq. [2.12], is too long to reproduce here.

For run 1-2, for example, where \( \kappa a = 1.97 \) and \( \zeta_{pe} = -80.5 \) mv \( (\zeta_p = -95.9 \) mv), it was found that \( \phi = \phi_{edl} + \phi_{vdw} = kT \) when \( a_e = 2.26 a \), assuming that the Hamaker constant \( A = 10^{-13} \) ergs. When this value of \( a_e \) is substituted into Eq. [4.26] the curve shown as a dashed line on Fig. 4.10 is obtained. As can be seen from Fig. 4.10, Eq. [4.26] with \( a_e/a = 2.26 \) predicts the attainment of a much higher surface coverage than is actually observed (at \( t \to \infty, \theta \to 0.196 \)). Although increasing \( a_e \) would reduce \( \theta \) further, it is in fact very likely that \( a_e \) has already been overestimated rather than underestimated, for the reasons mentioned above. In addition, the exponential shape of the theoretical curve does not correspond to that of the experimental curve.

A second problem with the model of Ruckenstein et al. is that it does not correctly account for the finite size of the depositing particles. It effectively deals only with particle centres which are assumed to deposit anywhere on the uncovered surface. In fact, a particle centre cannot approach to a distance less than \( 2a_e \) from the centre of a previously deposited particle. Thus, the surface area available for the deposition of particle centres at any given stage of the process is likely to be less than is suggested by the model just developed. In addition, a correct accounting for the finite size of the depositing particles leads to the possibility of some areas of the uncovered surface being totally excluded from further deposition. For example,
Figure 4.10. Comparison of measured surface coverages (solid line) with those predicted assuming minimum geometric exclusion (dashed line) and maximum geometric exclusion (dot-dash line). Run I-2.
if one particle centre deposits within $4a_e$ of a second particle centre, a
good part of the area between the two particles will no longer be available
for deposition.

In order to correctly account for the finite size of depositing
particles, it is necessary to know something about the geometric distribution
of all of the particles which have previously deposited on the surface.
Hull (139) showed that the deposition of negatively charged polystyrene
spheres onto a positively charged 2VP/S substrate followed a Poisson distri­
bution, i.e. the process was completely random. As a random distribution is
rather difficult to deal with, let us consider instead the extreme case
where all of the deposited particles are assumed to position themselves a
maximum distance away from one another at all stages of the process. Thus,
as is depicted in Fig. 4.11, the particles will be located on the intersection
points of a square grid whose spacing is equal to $1/\sqrt{C_w}$. Whereas in the
previous version of this model, the fractional area available for deposition
was given by $\alpha = 1 - \left(\frac{a_e}{a}\right)^2 \theta$, in the present case $\alpha$ (shaded area/area of
rectangle) is given by

$$\alpha = 1 - \pi \left(\frac{a_e}{a}\right)^2 \theta, \quad \theta \leq \frac{a^2}{4a_e^2}$$

$$= 1 - \left(4 \left(\frac{a_e}{a}\right)^2 \theta - 1\right) - \frac{a_e}{2} \theta \sin^{-1} \left(\frac{a_e^2}{2a_e^2 \theta} - 1\right),$$

$$\frac{a^2}{4a_e^2} \leq \theta \leq \frac{a^2}{2a_e^2}.$$  \[4.28\]

where $\theta = 4a^2C_w$ as before. In general, the differential equation relating
the change in surface coverage with time is given by
Figure 4.11. Surface area available for further deposition (cross-hatched region) assuming particles deposit in a square array.
\[ \frac{d\theta}{dt} = 4a^2 \alpha J_D \]  

subject to the initial condition \( \theta = 0 \) at \( t = 0 \). Upon substituting Eq. [4.28] into [4.29] and integrating, the following relationship for \( \theta \) is obtained:

\[ \theta = \frac{a^2}{n a_e^2} \left( 1 - e^{-4\pi a^2 J_D t} \right), \quad \theta \leq a^2/4a_e^2 \]

\[ \int_a^\theta \frac{d\theta}{4a_e^2 \left[ 1 - \left( \frac{4a_e^2 \theta}{a^2} - 1 \right)^{1/2} - \frac{2a_e^2 \theta}{a^2} \sin^{-1}\left[ \frac{a_e^2 \theta}{2a_e^2} - 1 \right] \right]} = 4a^2 J_D t + \frac{a^2 \ln(1 - \pi/4)}{na_e^2}, \quad \frac{a^2}{4a_e^2} \leq \theta \leq \frac{a^2}{2a_e^2} \]  

[4.30]

Eq. [4.30] predicts that the maximum surface coverage attained will be \( \frac{a^2}{2a_e^2} \), or exactly half of the asymptotic coverage predicted by Eq. [4.26]. At \( \theta > \frac{a^2}{2a_e^2} \), the space remaining between four adjacent particles on the grid will not be large enough to receive another particle. Thus, \( \theta = a^2/2a_e^2 \) represents the coverage at which the maximum possible geometric exclusion can occur.

For run I-2, assuming again that \( a_e/a = 2.26 \), Eq. [4.30] yields the dash-dot line shown in Fig. 4.10. (The second expression in Eq. [4.30] was integrated numerically by Simpson's Rule for fixed values of \( \theta \) in the range indicated, and then solved for \( t \).) As can be seen from Fig. 4.10, Eq. [4.30] appears to give results in reasonable accord with those obtained experimentally, both in terms of quantitative agreement and in the shape of
the curve produced. However, it should be kept in mind that the distribution assumed in deriving Eq. [4.30] represents an extreme case. It not only requires that the initially deposited particles be arranged in a square array, but also that, with each subsequent deposition, all particles redistribute themselves on the surface so as to maintain this pattern. Thus, quantitative agreement between the measured coverages and those predicted by Eq. [4.30] would not generally be expected.

It can be argued that Eq. [4.26] represents the opposite extreme. If each particle deposits as closely as possible to those which have already preceded it to the surface such that large patches of close-packed particles are formed, then as long as the patch size greatly exceeds $a_e$, the remaining fractional area available for deposition will be approximately $\theta = 1 - a_e^2 \theta / a^2$ at all stages of the process. This is exactly the expression for $\alpha$ assumed in deriving Eq. [4.26]. Thus, Eqs. [4.26] and [4.30] represent the extremes of minimum and maximum geometric exclusion, respectively. The accumulation curves produced by a completely random deposition process would be expected to lie somewhere between the curves predicted by these two extreme relationships.

The results of run I-2 (Fig. 4.10) appear to correspond to this hypothesis. However, for most other runs (primarily because $\kappa a$ was generally larger and hence the ratio $a_e / a$ correspondingly smaller) it was found that the measured surface coverages were well below the envelope of possible results predicted by the two relationships. Thus, it is apparently not enough to account for the double layer interaction between deposited particles and the geometric exclusion caused by their random distribution on the channel wall. There must exist some other contributing factor which assists in creating the rather low surface coverages observed in most experiments.
It is believed that this additional effect arises from the fact that the suspension is flowing. Consider a fluid which is in laminar flow over a flat surface. The fluid streamlines form planes which are parallel to the underlying surface. When a particle deposits on a surface, the fluid streamlines are forced to move over and around the obstruction. At very low surface coverages, when the randomly deposited particles are a relatively long distance apart, the distribution of streamlines over the bare portion of the wall is probably little affected. However, when this distance becomes only a few particle diameters, the distribution of streamlines over the bare wall is influenced by the presence of deposited particles; the closer these particles are to each other, the more the streamlines are pushed away from the wall.

In the region where the interaction energy is less than ±kT, each suspended particle is transported only by convection and diffusion. Because of the size of the particles used in the present investigation, their Brownian component is always much smaller than their convective component. Thus, over axial distances of at least several diameters, the suspended particle will tend to travel along a fluid streamline. When this particle passes over or around a deposited particle, the minimum distance of separation between the centre of the former and the surface of the latter will be approximately $2a_e - a$. This distance defines the position of the streamline which convects the particle's centre as close as possible to the wall. When the deposited particles are within a few diameters of one another the streamline over the bare wall will be displaced slightly such that the minimum separation between the particle and the wall is greater than $2a_e - a$. Thus, it is hypothesized that, as the spacing between deposited particles decreases, the probability of a particle diffusing the increased distance to the wall will be greatly reduced.
As a result, it is expected that this hydrodynamic exclusion effect would begin exerting itself at relatively low surface coverages (e.g. $\theta = 0.05$ corresponds to an average particle spacing of 4.5 diameters) and would become more noticeable at higher suspension flow rates. Although the results would have been more convincing had the runs been continued longer, hydrodynamic exclusion appears to be the explanation of the trend observed in Fig. 4.7, i.e. increasing the fluid flow rate under otherwise constant conditions decreases the maximum surface coverage obtained. It is believed that this effect also explains the rather sharp decline in deposition which causes the distinctive shape of most accumulation curves. In addition, because larger particles have smaller diffusivities and project higher above the surface when deposited, it might be expected that increasing the particle size would enhance the hydrodynamic exclusion. Again, this observation is in agreement with the measured results (Fig. 4.8).

Hydrodynamic exclusion also provides a rationalization for the anomalous effect of the double layer thickness on the surface-coverage-dependent deposition. Earlier, it was observed that a maximum suppression of the accumulation results occurred when $0.04 \leq 1/\kappa \leq 0.07 \mu m$. When $1/\kappa \geq 0.07 \mu m$, the surface coverage appeared to increase with increasing double layer thickness while for $1/\kappa \leq 0.04 \mu m$, the opposite trend was observed. The latter trend could be reasonably interpreted in terms of the exclusion (implicit in the use of $a_e$) caused by the interaction of the double layers surrounding each particle. It is postulated here that the former trend can be attributed to the inhibition of the hydrodynamic exclusion effect at larger double layer thicknesses.

This inhibition occurs because the effective radius of influence is less for the interaction between two particles ($a_e^{p-p}$) than for the
interaction between a particle and the wall \( (a_{e}^{p-w}) \). The double layer and van der Waals interactions are much stronger for the sphere-plate geometry than for the sphere-sphere geometry. Furthermore, these two interaction forces are both attractive and hence are additive in the sphere-plate case. Thus, if \( h_{e}^{p-w} \) is the separation between a particle and a wall at which \( |\theta_{ed} + \phi_{vdw}| = kT \) and if the effective radius of influence for the particle-wall interaction is defined as \( a_{e}^{p-w} = a + h_{e}^{p-w}/2 \), then, in general, \( a_{e}^{p-w} - a_{e}^{p-p} > 0 \) and the difference increases with increasing \( 1/\kappa \). Therefore, although a particle centre may be restricted by hydrodynamic exclusion to a distance of approach greater than \( 2a_{e}^{p-p} - a \) from the wall, it may still be in a region where the distance is less than \( 2a_{e}^{p-w} - a \). As a result, its transport to the wall will be facilitated by its interaction with the wall. Thus, even though there is less surface area available for deposition, it is suggested that this facilitated transport effectively suppresses the hydrodynamic exclusion and hence increases the coverage at large \( 1/\kappa \).

The model cannot be satisfactorily modified to account for the anomalously low surface coverages obtained for those runs (eg. 11-9, -12) where the initial wall \( \xi \)-potentials was very small. However, as will be shown in the next section, this phenomenon may be attributed to an altogether different effect.

Thus, because it is able to provide a qualitative explanation for many of the trends observed in the measured accumulation-time curves, the surface coverage model which accounts explicitly for the heterogeneities introduced by the depositing particles appears to be the more fundamentally correct one. However, much effort must still be expended in order to develop a useful quantitative theory for the time-dependent deposition process. In
particular, the inclusion of effects such as random deposition and hydrodynamic exclusion poses a rather difficult challenge.

It is of interest to note that for this second model, the change in the wall $\zeta$-potential with time is not a determinant but a direct result of the deposition process. In fact, if it is assumed that the measured $\zeta_w$ is a surface area average of the initial wall and particle $\zeta$-potentials, then it is possible to reproduce the experimental $\zeta_w$-time curves reasonably accurately on the basis of the accumulation results.

4.3.2 Negatively Charged Substrates

When a suspension of negatively charged silica particles was pumped through test sections whose walls were also negatively charged, it was found that the initial deposition rate was usually significantly less than the mass-transfer controlled rate. Figure 4.12 compares, for example, the accumulation curves obtained for runs I-5 and I-6. Both runs were operated under similar mass-transfer conditions and in both cases the test sections were coated with the 2VP/S copolymer. However, a slight pH shift between runs resulted in an initial wall $\zeta$-potential of -5.7 mv. in run I-5 compared to +3.5 mv. in run I-6. The mass-transfer controlled deposition rate as predicted from Eq. [4.3] was $2.1 \times 10^4$ particles/cm$^2$-sec. for both runs. The experimental values, obtained as the initial slopes of the measured accumulation curves, were $4.4 \times 10^2$ and $2.1 \times 10^4$ particles/cm$^2$-sec. for runs I-5 and I-6, respectively. Thus, it is apparent that the repulsive interaction between the two similarly charged double layers encountered in run I-5 led to a substantial resistance to deposition at the channel walls.

In fact, for all cases involving negative particles and negative substrates investigated in the present study, it was found that the wall
Figure 4.12. Comparison of deposition results obtained for a positively charged substrate (run I-6) with those measured for a negatively charged substrate (run I-5) under otherwise similar conditions.
resistance was generally much greater than the mass-transfer resistance, and hence, was the controlling resistance in the deposition process. It can be shown that for the wall resistance to predominate under the present circumstances, the interaction energy barrier will always have a maximum greater than 5 kT. Furthermore, because the deposition process is controlled by the surface reaction, the suspension concentration at every point in the core region of the channel must be very close to $C_{0}$. As a result, the concept of a concentration boundary layer becomes meaningless and the theoretical assumption requiring that the thickness of the wall region be small compared to the thickness of the boundary layer can be relaxed. Thus, all of the initial deposition rates measured here for negatively charged substrates should be represented by the theory derived in Sect. 2.2.

To test the validity of the proposed model, it is necessary to investigate how each one of the experimental parameters independently influences the initial deposition rate. Thus, the role played by those variables which affect the interaction energy (e.g. wall and particle $\zeta$-potentials, double layer thickness, system Hamaker constant, particle size, and temperature) and those which affect bulk mass transfer rates (e.g. initial suspension concentration, particle diffusivity, flow rate, and channel dimensions) should be examined. Unfortunately, the time available did not allow an extensive investigation of all these parameters. Even more regrettably, experimental difficulties restricted the usefulness of some of the results which were obtained.

The series I experimental runs ($a = 0.201 \mu m$) were considered to be of a trial nature and hence the effect of independently changing the concentration of neutral electrolyte (NaCl) and pH(NaOH) was only briefly studied. In series II ($a = 0.324 \mu m$), the consequences of varying the
counterion concentration were fairly extensively investigated. In these runs, the NaCl concentration was gradually increased at constant pH from a low value of $4 \times 10^{-5}$ moles/\(\ell\). to a maximum of $3 \times 10^{-2}$ moles/\(\ell\), the point at which observable particle coagulation began to occur. Because good reproducibility was demonstrated for two pairs of runs (II-13, -14 and II-15, -16), it was felt that all of the results obtained in this series could be considered fairly reliable.

The same claim could not be made for the series III runs (\(a = 0.300 \ \mu\text{m}\)). The objective in this series was to investigate a wide range of factors which affect deposition onto negative substrates including changes in counterion concentration, suspension pH, suspended particle concentration, solution temperature, and substrate material. However, soon after the completion of the first set of runs which involved increasing the counterion concentration to $3 \times 10^{-3}$ moles/\(\ell\), it was observed that the suspension began to coagulate, a problem which worsened as the series progressed. This unfortunate occurrence was rather unexpected, as the series II suspension had appeared quite stable at the same NaCl concentration. Furthermore, the series III non-radioactive suspension under identical electrolyte conditions did not coagulate significantly. Thus, it is suspected that this unexpected coagulation of the series III radioactive particles was due primarily to the accidental introduction of contaminants into the system, e.g. chromic acid, introduced by an improperly flushed test section, had been earlier demonstrated to have a pronounced effect on suspension stability (see Sect. 3.3.1). Because the bulk of the particles had already been committed to the experiment, there was no option left but to continue the series in the hope that some sense could be made of the subsequent results. However, starting with run III-8 onwards, the measurements presented no consistent pattern and
attempts at obtaining reproducibility (runs III-9, -13 and runs III-15, -16, -17) met with complete failure. The inconsistency of these results suggests that the presence of surface-active contaminants is the major source of the problem rather than any inherent instability of the suspension itself.

Thus, the discussion which follows is restricted to those measurements of particle deposition onto a negative substrate which are considered to be reasonably reliable. The results of the other experiments, however, have been included in Appendix C.3 for further reference.

The accumulation results obtained when the concentration of neutral electrolyte (NaCl) was varied under constant pH conditions are shown in Figs. 4.13, 4.14, and 4.15 for series I, II, and III, respectively. In all cases, the deposition substrate is a thin (~200 Å) film of Formvar. For all three series, it can be observed that as the NaCl concentration increases at a constant pH, the initial rate of deposition (given by the slope of the dashed lines) also increases. This phenomenon can be explained on two counts. First, an increase in the counterion (Na\(^+\)) concentration causes the double layer thickness (1/\(\kappa\)) to decrease in accordance with Eq. [2.2]. As was earlier observed in Fig. 2.5, decreasing the double layer thickness under otherwise constant conditions decreases the height and breadth of the interaction energy barrier and hence reduces the resistance to deposition. Secondly, increasing the NaCl concentration also increases the equilibrium adsorption of counterions into the Stern layer surrounding each surface. As a result, the surface potential (which is determined by the concentration of potential determining OH\(^-\) ions in solution) remains unchanged, but the potential at the outer Helmholtz plane and hence the \(\zeta\)-potential is lowered. This result is demonstrated quite clearly by Fig. 4.16, which shows the particle and wall \(\zeta\)-potentials measured for the experimental conditions encountered in
Figure 4.13. Effect of counterion concentration on deposition onto a negative Formvar substrate. Series I. Run I-9: \([Na^+] = 4.60 \times 10^{-5} \text{ M}\), run I-10: \([Na^+] = 1.00 \times 10^{-3} \text{ M}\), run I-11: \([Na^+] = 1.02 \times 10^{-2} \text{ M}\).
Figure 4.14. Effect of counterion concentration on deposition onto a negative Formvar substrate. Series II. Run II-13: $[\text{Na}^+] = 3.99 \times 10^{-5}$ M, run II-16: $[\text{Na}^+] = 1.46 \times 10^{-4}$ M, run II-17: $[\text{Na}^+] = 1.00 \times 10^{-3}$ M, run II-18: $[\text{Na}^+] = 2.85 \times 10^{-3}$ M, run II-19: $[\text{Na}^+] = 9.40 \times 10^{-3}$ M, run II-20: $[\text{Na}^+] = 2.80 \times 10^{-2}$ M.
Figure 4.15. Effect of counterion concentration on deposition onto a negative Formvar substrate. Series III. Run III-2: [Na$^+$] = 4.29 x 10$^{-5}$ M, run III-3: [Na$^+$] = 3.51 x 10$^{-4}$ M, run III-6, [Na$^+$] = 2.81 x 10$^{-3}$ M.
Figure 4.16. Effect of counterion concentration on particle and wall ζ-potentials. Series II. pH = 6.7.
series II. The open symbols represent the ζ-potentials actually measured during runs II-13 to -20 whereas the solid points were obtained using artificial suspensions prepared from the series II particles. According to the theory developed in Chapter 2, if the magnitude of the ζ-potential of one or both interacting double layers is decreased, the height of the repulsive energy barrier should also decrease. Thus, increasing the concentration of neutral electrolyte decreases the double layer thickness as well as the magnitudes of both the particle and the wall ζ-potential and, as a result, increases the rate of particle deposition.

Figures 4.17 and 4.18 show the effect of altering the suspension pH under conditions where the double layer thickness remains relatively constant for series I and series III, respectively. [Of course, it is impossible to maintain an absolutely constant counterion concentration while adding NaOH to change the pH. However, a good approximation of this condition can be achieved in practise by utilizing a relatively high salt concentration throughout each set.] Again, the substrate was Formvar in all cases. Although the data are rather scanty, the same trend can be observed in both sets, i.e. increasing the pH markedly decreases the initial deposition rate. As in the case of the changing counterion concentration, the explanation for these results also seems to follow directly from the theory developed in Chapter 2. The OH⁻ ion is a potential-determining ion for both silica and Formvar surfaces. Increasing the concentration of OH⁻ ions in the solution increases the specific adsorption of OH⁻ ions on or the release of H⁺ ions from (the two mechanisms are indistinguishable) the surfaces of both materials. As a result, the surface potential and hence the ζ-potential of both the particles and the wall increase in magnitude. For example, changing the pH from 6.2 to 8.6 in series I and from 6.0 to 7.0 in series III caused the
Figure 4.17. Effect of pH on deposition onto a negative Formvar substrate. Series I. Run I-11: pH = 6.2, run I-12: pH = 8.6.
Figure 4.18. Effect of pH on deposition onto a negative Formvar substrate. Series III. Run III-6: pH = 6.0, run III-7: pH = 7.0.
magnitudes of $\zeta_p$ to increase from -55 to -80 mv and from -59 to -68 mv, and of $\zeta_w$ to increase from -12 to -21 mv and from -10 to -14 mv, respectively. As was observed earlier in Fig. 2.4, increasing the magnitude of one or both similarly charged $\zeta$-potentials under otherwise constant conditions increases the height of the interaction energy barrier and hence reduces the deposition rate.

Thus, the theory developed in Chapter 2 appears to provide an accurate qualitative description of the experimental results obtained for the deposition of negatively charged silica particles onto negatively charged Formvar surfaces. It is of interest to determine how well the theory performs on a quantitative basis.

From the measured initial deposition rates, $J_{D_{\text{expt}}}$, it is possible to estimate the dimensionless reaction rate constants, $K_{\text{expt}}$, using Eq. [4.5]. $K_{\text{expt}}$ values are tabulated in Table 4.2 for all of the accumulation curves shown in Figs. 4.13-4.15, 4.17, and 4.18. From knowledge of the particle and wall $\zeta$-potentials, the double layer thickness, the particle radius, and the system Hamaker constant, it is also possible to predict a theoretical $K$-value, $K_{\text{theory}}$, for each experiment by integrating Eq. [4.4]. In this case, the values of $\delta$ was increased until the integral became insensitive to further changes in $\delta$. A computer program which evaluates $K_{\text{theory}}$ by numerical integration is listed in Appendix D, Sect. D.2. The $K_{\text{theory}}$ values shown in Table 4.2 for comparison with the experimental $K_{\text{expt}}$ were obtained under the conditions that the surface potentials of each particle and the wall remain constant during the interaction (i.e. $\phi_{ed\zeta}$ is given by Eq. [2.1]) and that the system Hamaker constant $A = 10^{-13}$ ergs.

As can be seen from Table 4.2, although the predicted $K$-values generally follow the same qualitative trends as those measured experimentally,
Table 4.2
Initial Deposition Rates - Repulsive Double Layer Interactions

<table>
<thead>
<tr>
<th>Run</th>
<th>κa</th>
<th>pH</th>
<th>$\zeta_p$ (mv.)</th>
<th>$\zeta_w$ (mv.)</th>
<th>$j_D^{\text{expt}}$ (particles/cm²-sec)</th>
<th>$K_{\text{expt}}$</th>
<th>$K_{\text{theory}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-9</td>
<td>4.48</td>
<td>6.6</td>
<td>-78</td>
<td>-11*</td>
<td>$8.58 \times 10^2$</td>
<td>1.62</td>
<td>$1.56 \times 10^{-17}$</td>
</tr>
<tr>
<td>I-10</td>
<td>20.9</td>
<td>6.3</td>
<td>-100</td>
<td>-15</td>
<td>$2.25 \times 10^3$</td>
<td>4.69</td>
<td>$7.63 \times 10^{-33}$</td>
</tr>
<tr>
<td>I-11</td>
<td>66.7</td>
<td>6.2</td>
<td>-55</td>
<td>-12</td>
<td>$4.08 \times 10^3$</td>
<td>9.51</td>
<td>$6.21 \times 10^{-12}$</td>
</tr>
<tr>
<td>I-12</td>
<td>65.4</td>
<td>8.6</td>
<td>-80</td>
<td>-21</td>
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<td>1.22</td>
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<td>$2.31 \times 10^{-43}$</td>
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* $\zeta_w$-values obtained by streaming potential measurement; otherwise the electro-osmotic technique was used. Substrate was Formvar in all cases.

** measured mobility was greater than permitted by W.L.O. theory. $\zeta_p$ and $\zeta_w$ obtained by interpolation from Fig. 4.16.

*** $K_{\text{theory}} < 10^{-99}$. Calculations limited by computer capability.

**** $\phi_{\text{max}} < 10 kT$. 
quantitative agreement is rather poor. In addition, the discrepancy between theory and experiment appears to worsen as conditions change to promote a larger resistance to deposition. In fact, the theory predicts that under these less favourable circumstances no deposition should take place, whereas measurable deposition occurred in all cases. A very similar trend was observed by Ruckenstein and Prieve (10) in their analysis of the reaction-rate controlled deposition results obtained by Hull and Kitchener (17). The latter authors measured the rate of deposition 0.308 μm dia. polystyrene spheres onto a rotating disc coated with Formvar (both surfaces negatively charged) for varying concentrations of NaCl (0.03-0.3 moles/ℓ.) in the presence of the surface active agent sodium dodecyl sulphate. Ruckenstein and Prieve found that K-value predictions based upon the experimental conditions of Hull and Kitchener were generally orders of magnitude smaller than those observed experimentally and that the disagreement increased with conditions which favoured lower deposition.

There are many possible explanations for these discrepancies. For example, the experimentally measured deposition rates may be greatly in error. However, the good agreement between theory and experiment obtained for the positively charged substrates attests to the accuracy of the measuring technique and to the fact that at least the mass transfer assumptions required by the theory were being met experimentally. Traces of surface active contaminants, which were unavoidably present in most runs, very likely alter the deposition rate. However, they do so by affecting the ζ-potentials of the particles and the substrate. It was for this reason that all electrokinetic measurements were carried out either in situ or by using an actual sample of the suspension taken at the beginning of each run.
Another possibility which would lead to much higher experimental rates than expected is that deposition may be occurring into the "secondary minimum" of the interaction potential energy curve (see Sect. 2.1.2). This explanation can also be discounted for two reasons. First, the release rate measurements (Sect. 4.2) showed that all particles which were deposited on the wall were retained there indefinitely. Because its depth is at most only a few kT (e.g. see Fig. 2.5), particles captured in a secondary minimum would easily diffuse back into the bulk suspension. Secondly, the fact that the measured deposition rates were always less than the mass-transfer controlled rates indicates that each deposited particle must have surmounted a potential barrier in order to get to the wall. There is no potential barrier to deposition into a secondary minimum.

Thus, it would appear that the main source of discrepancy lies with the predicted K-values. Because K is approximately proportional to $e^{-\phi_{\text{max}}/kT}$, it is apparent that even moderate changes in $\phi_{\text{max}}$ can lead to rather catastrophic changes in the rate constant. Thus, it is conceivable that refinements of the expressions used to describe the interaction energy may bring the theoretical K-values into closer conjunction with those obtained experimentally.

In order to derive an analytic expression for the double layer interaction energy given by Eq. [2.1], Hogg et al. (25) found it necessary to make a number of simplifying assumptions, namely, that the distribution of charge and potential is governed by the Poisson-Boltzmann equation, that the linearized form of this equation can be adopted (low potential approximation), that the surface potentials of the two bodies remain constant during the interaction, and that the double layer thickness is small compared to the size of the particle (Derjaguin's approximation). Of these, only the
last is met with any certainty in the experimental runs listed in Table 4.2. It is therefore of some interest to examine how failing to comply with the other assumptions can effect the double layer interaction and hence, $\phi_{\text{max}}$.

It is generally recognized that the Poisson-Boltzmann equation is not always applicable, especially at higher electrolyte concentrations (20, p. 129). Sparnaay (157) introduced the effects of finite ionic sizes and a concentration dependent dielectric constant into his integration of the P.-B. equation, and found an increase in double layer repulsion between similar parallel plates at a given separation distance. However, the correction was negligibly small for electrolyte concentrations less than $10^{-3}$ moles/\text{l.} and contributed only an additional 10-20% at a concentration of $10^{-2}$ moles/\text{l.}

In a more complete treatment of the problem, Levine and Bell (158) have obtained corrections to the P.-B. equation for the effects of ion size, discreteness of charge, dielectric saturation, medium compressibility, and the so-called cavity potentials. They found that many of these effects tend to compensate for one another such that, only at electrolyte concentrations as high as 0.1 molar was there any significant change in the interaction energy between two similar plates, and this small change was a decrease rather than an increase.

Since Eq. [2.1] was derived using the linearized Poisson-Boltzmann equation, its validity is restricted to situations of low surface potential (< 25 mv.), although Hogg et al. (25) claim that it gives a reasonably good estimate of the double layer interaction energy for potentials twice this value. In the present study, the magnitude of the measured wall $\zeta$-potentials usually fell within this range but that of the particles always exceeded 50 mv. By comparing the interaction energies for identical spheres obtained by Honig and Mul (159), who used the exact P.-B. equation in conjunction with
Derjaguin's approximation, with those estimated from Eq. [2.1], Kar et al. (27) found that for large potentials, the latter expression overestimates the energy at all separations. A comparison of the exact (32) and approximate (25) results for the interaction energy between two identical parallel plates leads to a similar conclusion. For both spheres and plates, the error incurred is negligible at potentials less than 25 mv., but increases with increasing potential beyond this range.

Thus, it seems likely that for the interaction between a sphere and plate, the magnitude of whose potentials exceeds 25 mv., use of Eq. [2.1] in place of a solution based on the exact P.-B. equation will yield a value of \( \phi_{\text{max}} \) which is too high. Bell et al. (28) and Bell and Peterson (33) have given approximate (and much more complicated) methods for estimating the interaction energy between dissimilar spheres (including a sphere and a plate) at high potentials. However, although such refinements may lead to a large increase in the predicted rate constants, they are unlikely to result in the many orders of magnitude changes required to bring theory and experiment into alignment.

Use of the constant surface charge boundary condition in place of the constant potential assumption increases the repulsion at close distances of approach and hence yields a larger \( \phi_{\text{max}} \) (e.g. see Fig. 2.7). Recently, Prieve and Ruckenstein (160) have numerically evaluated the energy of interaction between a sphere and a plate under conditions where both surfaces are composed of acid and base ionogenic groups which remain in equilibrium with the intervening electrolyte as one body approaches the other. Under these circumstances, neither the surface charge densities nor the surface potentials remain constant during the interaction, but instead both change in accordance with the equilibrium constants assigned to the two types of
dissociation reactions. However, the calculated energies are still bounded by the two extreme conditions; interaction at constant potential (Eq. [2.1]) and interaction at constant charge (Eq. [2.3]). Thus, although this approach may provide a more realistic representation of the interaction boundary condition, it still yields rate constants which are too small.

Errors in some of the experimental parameters introduced into Eq. [2.1] could also be the source of discrepancies in the estimated double layer interaction energy. For example, because of uncertainties in the electrokinetic measurements and their interpretation, the values obtained for the particle and wall \( \zeta \)-potentials may not be reliable. However, in order to eliminate the differences between experiment and theory, the actual values of these parameters would, in general, have to be less than half of those listed in Table 4.2. In view of the fact that the measured potentials seem to be in line with values available in the literature for amorphous silica (103) and Formvar (139), this possibility seems very unlikely. Cooper (161) has shown that failure to account for the polydispersity of the particle size distribution can lead to an under-estimation of the initial rate of coagulation for a real suspension. Because the double layer interaction energy between two spheres (or a sphere and a plate) is proportional to the radius of the sphere, the initial rate of coagulation (or deposition) is heavily skewed towards that of the smallest particles in the distribution. This effect could become quite pronounced in the series II and III runs, where the actual size distributions are bimodal (see Table 3.2) rather than normal, as Cooper had assumed in his analysis. However, even if the radii of the smaller particles (0.265 \( \mu \)m in series III) are used in the calculations for these runs, the estimated rate constants are still many orders of magnitude too low.
It is recognized that the expression used to represent the distance variation of the van der Waals attraction energy (Eq. [2.12]) is fundamentally incorrect. However, until a more tractable expression for the sphere-plate geometry based on the Lifshitz theory is available, it is difficult to speculate how the inaccuracies implicit in Eq. [2.12] affect the overall interaction energy curves. When the latter expression is used, the magnitude of the van der Waals attraction at all distances is proportional to the value chosen for A, the Hamaker constant. Thus, one possible means of obtaining better agreement between theory and experiment would be to choose a value of A which would lead to an appropriate balancing of the repulsive energy in each case. However, this scheme results in a large range of A-values which show a strong functional dependence on the electrolyte concentration and solution pH. Furthermore, with the exception of run II-20, all of the Hamaker constants thus calculated are much higher than the expected range for colloid interactions in water, i.e. $A = 10^{-14} - 10^{-13}$ ergs.

In deriving the theory of particle deposition presented in Sect. 2.2, the effects of such forces as Born and "steric" repulsion and shear-induced lift forces were disregarded. Inclusion of these effects could conceivably influence the outcome of the analysis. However, it can be argued that if these forces play any role in the deposition process, it is more likely one of reducing rather than increasing the initial deposition rate. For example, "steric" and Born forces, being repulsive, would tend to slow down the deposition process. Because a suitable mathematical description of the lift force in the wall region is lacking, it is difficult to speculate on its role in the process. However, Vasseur and Cox (59) have shown that, for more dense particles in a downflow in a parallel-plate channel (as is the case here), the equilibrium position (zero force) approaches the wall.
only asymptotically as the density difference between particle and fluid increases. Thus, it is expected that the lift force on a particle in the vicinity of the wall will always be away from this surface. Certainly no cases of enhanced deposition which could be attributed to a lift force were observed for the positively charged substrate (Sect. 4.2.1).

In deriving Eq. [4.4] for the reaction rate constant $K$, it was assumed that the inertia of the particles could be ignored. In view of the fact that large changes in the interaction force field take place over very small distances, it is conceivable that a particle's inertia could assist it in surmounting the potential energy barrier and greatly improve its chances of arriving at the wall. To ascertain the importance of particle inertia, a second expression (Eq. [2.62]) for the reaction rate constant $K (= bK_1/D_\infty)$ was obtained by solving a more general wall region diffusion equation, the Fokker-Planck equation, which is valid for rapidly changing potential energy fields. As was discussed in Sect. 2.2.1.2, this solution is valid only when surface interactions result in a potential energy maximum, $\phi_{\text{max}} \geq 10kT$.

For those runs where $\phi_{\text{max}}$ exceeded this value, the rate constants were re-evaluated using Eq. [2.62] and are shown in Table 4.2 for comparison with the $K_{\text{theory}}$-values obtained from the more restrictive Eq. [4.4]. The close agreement which can be observed between each pair of theoretical $K$-values indicates that inertial effects can be considered of negligible importance in the present deposition problem. This agreement occurs because the value of the parameter $(4\gamma)/(m\beta_m^2)$ is in all cases much smaller than unity. It is of interest to note that if this parameter is evaluated using the bulk value of $\beta(= \beta_m/\alpha_m)$ in place of $\beta_m$, then this condition is no longer fulfilled. Thus, it is primarily the viscous damping forces which occur at small distances of separation that prevent particle inertia from being an important consideration.
Although some of the many refinements to the theory of particle deposition discussed above could conceivably result in large changes to the calculated rate constants, it is doubtful whether they could account for the order of magnitude differences observed between theory and experiment. It appears that the explanation to this problem lies elsewhere.

It is believed that the shape of the accumulation curves illustrated in Figs. 4.13-.15, 4.17, and 4.18 provides the clue needed to understand this mystery. One common characteristic of all of the curves shown is that the accumulation of negative particles onto negative substrates is not linear with time. Instead, the accumulation rate steadily decreases as the channel wall becomes progressively covered with particles. As was pointed out in Sect. 4.2, this decrease cannot be attributed to the release of particles from the wall. Also, deviations from linearity begin to occur at coverages (θ << 1) which are far too low for this effect to be ascribed to saturation of the wall in the sense that this term might be used to describe the effect of surface coverage on the rate of deposition onto a positively charged substrate.

In the theoretical analysis, it was assumed that the interacting surfaces were perfectly smooth and homogeneously charged. In reality, however, all solid surfaces are geometrically and energetically heterogeneous. Because of this heterogeneity, the interactions between all particles and the wall are no longer characterized by a single potential energy curve, but instead, may be represented by a range (apparently wide) of such curves. Thus, it is postulated that deposition takes place preferentially onto more favourable sites, i.e., areas of the substrate where the interaction energy maxima are significantly less than the average value. As a result, the initial deposition rate is much faster than the rate predicted by the
characteristic interaction energy curve. Moreover, because these "more active" sites are rapidly filled, the rate of deposition falls off quickly with time.

It is suggested that the existence of preferred sites is due to a heterogeneous distribution of surface charge and to the presence of surface microroughness on both interacting bodies. In general, surfaces become charged by the specific adsorption of potential-determining ions from solution or by the dissociation of surface groups. From knowledge of their $\xi$-potentials, it is possible to estimate approximately the density of surface charges on the wall and the particles using Eqs. [4.15] and [4.16], respectively. Typically, if it is assumed that the charge sites are located in a square array, their average separation is found to be 20-40 Å. Of course, in reality, the distribution of surface charge is much more random. Thus, it seems likely that there could exist comparatively large areas on both interacting surfaces which are relatively weakly charged (or perhaps even uncharged) compared to the average. For the interaction of macroscopic bodies, such areas would be insignificantly small. However, for the interaction of a submicron sphere with a plate (or of two submicron spheres), the size of these weakly charged areas begins to approach the effective area over which the bulk of the interaction takes place. For example, at the highest electrolyte concentration used (e.g. Run II-20), the range of the double layer interaction is only ~50 Å. Thus, even when the two bodies are in contact, the effective area exerting a force on the sphere is confined to a spot about 500 Å in radius.

Heterogeneities in surface geometry can also lead to localized reductions in the double layer interaction between two approaching surfaces. Consider, for example, the hypothetical interaction between a sphere of radius $a$ and a hemispherical projection of radius $a'$ on the wall. Under
conditions where Derjaguin's approximation can be applied, the interaction energy between two dissimilar spheres is proportional to \((aa')/(a + a')\) (25). When \(a' \to \infty\) (i.e. flat plate), \(\phi_{ed} \propto a\). However, if it is assumed for the moment that the interaction with the rest of the plate can be ignored, when \(a' \ll a\), then \(\phi_{ed} \propto a'\). A similar result is obtained when the interaction between a smooth plane and an artificial roughness hump on the sphere is considered. Thus, it is expected that local roughness elements will reduce the local repulsion between a particle and the wall (or between two particles).

The inclusion of surface heterogeneities, therefore, leads to a wide distribution of possible double layer interaction curves for the deposition of particles onto a macroscopically flat substrate. For negative particles and negative walls, because the process is reaction-rate controlled, the rate of deposition is very sensitive to changes in the repulsive maximum in the potential energy curve. Thus, the accumulation curves for this case are characterized by an initial rate of deposition which is very much greater than predicted from the average interaction energy curve, followed by a rapid decline in rate as the sites of lowest energy are filled. For the deposition of negatively charged particles onto non-weakly positively charged substrates, on the other hand, the same surface heterogeneities exist but the process is mass-transfer controlled. Thus, it was earlier observed that the accumulation of particles on this substrate remains approximately linear with time until the previously deposited particles begin excluding a significant fraction of the substrate area from further deposition. When the average substrate potential is very close to zero, it would be expected that a wide distribution of interaction energies might cause a combination of both types of behaviour. Thus, the initial deposition rate would be close to (but less
than) the mass-transfer controlled rate but the effect of surface coverage would be felt sooner than for the more positively charged substrates. This is exactly the type of behaviour observed in Runs II-9 and II-12, where the initial wall ζ-potentials were -4.1 and 0.3 mv., respectively.

Strong evidence for the existence of surface heterogeneities has been recorded in the literature on particle adhesion. For example, Visser has measured the force required to remove carbon-black (64) and polystyrene (65) spheres from a flat cellulose film when the substrate and adhering particles are immersed in an aqueous solution. Typically, it was found that all of the particles were not removed by a single force, but rather, a wide range of forces was required. Although some of this variation could be attributed to the polydispersity of the particles used, it is likely, for the most part, that the distribution is a reflection of the heterogeneous nature of the surfaces involved. For example, almost an order of magnitude range of removal forces was required to detach the middle 95% of the relatively monodisperse polystyrene particles in a 10^{-3} molar solution of NaCl at pH 5.5.

The existence of surface heterogeneity may be the explanation for the quantitative deviations from the DLVO theory frequently observed in studies of colloid coagulation. In recent years, a number of investigations on the kinetics of the coagulation of model colloid systems consisting of spherical monodisperse particles have been reported (39,40,162,163). Many of the results of these studies bear a strong qualitative resemblance to the deposition measurements obtained in the present investigation. For example, it is generally found that, at a given pH, increasing the concentration of an indifferent electrolyte causes the rate of coagulation to increase. However, once a certain electrolyte concentration, termed the critical coagulation concentration, is reached, further increases no longer affect the
coagulation rate; instead, it remains constant at a value determined solely by mass transfer considerations. The critical coagulation concentration (c.c.c.) is, therefore, the electrolyte concentration at which the double layer and van der Waals interaction forces balance each other such that \( \phi_{\text{max}} = 0 \). It is found that the experimental value of the Hamaker constant \( A \) which makes this equality true at the c.c.c. usually agrees quite closely with \( A \) predicted by purely theoretical means. This agreement is considered as one of the proofs for the correctness of the DLVO theory. However, at concentrations less than the c.c.c., where the sols are more stable, coagulation rates predicted from the DLVO theory are invariably orders of magnitude lower than those actually measured, with the discrepancy between theory and experiment increasing with increasing stability.

There have been many reasons put forward to explain these discrepancies, including a number of those which have already been discussed in detail above. Of the many deliberations on this subject, none has ever specifically mentioned the possible effects of surface heterogeneities. Cooper (161), however, has examined theoretically the consequences of allowing the particles to have a Gaussian distribution of surface potentials around a mean value without citing a cause for this variation. Although his calculations are not extensive, they show that even a small spread in surface potentials leads to a large increase in the initial coagulation rate over the uncorrected value based on the mean potential. Furthermore, the difference between the corrected and uncorrected rates increases with increasing variance of the distribution and increasing stability of the sol. Of course, if the particles are large enough, there is probably very little variation in the average surface potential of each particle in the sol. However, because of surface heterogeneities, the interaction energy between
two approaching particles is not a function of their average potentials, but instead is controlled by the local roughness and charge density of the parts coming into contact. One way of representing these two types of heterogeneities is to allow the population of particles in the sol to have a distribution of surface potentials. However, because surface roughness always leads to a reduction in the interaction energy, it is doubtful whether this pseudo-distribution would be normally distributed around the mean obtained from electrokinetic measurements.

Incorporating the influence of surface heterogeneity into a theory of particle deposition is even more difficult than is the case for the process of particle coagulation. Whereas the latter process deals only with surfaces sharing similar characteristics, the deposition process is generally concerned with two materials which not only have different macroscopic dimensions but also have very different microstructures and charge characteristics. Thus, the representation of surface heterogeneities on the two different surfaces as two separate distribution of surface potential leads to an over-determined problem, as it is clear that any number of pairs of assumed distributions could be forced to fit the measured data.

Instead, what is required to improve the present-day understanding of both coagulation and deposition processes is a revised theory of electrical double layer interactions which successfully accounts for the effects of surface heterogeneity. Because heterogeneity of geometry always reduces the interaction energy whereas heterogeneity of surface charge can either increase or reduce it, it is apparent that the improved theory should deal with both aspects separately. In addition, experimental methods of characterizing the heterogeneity of surfaces are also required. Because the
mass-transfer conditions can be uniquely and reproducibly defined in simple channel flows, studies of particle deposition in these systems may be the optimal technique for obtaining such information.
Chapter 5

SUMMARY AND CONCLUSIONS

The deposition of spherical, uniformly-sized, colloidal particles from a suspension in steady fully-developed laminar flow onto the walls of geometrically simple channels has been investigated theoretically and experimentally.

Under these idealized circumstances, deposition takes place by means of Brownian diffusion in the presence of a velocity field (due to the movement of the suspension) and a force field (due to the electrical double layer, London-van der Waals, and viscous interactions between each suspended particle and the channel wall). In general, it is not possible to solve analytically the partial differential equation which results when both fields are simultaneously taken into account. However, under conditions where the interaction forces act over distances which are small compared to the diffusion boundary layer thickness and where the double layer interaction leads to a net repulsive energy maximum which exceeds $5\ kT$, the velocity and force fields can be approximately uncoupled and, as a result, the effect of the various interactions can be lumped into a boundary condition on the equation which treats convection and diffusion only. This boundary condition takes the form of an irreversible first-order chemical reaction at the channel wall. Explicit expressions for the surface reaction rate
constant have been derived in terms of the various parameters which affect the three interaction forces.

The resulting convective-diffusion problem which is an extension of the classical Graetz heat-transfer problem, has been solved for both parallel-plate and cylindrical channels. The use of confluent hypergeometric functions combined with asymptotic techniques allowed a more accurate evaluation of these infinite series solutions than had been previously attained, especially for the deposition of colloids and for cylindrical channels. In addition, because the diffusion coefficients of sub-micron size particles are extremely small, simple Leveque-type asymptotic solutions have also been obtained for the case of large Peclet numbers. It has been shown that the latter solution is applicable under all of the mass transfer conditions encountered in the present experiments. Because the channel wall is modified by the presence of deposited particles, these solutions describe only the initial state of the deposition process.

The rather stringent mass-transfer requirements of the theoretical analysis were met experimentally by using a well-dispersed suspension of uniform, spherical silica particles (0.01-0.05% v/v) and a parallel-plate channel formed from glass and coated with different plastics. The measurement of deposition and release was greatly facilitated by employing particles doped with the $\gamma$-emitter Co$^{58}$ and using a collimated scintillation detector mounted on the channel walls.

Under the conditions of the present experiments, it was found that the rate of particle release from the channel surface was negligibly small. In other words, the adhesion force acting to hold the particle on the wall at the primary minimum of the interaction energy curve was too strong to permit significant diffusion from the surface even in the presence of fluid shear, or significant erosion by collisions with suspended particles.
Thus, the declining rate of accumulation with time observed in most runs could not be attributed to particle release but instead was a result of a declining deposition rate.

The initial rate of deposition of negatively charged silica spheres onto a positively charged plastic substrate was found to be essentially mass-transfer controlled. In fact, in the range of double layer thickness $0.04 \leq 1/\kappa \leq 0.10 \ \mu\text{m}$, the measured rates demonstrated an average deviation of only 10% from the values predicted from the purely diffusion-controlled (i.e. $K = \infty$) Leveque equation. However, a closer inspection of the results revealed that deviations from the Leveque theory (which were more apparent at higher and lower $1/\kappa$) could be explained for the most part by an empirical consideration of the roles played by the various interaction forces. The overall effect of these forces was enhanced under the present circumstances because one or more of them extend much further into the developing concentration boundary layer than is permitted by the theory. Thus, the developed theory (with $K = \infty$) yields only an estimate of the initial deposition rate for the case where particles and wall are oppositely charged. For this case, a better solution could be obtained by numerically solving the coupled mass transfer equation.

The rate of deposition onto a positively charged substrate did not maintain its initial value but instead decreased with time for all runs. For those runs which were reasonably long-lived, it was observed that the concentration of deposited particles approached an asymptotic value at surface coverages which never exceeded 10%. The surface coverage dependent deposition rate was apparently influenced by a number of experimental parameters. For example, higher asymptotic surface coverages could be obtained by decreasing the double layer thickness in the range $1/\kappa \leq 0.04 \ \mu\text{m}$, increasing $1/\kappa$
in the range $1/\kappa \gtrsim 0.07 \mu m$, decreasing the suspension flow rate, decreasing the particle size, and increasing the magnitude of the (positive) wall $\zeta$-potential. It was found that these effects were best interpreted by a model of surface-coverage-dependent deposition which accounted for the surface heterogeneity introduced by the depositing particles. This model is based on the simple premise that, because of coverage, the surface area available for deposition decreases, and hence the overall rate of deposition decreases with time. Qualitative and quantitative arguments were used to show that this coverage effect is enhanced by double layer exclusion (due to the repulsive interaction of the diffuse layers surrounding each particle), by geometric exclusion (due to the finite size of particles and their random deposition on the channel wall) and hydrodynamic exclusion (due to the movement of fluid around the deposited particles).

The initial rate of deposition of negatively charged particles onto a negatively charged plastic substrate was generally much less than onto a positively charged surface and, in fact, was found to be primarily surface-reaction-rate controlled. For negative substrates, the developed theory of particle deposition provided an accurate qualitative description of the measured results. For example, decreasing the double layer thickness (by adding neutral salts) or decreasing the magnitude of the particle and wall $\zeta$-potentials (by lowering the suspension pH) both served to increase the initial deposition rate in accordance with the theoretical prediction. However, the measured values were usually orders-of-magnitude greater than those predicted theoretically. Furthermore, the disagreement between theory and experiment increased with conditions which favoured lower deposition rates. These findings are in line with results obtained by earlier investigations for deposition onto a rotating disc and for coagulation of spherical, monodisperse particles.
Because the deposition process is reaction-rate controlled and because the reaction rate constant is very sensitive to changes in the overall interaction energy, this radical disagreement may be partly attributable to the approximate nature of the expressions used for estimating $\phi$. Thus, for example, using solutions for the double layer interaction based on the exact Poisson-Boltzmann equation and for the van der Waals interaction based on Lifshitz theory, and accounting for the polydispersity of the particle suspension, may well serve to reduce the repulsive maximum and, as a result, bring theory and experiment somewhat closer together. However, it is doubtful whether such refinements could account for the orders of magnitude differences observed.

A better explanation, and one which also rationalizes the shape of the accumulation-time curves observed for the negative substrate case, is that these discrepancies are largely due to the failure of the interaction theory to account for the small-scale heterogeneities which characterize all real surfaces. Because of micro-roughness and a non-uniform distribution of charge sites on each surface, the interaction between a given particle and the substrate is strongly dependent upon the nature of the local areas coming into contact. As a consequence, the interaction of real surfaces may be represented by a wide distribution of possible interaction energy curves. Thus, deposition occurs preferentially onto locally favourable areas of potential and geometry resulting in an initial deposition rate which is much more rapid than predicted by the interaction energy based on electrokinetic measurements. Moreover, because these "more active" sites are rapidly filled, the rate of deposition falls off quickly with time at surface coverages which are characteristically low. Although the same surface heterogeneities are
also present in the case of particle deposition onto a positively charged substrate, they have a negligible influence because the latter process is mass-transfer controlled.

In order to rectify this problem, the DLVO theory must be revised to account for the effects of surface heterogeneity. This is a rather difficult undertaking, especially since there are at present no experimental methods for characterizing either the micro-roughness or the distribution of charge on real surfaces. In view of these uncertainties, the best solution for the moment might be an empirical one: correlating the measured K-values with the experimental parameters which are presently accessible. Due to the innovations of Ruckenstein and Prieve and of Spielman and Friedlander, reaction rate constants obtained for one flow geometry may then be applied to other systems. Because its mass-transfer conditions are uniquely and reproducibly defined, the parallel-plate channel would appear to be the geometry best suited to this task.
Chapter 6

SUGGESTIONS FOR FURTHER WORK

As improved understanding of the particle deposition process under the present idealized circumstances could be obtained by making the following theoretical and experimental modifications.

To better describe the initial rate of deposition of negative particles onto positive substrates (i.e. oppositely charged surfaces), a numerical solution to the coupled transport equation involving convection and diffusion in a field of force is required. Such a solution would be particularly useful in analyzing the results of the present experiments since, even though the deposition process is essentially mass-transfer controlled, one or more of the interaction forces extend far enough into the developing concentration boundary layer to have a significant effect on the overall deposition rate. The numerical solution would also allow a complete evaluation and hence, an improved assessment, of the homogeneous surface-coverage-dependent deposition model due to Wnek et al. An especially challenging task would be to extend the heterogeneous model of surface-coverage-dependent deposition for positively charged substrates to include the effects of random deposition and fluid flow. Once an acceptable model of surface-coverage-dependent deposition has been obtained, attempts should be made to incorporate it into a time-dependent theory for the entire channel surface, i.e. one in which the upstream as well as the local effects are accounted for.
Since the expressions obtained here for the surface reaction rate constant apply to a generalized interaction energy curve, it may be worthwhile to re-assess the present reaction rate controlled theory for the deposition of negative particles onto negative substrates (i.e. similarly charged surfaces) using K-values estimated from the more refined expressions for the double layer (higher potential) and the van der Waals (Lifshitz theory) interaction energies presently available in the literature. However, in order to rationalize the discrepancies which will likely remain between theory and experiment, it is apparent that a new theory for the interaction of dissimilar spheres which successfully accounts for the existence of surface heterogeneities is needed. Although the development of such a theory may prove to be an enormous task, its benefits should have a far-reaching impact in the fields of deposition and coagulation, because heterogeneities of potential and geometry are probably characteristic of all real surfaces. The new theory would yield a distribution of K-values which changes with time as the more preferred deposition sites on the wall are occupied. As a result, it again becomes necessary to solve a time-dependent deposition problem. However, since the deposition process is essentially reaction rate controlled, the solution is much simpler in the case of negatively charged substrates, because all changes occur simultaneously over the entire surface of the channel.

Improved experimental results using the present deposition system could probably be obtained if the measuring loop were modified to rigorously exclude the introduction of contaminants. In particular, a better technique for assembling test sections should be devised which would eliminate the carry-over of chromic acid (or any other surface active cleaning agent) to
the closed loop system. The new assembly method would be additionally advantageous if it also allowed easy dismantling such that the deposition surfaces could be examined under an optical microscope and then thoroughly cleaned for re-use. The optical examination would not only give a corroborative measurement of the final concentration of deposited particles but would also yield valuable information about the distribution of these particles on the surface. Once the apparatus has been successfully modified, the measurements should be extended over a wider range of parameters to provide a more complete investigation of the surface-coverage-dependent deposition onto positive substrates, a more thorough examination of the initial rate of deposition onto negative substrates, and a search for conditions which lead to significant particle release.

In addition to the improvements on the present idealized system, studies of more complex systems which are more representative of practical deposition situations should also be undertaken. Many of the same experimental and theoretical approaches adopted in the present study could be progressively extended to include such complicating factors as turbulent flow, polydisperse particles, non-spherical particles, coagulating suspensions, and rough channel walls. Again, many of these complexities lead to a time-dependent deposition problem.
NOMENCLATURE

Only those symbols used in the main text of the thesis are defined here. Those used in the Appendices are defined in the particular section in which they occur. The units (given in brackets) are those which are most frequently employed.

a \quad \text{particle radius (cm)}

a \quad \text{half-width of flat electrophoresis cell, Sect. 3.5.2 (cm)}

a \quad \text{displacement of interference fringes, Fig. 3.10 (cm)}

a' \quad \text{radius of hemispherical projection on surface (cm)}

A \quad \text{Hamaker constant (ergs)}

A \quad \text{cross-sectional area of flat cell at measuring plane, Sect. 3.5.2 (cm}^2\text{)}

A_1,A_2 \quad \text{constants in Eq. [2.73]}

b \quad \text{half-thickness of parallel-plate channel (cm)}

b \quad \text{half-thickness of flat electrophoresis cell, Sect. 3.5.2 (cm)}

b \quad \text{distance between interference fringes, Fig. 3.10 (cm)}

B = B(x), normalization constant used in Eq. [2.46]

B,C,D,E \quad \text{constants used in Eq. [2.12]}

c \quad \text{electrolyte concentration used in Eq. [3.8] (moles/cm}^3\text{)}

C = C(x,y), \text{concentration of suspended particles (particles/cm}^3\text{)}

C_0 \quad \text{homogeneous suspension concentration at channel inlet (particles/cm}^3\text{)}

C_S \quad \text{suspension concentration at channel wall, Eq. [4.6] (particles/cm}^3\text{)}

C_W \quad \text{concentration of deposited particles (particles/cm}^2\text{)}
\[ C_\delta = C_\delta(x), \] suspension concentration at \( h = \delta \) (particles/cm\(^3\))

\[ D_n \] constant coefficients of Eq. [2.68]

\[ D \] particle diffusion coefficient (cm\(^2\)/sec)

\[ e_0 \] elementary charge = \( 4.80298 \times 10^{-10} \) cm\(^{3/2}\) g\(^{3/2}\) sec\(^{-1}\)

\[ E_n \] coefficients used in Eq. [2.82]

\[ E_\gamma \] energy of \( \gamma \)-radiation (kev)

\[ \Delta E \] potential difference (mv)

\[ \Delta E_{str} \] streaming potential at zero net current flow (mv)

\[ f \] coefficient of dynamic friction (g/sec)

\[ f = f(p) \] fitted correction factor used in Eq. [2.10]

\[ F \] Faraday constant = \( 9.64870 \times 10^3 \) cm\(^2\) g\(^{2/3}\) moles\(^{-1}\)

\[ G = p v^2 a^2 / 2b k T, \] parameter used in determining relative importance of lift force and diffusion in transporting neutrally-bouyant spheres in parallel-plate channel, Sect. 2.1.1.4 (dimensionless)

\[ h \] distance of separation between surface of sphere and surface of plate (cm)

\[ h_0 \] separation distance of closest approach (cm)

\[ h_{\text{max}} \] separation distance at which \( \phi \) is maximum (cm)

\[ H \] distance from \( h_{\text{max}} \) defined by Eq. [2.48] (cm)

\[ I_{11}, I_{3-3} \] factors used in Eq. [2.12]

\[ J \] particle flux (particles/cm\(^2\)-sec)

\[ J_D = D_\infty C_0 J'_D / b, \] dimensionless particle deposition rate

\[ k \] Boltzmann constant = \( 1.38054 \times 10^{-16} \) erg °K\(^{-1}\)

\[ K = b K_1 / D_\infty, \] dimensionless surface reaction rate constant
$K_1$ surface reaction rate constant (cm/sec)

$K_\delta$ pseudo-K-value used as a correlation parameter in Fig. 4.4 (dimensionless)

$l$ interelectrode distance for electrophoresis cell (cm)

$L$ length of test section (cm)

$L_+ , L_-$ cation and anion mobilities, respectively, used in Eq. [3.8] (cm³/sec-mole)

$m$ particle mass (g)

$n$ counterion concentration used in Eq. [2.2] (ions/cm³)

$p = 2\pi h/\lambda$, parameter used in Eq. [2.10] (dimensionless)

$p$ parameter defined by Eq. [2.53]

$Pe = 4v_m b/D_\infty$, Peclet number for parallel-plate channel (dimensionless)

$q$ parameter defined by Eq. [2.53]

$\hat{q}_p$ effective particle charge (coulombs)

$Q$ flow rate (cm³/sec)

$r$ half-distance of separation between centres of two interacting spheres, Sect. 4.3.1.2 (cm)

$R$ universal gas constant $= 8.3143 \times 10^7$ erg °K⁻¹ mole⁻¹

$R$ electrical resistance (ohm)

$Re = 4v_m b\rho/\nu$, Reynolds number for parallel-plate channel (dimensionless)

$t$ time (sec)

$t_\text{expt}$ thickness of coated plastic film, Sect. 3.3.2 (Å)

$t_{1/2}$ half-life of radioactive species (days)

$\tilde{t} = 4a^2 J_{D_{\text{expt}}}$, dimensionless time

$T$ absolute temperature (°K)

$u$ instantaneous particle velocity (cm/sec)

$u_s$ settling velocity of particle used in Eq. [3.1] (cm/sec)
\( v_0 \) apparent electrophoretic velocity at mid-plane, Sect. 3.5.3.1 (cm/sec)

\( v_E \) true electrophoretic velocity at stationary levels, Sect. 3.5.3.1 (cm/sec)

\( v_m \) average suspension flow velocity in parallel-plate channel (cm/sec)

\( dV \) volume element (cm\(^3\))

\( W \) width of test section (cm)

\( W = W(x,h,u)dh\ du \), probability function used in Eq. [2.44]

\( W^* = W^*(x,h)dh \), probability function used in Eq. [2.56]

\( x \) longitudinal distance (cm)

\( X = (2/9\gamma)^{1/3} \xi \), transformation used to solve Eq. [2.86]

\( X \) applied potential gradient, Sect. 3.5.3.1 (volts/cm)

\( y \) distance normal to median plane of parallel-plate channel (cm)

\( y \) distance normal to median plane of flat electrophoresis cell, Sect. 3.5.2 (cm)

\( Y_n = Y_n(\lambda) \), eigenfunctions used in Eq. [2.68]

\( z \) valence

\( z = (2\lambda)^{1/2} \eta \), transformation used to solve Eq. [2.69]

\( \alpha \) Stokes' law correction factor defined by Eq. [2.16] (dimensionless)

\( \alpha = \alpha(t) \), fractional area available for deposition, Sect. 4.3.1.2 (dimensionless)

\( \beta \) parameter defined by Eq. [2.45] (sec\(^{-1}\))

\( \gamma = (1/Pe)(8x/3b) \), dimensionless longitudinal distance

\( \gamma \) parameter defined by Eq. [2.39] (erg/cm\(^2\))

\( \delta \) thickness of wall region (cm)

\( \delta_c \) thickness of concentration boundary layer (cm)

\( \delta' \) innermost boundary of region \((\delta' \leq h \leq \delta)\) where Maxwell-Botzmann distribution is approximately realized

\( \varepsilon \) dielectric constant, \( \varepsilon_{H_2O} \) at 25 °C = 78.30 (120, p. E-61)
\( \varepsilon_\lambda \) wavelength-dependent dielectric constant used in Eq. [2.13]
\( \zeta \) zeta potential (mv)
\( \eta \) = \( y/b \), dimensionless distance normal to median plane of parallel-plate channel
\( \theta \) = \( C/C_0 \), dimensionless suspension concentration
\( \theta \) = \( 4a^2C_w \), dimensionless surface coverage, Sect. 4.3.1.2
\( \theta_0 \) surface coverage at which \( \zeta_w = 0 \), Sect. 4.3.1.2
\( \theta_m \) dimensionless mean concentration
\( \kappa \) inverse double layer thickness defined by Eq. [2.2] (cm\(^{-1}\))
\( \lambda \) conductivity (mho/cm)
\( \lambda \) wavelength of atom dipole fluctuation, Sect. 2.1.1.2 (Å)
\( \lambda \) wavelength of monochromatic light used in interference measurements, Sect. 3.3.2; \( \lambda_{Na} = 5890 \) Å
\( \lambda_n \) eigenvalues used in Eq. [2.68]
\( \lambda_s \) surface conductance (mho)
\( \lambda' \) = \( \lambda + \lambda_s/b \), overall conductance of test section (mho/cm)
\( \Lambda \) geometric factor used in Eq. [2.7] (dimensionless)
\( \mu \) fluid viscosity, \( \mu_{H_2O} \) at 25 °C = 0.008904 g/cm-sec (120, p. F-49)
\( \xi \) = \( h/b \), dimensionless distance normal to parallel-plate channel wall
\( \xi \) parameter defined by Eq. [2.53]
\( \rho \) fluid density, \( \rho_{H_2O} \) at 25 °C = 0.997075 g/cm\(^3\) (120, p. F-5)
\( \rho, \rho' \) parameters used in Eq. [2.12] (cm)
\( \rho_f, \rho_s \) fluid and particle density, respectively, used in Eq. [3.1] (g/cm\(^3\))
\( \sigma \) surface charge density (coulomb/cm\(^2\))
\( \sigma_1, \sigma_2 \) systemic constants used in Eq. [3.6] (cm\(^{-1}\), cm\(^{-3}\))
\( \Sigma_1, \Sigma_2 \) systemic constants used in Eq. [3.5] (cm)
\( \phi \) interaction energy (ergs)
\[ \phi_{\text{max}} \] maximum value of \( \phi \) (ergs)

\[ \psi = \psi(h) \] potential distribution in the double layer (mv)

\[ \psi_0 \] surface potential (mv)

\[ \psi_1, \psi_2 \] Stern potential of particle and wall, respectively (mv)

\[ \psi_0^* \] Stern potential (mv)

\[ \Omega \] geometric parameter used in Eq. [2.16] (dimensionless)

**Subscripts**

- \( a \) circulation loop excluding test section
- \( e \) effective value
- \( \text{edl} \) electrical double layer interaction
- \( \text{expt} \) experimentally measured value
- \( i,j,n \) dummy indices = 1,2,3,...
- \( m \) evaluated at \( h = h_{\text{max}} \)
- \( p \) particle
- \( \text{ret} \) retarded
- \( t \) test section
- \( \text{theory} \) theoretically predicted value
- \( \text{vdw} \) London-van der Waals interaction
- \( w \) channel wall
- \( 0 \) initial value
- \( 1 \) wall region
- \( 2 \) core region
- \( \infty \) bulk property
Superscripts

- a-a interaction between two identical atoms
- p-p interaction between two identical particles
- p-w interaction between a particle and a channel wall
- ret retarded
- σ-σ interaction between two surfaces at constant charge
- σ-ψ,ψ-σ interaction between one surface at constant charge with a second at constant potential
- ψ-ψ interaction between two surfaces at constant potential
- 0 initial value
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APPENDIX A

PARTICLE DEPOSITION - FURTHER THEORETICAL CONSIDERATIONS

A.1 Theory of Particle Deposition in a Cylindrical Channel

Consider now the analogous problem of particle deposition in a cylindrical channel of radius R (Fig. A.1). When \( \kappa R >> 1 \) and \( R/a >> 1 \), the wall region is of such limited extent that curvature effects in this region can be ignored. Under these conditions, arguments similar to those applied to the parallel-plate channel can be used to show that this new problem is also rationalized as equivalent to mass transfer in the bulk with a first-order reaction at the walls. The core-region convective-diffusion equation for \( C_2 = C_2(x,r) \) corresponding to Eq. [2.26] now becomes

\[
2 \left( 1 - \frac{r^2}{R^2} \right) \nu_m \frac{\partial C_2}{\partial x} = D \left( \frac{\partial^2 C_2}{\partial r^2} + \frac{1}{r} \frac{\partial C_2}{\partial r} \right) \tag{A.1}
\]

with boundary conditions

\[
C_2(0,r) = C_0, \quad \left[ \frac{\partial C_2(x,r)}{\partial r} \right]_{r=0} = 0 \tag{A.2}
\]

and

\[
D \left[ \frac{\partial C_2(x,r)}{\partial r} \right]_{r=R} = -K_1 C_2(x,R)
\]
Figure A.1: Cylindrical channel. Particle suspension with a fully-developed laminar velocity profile flows from a region where walls act as particle reflectors ($x < 0$) to a region where deposition can occur ($x \geq 0$).
Again, the first order reaction rate constant, \( K_1 \), is given by Eqs. [2.35], [2.38], [2.43] or [2.62] under the conditions where each of the expressions applies. In these equations, \( h \) is replaced by \( \tilde{h} = R-a-r \).

A.1.1 Core Region Solution

In dimensionless terms, Eq. [A.1] and its corresponding boundary conditions [A.2] may be written as

\[
(1 - \tilde{\eta}^2) \frac{\partial \theta}{\partial \tilde{\eta}} = \frac{\partial^2 \theta}{\partial \tilde{\eta}^2} + \frac{1}{\tilde{\eta}} \frac{\partial \theta}{\partial \tilde{\eta}} \tag{A.3}
\]

with

\[
(0, \tilde{\eta}) = 1 \tag{A.4}
\]

\[
\theta'(-\tilde{\eta}, 0) = 1 \tag{A.5}
\]

\[
\theta(-\tilde{\eta}, 1) + \frac{1}{K} \theta'(-\tilde{\eta}, 1) = 0 \tag{A.6}
\]

where \( \theta = \theta(-\tilde{\eta}, \tilde{\eta}) = C_2/C_0 \), \( K = RK_1/D_\infty \), \( \tilde{\eta} = r/R \), and if \( Pe = 2v_mR/D_\infty \) is the Peclet number, \( \tilde{\eta} = (1/Pe)(x/R) \). In this section the prime denotes differentiation with respect to \( \tilde{\eta} \). This "extended Graetz problem" has also received treatment in the literature. Sideman et al. (71) have given a solution to the constant wall resistance heat transfer analog, while Davis and Parkinson (164) have dealt with the semi-permeable cylinder problem.

By separation of variables, the solution of Eq. [A.3] is

\[
\theta(-\tilde{\eta}, \tilde{\eta}) = \sum_{n=1}^{\infty} D_n Y_n(\tilde{\eta}) e^{-\lambda_n^2 \tilde{\eta}} \tag{A.7}
\]

where \( Y_n(\tilde{\eta}) \) and \( \lambda_n \) are the eigenfunctions and corresponding eigenvalues, respectively, of
\[
\frac{d^2Y}{d\tilde{\eta}^2} + \frac{1}{\tilde{\eta}} \frac{dY}{d\tilde{\eta}} + \lambda^2 (1 - \tilde{\eta}^2) Y = 0
\]  
\[\text{[A.8]}\]

subject to boundary conditions

\[Y'(0) = 0\]  
\[\text{[A.9]}\]

\[Y(1) + \frac{1}{K} Y'(1) = 0\]  
\[\text{[A.10]}\]

Both Sideman et al. (71) and Davis and Parkinson (164) use the conventional power series to obtain a solution to Eq. [A.8]. Because of its superior convergence properties, the confluent hypergeometric function will again be employed here.

If \( \zeta = \lambda \tilde{\eta}^2 \) and \( \psi = \tilde{\eta} Y \), Eq. [A.8] is transformed to Whittaker's equation

\[
\frac{d^2\psi}{d\zeta^2} + \left[ \frac{1}{4\zeta^2} + \frac{\lambda}{4\zeta} - \frac{1}{4} \right] \psi = 0
\]  
\[\text{[A.11]}\]

The general solution is (75, p. 505)

\[\psi(\zeta) = B_1 e^{-\frac{\zeta}{2}} \zeta^{\frac{1}{2}} M\left(\frac{2-\lambda}{4}, 1, \zeta\right) + B_2 e^{-\frac{\zeta}{2}} \zeta^{\frac{1}{2}} U\left(\frac{2-\lambda}{4}, 1, \zeta\right)\]

which may be written

\[Y(\tilde{\eta}) = B_1 \lambda^\frac{1}{2} e^{-\frac{\lambda \tilde{\eta}^2}{2}} M\left(\frac{2-\lambda}{4}, 1, \lambda \tilde{\eta}^2\right) + B_2 \lambda^\frac{1}{2} e^{-\frac{\lambda \tilde{\eta}^2}{2}} U\left(\frac{2-\lambda}{4}, 1, \lambda \tilde{\eta}^2\right)\]  
\[\text{[A.12]}\]

where \( B_1 \) and \( B_2 \) are arbitrary constants and \( U(a,b,x) \) is a confluent hypergeometric function of the second kind. Using the appropriate relationships (75, 165) it can be shown that the boundary condition [A.9] implies that
B_2 = 0. Thus, if the confluent hypergeometric function is expanded in its series form, the solution of Eq. [A.8] becomes

\[ Y(n) = e^{-\frac{\lambda n^2}{2}} \left\{ 1 + \sum_{i=1}^{\infty} \frac{(2-\lambda) \cdots (4i-2-\lambda)}{4^i i! i!} \lambda^i n^{2i} \right\} \]  

[A.13]

where the constants B_i \lambda^{\frac{i}{2}} are absorbed into the coefficients D_n in Eq. [A.7].

The eigenvalues \lambda_n in Eq. [A.7] are the roots of the second boundary condition [A.10], which can be written

\[ F(\lambda) = Y(1) + \frac{1}{K} Y'(1) \]

\[ = e^{-\frac{\lambda}{2}} \left\{ 1 - \frac{\lambda}{K} + \sum_{i=1}^{\infty} \frac{(2-\lambda) \cdots (4i-2-\lambda)}{4^i i! i!} \lambda^i \left[ 1 + \frac{2i-\lambda}{K} \right] \right\} = 0 \]  

[A.14]

For large \lambda, it becomes necessary to use the asymptotic form (Appendix A, Sect. A.2.)

\[ F(\lambda) \approx \frac{2^{4/3} \Gamma(1)}{3^{2/3} \Gamma(2/3)} \left\{ \frac{3}{5K} - 1 \right\} \sin \left[ \frac{\lambda \pi}{4} - \frac{2\pi}{3} \right] \lambda^{-1/3} - \]

\[ \frac{2^{5/3} \Gamma(1)}{3^{4/3} K \Gamma(4/3)} \sin \left[ \frac{\lambda \pi}{4} - \frac{\pi}{3} \right] \lambda^{1/3} = 0 \]  

[A.15]

From the usual orthogonality arguments, the coefficients D_n in Eq. [A.7] are found to be

\[ D_n = \int_0^1 \tilde{n}(1-\tilde{n}^2) \frac{Y_n(\tilde{n})d\tilde{n}}{\int_0^1 \tilde{n}(1-\tilde{n}^2) Y_n^2(\tilde{n})d\tilde{n}} \]  

[A.16]

It has been shown (71) that
\[ \int_0^1 \bar{n}(1-\bar{n}^2) Y_n(\bar{n}) d\bar{n} = -\frac{Y_n'(1)}{\lambda_n^2} \]  

[A.17]  

and  

\[ \int_0^1 \bar{n}(1-\bar{n}^2) Y_n^2(\bar{n}) d\bar{n} = \frac{Y_n'(1)}{2\lambda_n} \left[ \frac{Y_n(1)}{\partial \lambda} + \frac{1}{K} \frac{Y_n'(1)}{\partial \lambda} \right]_{\lambda=\lambda_n} \]  

[A.18]  

Hence  

\[ D_n = -2 \left\{ \lambda_n \left[ \frac{\partial Y_n(1)}{\partial \lambda} + \frac{1}{K} \frac{\partial Y_n'(1)}{\partial \lambda} \right]_{\lambda=\lambda_n} \right\}^{-1} \]  

[A.19]  

where, from Eq. [A.14],  

\[ \frac{\partial F(\lambda)}{\partial \lambda} = e^{-\frac{1}{2}} \left\{ \frac{1}{2(K-1)} - \frac{1}{K} + \sum_{i=1}^{\infty} \left\{ \frac{(1-\lambda) \cdots \cdot (4i-2-\lambda)}{4^i i! i!} \right\} \right\} \]  

[A.20]  

The asymptotic form of \( \partial F/\partial \lambda \) is easily obtained from Eq. [A.15].  

Using Eq. [A.7], the local dimensionless particle deposition rate,  

\[ J_D = J_D(\bar{n}) \], is given by
\[ J_D(\tilde{\gamma}) = -\Theta'(\tilde{\gamma},1) = -\sum_{n=1}^{\infty} D_n Y_n'(1)e^{-\lambda_n^2 \tilde{\gamma}} \]  

[A.21]

where \( Y_n'(1) \) follows from Eq. [A.13]. For large \( \lambda \), the required asymptotic form (Appendix A, Sect. A.2) is

\[
Y_n'(1) \approx -\frac{2^{5/3} \Gamma(1)}{3^{4/3} \Gamma(4/3)} \sin\left(\frac{\lambda_n \pi}{4} - \frac{\pi}{3}\right) \lambda_n^{1/3} \\
+ \frac{2^{4/3} \Gamma(1)}{5 \Gamma(2/3)} \sin\left(\frac{\lambda_n \pi}{4} - \frac{2\pi}{3}\right) \lambda_n^{-1/3}
\]

[A.22]

For a cylindrical channel, the dimensionless mean concentration, \( \Theta_m = \Theta_m(\tilde{\gamma}) \), is

\[
\Theta_m(\tilde{\gamma}) = 4 \int_0^1 (1-n^2) e(\tilde{\gamma},n)dn \\
= -4 \sum_{n=1}^{\infty} \frac{D_n Y_n'(1)}{\lambda_n^2} e^{-\lambda_n^2 \tilde{\gamma}}
\]

[A.23]

using Eqs. [A.7] and [A.17]. The relevant expressions for the special case \( K = \infty \) are easily obtained from the above formulae by deleting those terms having \( K \) in the denominator. The exact values for the first 50 \( \lambda_n \) and \( D_n \) as well as the coefficients \( E_n = -D_n Y_n'(1) \) and \( F_n = -4 D_n Y_n'(1)/\lambda_n^2 \) appearing in Eqs. [A.21] and [A.23], respectively, are compiled in Table A.1.

A computer program for evaluating particle deposition rates and mean particle concentrations for a cylindrical tube as a function of \( \tilde{\gamma} \) and \( K \) is listed in Appendix D. A separate program is required for the special case \( K = \infty \). As in the case of the parallel-plate channel, the asymptotic forms provide a very good estimate of the eigenvalues and coefficients for \( n \geq 50 \). For example, when \( K = 1.0 \) the following exact (vs. asymptotic) values are obtained: \( \lambda_{50} = 197.347 \) (197.347), \( D_{50} = -0.0026798 \) (-0.0026797), and
Table A.1

First Fifty Eigenvalues and Coefficients for $K = \infty$.
Cylindrical Channel.

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\[ D_{50} Y_{50}(1) = -0.00035428 \] 

Thus, it can also be shown for the case of the cylindrical channel that the maximum error incurred by using asymptotic forms for \( n > 50 \) affects only the fifth significant figure of the result of interest. The total number of terms, \( N \), of Eqs. [A.21] and [A.23] required to yield a converged answer of four figure accuracy is again given by Table 2.2, with \( \bar{\gamma} \) replacing \( \gamma \). Table A.2 compares the deposition rates and mean concentrations obtained using the present analysis with results available in the literature for \( K = 1.0 \) and \( K = \infty \). As in the case of the parallel-plate channel, the table indicates that the five-term solution of Sideman et al. (71) should not be used for predicting \( J_D \) values where \( \bar{\gamma} \leq 10^{-2} \). Davis and Parkinson (164) obtained additional exact eigenvalues and coefficients for \( n > 5 \) by numerically integrating the differential equation [A.3]. Their 15-term solution for \( K = 1.0 \) and 20-term solution for \( K = \infty \) are accurate only when \( \bar{\gamma} \geq 10^{-3} \), as shown in Table A.2.

### A.1.2 Large Peclet Number Approximation

The nature of this approximation for a cylindrical channel is very similar to that of a parallel-plate channel for which a detailed explanation has already been given (see Section 2.2.3). Since the region of flow where the parabolic velocity profile can be replaced by its tangent line at the wall is so close to the wall that curvature effects can be ignored, in both cases the channel can be treated as a single flat plate. Under the conditions \( a/R \ll \bar{\xi} \ll 1 \) where \( \bar{\xi} = h/R \), the convective-diffusion problem described by Eqs. [A.3]-[A.6] becomes

\[
2\bar{\xi} \frac{\partial \theta}{\partial \bar{\gamma}} = \frac{\partial^2 \theta}{\partial \bar{\xi}^2} \tag{A.24}
\]
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Table A.2
Comparisons of Deposition Rates and Mean Concentrations in a Cylindrical Channel
with the single-wall boundary conditions

\[ \theta(0, \xi) = 1, \theta(\gamma, \infty) = 1 \]

and

\[ \frac{1}{K} \theta'(\gamma, 0) = 0 \]

where the prime in the last boundary condition now denotes differentiation with respect to \( \xi \). This new set of equations ([A.24] and [A.25]) is the same as the set ([2.86] and [2.87]) obtained earlier for a parallel-plate channel if \( \gamma \) is replaced by \( \gamma \) and \( \xi \) by \( \xi \). Thus, the solutions for \( \theta = \theta(\gamma, \xi) \) and \( J_D(\gamma) \) can be written immediately as

\[
\theta(\gamma, \xi) = \frac{\int_0^{(2/9\gamma)^{1/3}} e^{-u^3} du + (1/K)(2/9\gamma)^{1/3}}{\Gamma(4/3) + (1/K)(2/9\gamma)^{1/3}}
\]

[A.26]

and

\[
J_D(\gamma) = \frac{(2/9\gamma)^{1/3}}{\Gamma(4/3) + (1/K)(2/9\gamma)^{1/3}}
\]

[A.27]

The mean concentration \( \theta_m(\gamma) \), which depends on the channel geometry, is now given by

\[
\theta_m(\gamma) = 1 - 4 \int_0^\gamma J_D(\gamma) d\gamma
\]

\[
= 1 - \frac{8}{3K^2\Gamma(4/3)^2} \ln \left( 1 + \frac{K\Gamma(4/3)}{(2/9\gamma)^{1/3}} \right)
\]

\[
+ \frac{8}{3K\Gamma(4/3)^2(2/9\gamma)^{1/3}} - \frac{4}{3\Gamma(4/3)(2/9\gamma)^{2/3}}
\]

[A.28]
When $K = \infty$, it can be easily verified that the above solutions reduce to those obtained by Leveque (77). For this special case, Gormely and Kennedy (166) and subsequently Newman (167) have given a higher-order approximation which accounts for the parabolic shape of the velocity profile. Approximate values of $J_Q$ and $\theta_m$ predicted by Eq. [A.27] and Eq. [A.28], respectively, are included in Table A.2 for comparison with their exact (to four significant figures) counterparts.

The behaviour of $J_Q$ and $\theta_m$ as functions of $\tilde{\gamma}$ and $K$ for a cylindrical channel is very similar to that of the parallel-plate channel. The range of applicability of the approximate expressions, [A.27] and [A.28], can be seen from Figs. A.1 (along with Table A.2), and A.2, respectively. By comparing the approximate results to those obtained accurately using Eqs. [A.21] and [A.23], Figs. A.1 (with Table A.2) and A.2 show that Eqs. [A.27] and [A.28] may be applied for $\tilde{\gamma} \leq 10^{-4}$ and $\tilde{\gamma} \leq 10^{-3}$, respectively, when $K = \infty$, and for an ever increasing range of $\tilde{\gamma}$ as $K$ becomes smaller.

A.2 Asymptotic Approximation for Large Eigenvalues

For the case of real $\lambda$ where $\lambda \to \infty$ and $\eta \to 0$, the function

$$Y(\eta) = e^{-\frac{\lambda \eta^2}{2}} M(a,b,\lambda \eta^2)$$

[A.29]

is approximated by the asymptotic expansion (76)
Figure A.2. Dimensionless particle deposition rate $J_D$ in a cylindrical channel as a function of dimensionless axial distance $\bar{\gamma}$ for selected values of dimensionless reaction rate constant $K$. The solid lines refer to the modified Graetz solution and the dashed lines to the modified Leveque approximation for small $\bar{\gamma}$. 
Figure A.3. Dimensionless mean particle concentration $\Theta_m$ in a cylindrical channel as a function of dimensionless axial distance $\bar{\gamma}$ for various selected values of dimensionless reaction rate constant $K$. The solid lines refer to the modified Graetz solution and the dashed lines to the modified Leveque approximation for small $\bar{\gamma}$. 

\[\Theta_m = \frac{\text{EQ. [A.23]}}{\text{EQ. [A.28]}}\]
\[ \gamma(n) = \Gamma(b) \gamma_1 \left\{ \text{Ai}(\xi) + 3^{-1/3} \left[ \frac{1}{5} t^2 \text{Ai}'(\xi) + \alpha(t-\beta) \text{Ai}(\xi) \right] + 3^{-1/2} \alpha \beta \text{Bi}(\xi) \right\} \]

where

\[ \gamma_1 = \frac{1}{3^{1/3} (2k)^{b-2/3}} \left\{ 3^{1/3} \cos(a\pi) + \frac{2\alpha \beta \sin(a\pi + \pi/6)}{3^{1/2} (2k)^{2/3}} + 0(k^{-4/3}) \right\} \]

\[ \gamma_2 = \frac{1}{3^{1/3} (2k)^{b-2/3}} \left\{ 3^{1/3} \sin(a\pi) - \frac{2\alpha \beta \sin(a\pi + \pi/6)}{(2k)^{2/3}} + 0(k^{-4/3}) \right\} \]

\[ \alpha = (5b-2)/10 \quad , \quad \beta = \frac{1}{2} \left[ \Gamma(1/3)/\Gamma(2/3) \right] \]

\[ t = \frac{1}{2} \left( \frac{3}{2k} \right)^{1/3} \left( 4k - \lambda \eta^2 \right) \quad , \quad \tilde{t} = -3^{-1/3} t \]

\[ k = \frac{1}{2} b - a \]

Here, Ai and Bi are Airy function of the first and second kind, respectively (75, p. 446), and the prime denotes differentiation with respect to \( \eta \).
For both the parallel-plate channel (Eq. [2.73]) and the cylindrical channel (Eq. [A.12]), \( k = \lambda/4 \). Thus, as \( \eta \to 1 \), both \( t \) and \( t_0 \to 0 \). Since

\[
\text{Ai}(0) = 3^{-2/3}/\Gamma(2/3), \quad \text{Bi}(0) = 3^{-1/6}/\Gamma(2/3),
\]

it follows from Eq. [A.30] that

\[
Y(1) = 3^{-1/6} \frac{\Gamma(b)}{\Gamma(2/3)} \left(3^{-1/2} \gamma_1 + \gamma_2\right) \quad [A.31]
\]

Substituting for \( \gamma_1 \) and \( \gamma_2 \) in Eq. [A.31] yields

\[
Y(1) \approx \frac{2 \Gamma(b)}{3^{2/3} \Gamma(2/3)} \left(\frac{\lambda}{2}\right)^{2/3-b} \sin\left(a\pi + \frac{\pi}{6}\right) \quad [A.32]
\]

Furthermore, since

\[
\frac{dt}{d\eta} = -6^{1/3} \lambda^{2/3} \eta, \quad \frac{d\xi}{d\eta} = 2^{1/3} \lambda^{2/3} \eta
\]

and

\[
\text{Ai}'(0) = -3^{1/3}/\Gamma(1/3), \quad \text{Bi}'(0) = 3^{1/6}/\Gamma(1/3)
\]

then differentiating Eq. [A.30] yields at \( \eta = 1 \),

\[
Y'(1) = -3^{1/6} 2^{1/3} \frac{\Gamma(b)}{\Gamma(1/3)} \lambda^{2/3} \left(3^{-1/2} \gamma_1 - \gamma_2\right)
\]

\[
= \frac{4 \Gamma(b)}{3^{4/3} \Gamma(4/3)} \sin\left(a\pi - \frac{\pi}{6}\right) \left(\frac{\lambda}{2}\right)^{4/3-b}
\]

\[
- 2 \cdot 3^{1/3} \frac{\Gamma(b)}{5 \Gamma(2/3)} \sin\left(a\pi + \frac{\pi}{6}\right) \left(\frac{\lambda}{2}\right)^{2/3-b} \quad [A.33]
\]
Eq. [A.30] is a second-order asymptotic expansion to Eq. [A.29], whereas the asymptotic expansion first suggested by Sellars et al. (70) and later used by Colton et al. (72) for the parallel-plate Graetz problem is only first order, and in fact can be obtained from Eq. [A.30] by dropping the second-order terms in \( k \). The second-order term for \( Y(l) \) in Eq. [A.32] is identically zero. Thus, when \( K = \infty \), the eigenvalues, \( \lambda_n \), obtained as roots of \( Y(l) = 0 \), are correct to the second rather than the first order as conservatively surmised by Sellars et al. The second order term for \( Y'(l) \) in Eq. [A.33] is the one containing \( \lambda^{2/3} \). A comparison of the exact and asymptotic eigenvalues and coefficients (\( n \leq 50 \)) for a number of different values of \( K \) revealed that, in the case of the parallel-plate channel, the first-order asymptotic expansion always gave a better approximation than the second-order, while in the case of the cylindrical channel, the reverse was true. Thus, in the analysis presented here, the second-order asymptotic expansion is used for the cylindrical channel while only the first is employed in the case of parallel plates.
B.1 Electro-osmotic Flow in a Rectangular Channel

Consider a rectangular channel of half-width $a$ and half-thickness $b$ (Fig. B.1). When a potential gradient is applied along the length of the channel, the force exerted by the field on the excess ions in the diffuse part of the double layer is transferred to the molecules of the solvent. Under the conditions that $\kappa a \gg 1$ and $\kappa b \gg 1$, Smoluchowski (141) has shown that the resulting electro-osmotic motion manifests itself as a constant fluid velocity acting along the walls of the channel. The electro-osmotic velocity, $u_w$, is given by

$$u_w = \frac{\varepsilon \zeta_w X}{4\pi \mu}$$

[B.1]

where $\varepsilon$ is the solution dielectric constant, $\zeta_w$ the zeta potential of the wall material, $X$ the externally applied potential gradient, and $\mu$ the solution viscosity. In the derivation of Eq. [B.1], it is further assumed that both $\varepsilon$ and $\mu$ maintain their bulk values up to the electrokinetic slip-plane.

A solution to the equation of motion for fully developed laminar flow in a rectangular duct has been obtained by Cornish (129) in the form of an infinite series. For the condition of no-slip at the channel walls, Cornish gives the following expression for the velocity distribution $u(x,y)$:
Figure B.1. Cross-sectional co-ordinates of a rectangular electrophoresis cell ($a > b$).
\[ u(x,y) = \frac{-P}{2\mu} \left\{ b^2 \left[ 1 - \frac{32}{\pi^3} \left( \cosh \frac{\pi x}{2b} \cdot \cos \frac{\pi y}{2b} \right) \right. \right. \\
\left. \left. - \frac{1}{3^3} \cosh \frac{3\pi x}{2b} \cdot \cos \frac{3\pi y}{2b} + \cdots \right] - y^2 \right\} \]  \[ \text{[B.2]} \]

where \( P \) is the pressure gradient. For a constant slip velocity \( u_w \) at the walls, Eq. [B.2] is easily amended to yield

\[ u(x,y) = \frac{-P}{2\mu} \left\{ b^2 \left[ 1 - \frac{32}{\pi^3} \left( \cosh \frac{\pi x}{2b} \cdot \cos \frac{\pi y}{2b} \right) \right. \right. \\
\left. \left. - \frac{1}{3^3} \cosh \frac{3\pi x}{2b} \cdot \cos \frac{3\pi y}{2b} + \cdots \right] - y^2 \right\} + u_w \]  \[ \text{[B.3]} \]

When an electro-osmotic flow is generated in an open channel, \( P = 0 \), and Eq. [B.3] shows that the velocity everywhere in the channel is equal to \( u_w \). However, in the present case, the electrophoresis cell is closed. The flow of liquid down the walls of the channel creates an opposing pressure gradient which causes a return flow in the centre region of the channel. At steady state, the net flow at any cross-section of the channel must be zero. Thus,

\[ \int_{y=-b}^{y=b} \int_{x=-a}^{x=a} u(x,y) \, dx \, dy = 0 \]  \[ \text{[B.4]} \]

By substituting Eq. [B.3] into Eq. [B.4] and integrating, it is found that
\[ P = \frac{3\mu u_w}{b^2} \left( 1 - \frac{192 b}{\pi^5} \left( \frac{\pi a}{2b} \tanh \frac{3\pi a}{2b} + \frac{1}{3^5} \tanh \frac{3\pi a}{2b} + \cdots \right) \right)^{-1} \]  

[B.5]

Substituting for \( P \) in Eq. [B.3] now gives the electro-osmotic velocity distribution in a closed cell as

\[
u(x,y) = \frac{-3u_w}{2b^2} \left( \frac{b^2}{1 - \frac{192 b}{\pi^5} \left( \frac{\pi a}{2b} \tanh \frac{\pi a}{2b} + \frac{1}{3^5} \tanh \frac{3\pi a}{2b} + \cdots \right) - y^2} \right) + u_w
\]

[B.6]

The velocity profile at the measuring plane of the cell \( (x = 0) \) can be written immediately, since \( \cosh(0) = 1 \), as

\[
u(0,y) = \frac{-3u_w}{2b^2} \left( \frac{b^2}{1 - \frac{192 b}{\pi^5} \left( \frac{\pi a}{2b} \tanh \frac{\pi a}{2b} + \frac{1}{3^5} \tanh \frac{3\pi a}{2b} + \cdots \right) - y^2} \right) + u_w
\]

[B.7]

It is of interest to find an approximation for Eq. [B.7] when the ratio \( a/b \) becomes large. For example, for the rectangular cells used in the present study, \( a/b \sim 10 \). It can be easily shown that for \( z \geq 3 \), \( \tanh z \sim 1 \), and \( \cosh z \sim e^{z/2} \). Thus, when \( a/b \geq 2 \), Eq. [B.7] simplifies to

\[
u(0,y) \approx \frac{u_w}{2} \left( \frac{3y^2}{b^2} - \left( 1 + \frac{384 b}{\pi^5 a} \right) \right)
\]

[B.8]
When $b/a \to \infty$, Eq. [B.8] becomes

$$u(0,y) = \frac{u_w}{2} \left( \frac{3y^2}{b^2} - 1 \right)$$  \[B.9\]

which is the velocity distribution for closed electro-osmotic flow in a parallel-plate channel first derived by Smoluchowski (141).

If $u(0,y)$ could be evaluated at a known position in the channel for some applied potential gradient, $X$, it would then be possible to determine $u_w$ (from Eq. [B.8]) and hence $\zeta_w$ (from Eq. [B.1]). However, it is not possible to determine $u(0,y)$ directly in an electrophoresis cell. But it is possible to determine $u(0,y)$ indirectly during an electrophoresis measurement. When the potential gradient is applied, the resulting particle electrophoretic velocity, $v_E$, is constant relative to the solution. Thus, if $v(0,y)$ is the particle velocity relative to the stationary observer, then

$$v(0,y) = u(0,y) + v_E$$  \[B.10\]

The electrophoretic velocity, $v_E$, is obtained by measuring the particle velocity at the "stationary levels," i.e. where $u(0,y) = 0$ and hence, where

$$\frac{3y^2}{b^2} - \left( 1 - \frac{384}{\pi^5} \frac{b}{a} \right) = 0$$

or

$$\frac{y}{b} = \pm \left( \frac{1}{3} + \frac{128}{\pi^5} \frac{b}{a} \right)^{1/2}$$  \[B.11\]

[Note that the stationary levels for a parallel-plate channel are given by]$y/b = \pm \sqrt{7/3}$ (141).]

Thus, if $v(0,y)$ were measured at any other position in the cell, it would be possible to obtain $u(0,y)$ at that position from Eq. [B.10] and hence also the wall zeta potential. One obvious position to make this second measurement is at the cell wall. However, measurements made at this location
suffer two distinct disadvantages. First, the slope of the observed particle velocity profile, \( v(0,y) \), is at a maximum at the wall and therefore leads to a maximum depth-of-field error. Secondly, the particle motion near the wall is affected by the presence of the wall, particularly if the wall is contaminated by the deposition of other particles. The preferred position for making the second measurement is at the centre of the channel, where the depth-of-field error is at a minimum.

At the centre of the channel \( (y = 0) \),

\[
v(0,0) = v_0 = u(0,0) + v_E
\]

\[
= -\frac{u_w}{2} \left( 1 + \frac{384}{\pi^5} \frac{b}{a} \right) \left( 1 - \frac{192}{\pi^5} \frac{b}{a} \right) + v_E
\]

using Eq. [B.8]. Substituting Eq. [B.1] into [B.12] and solving for \( \zeta_w \) yields

\[
\zeta_w = \frac{8\pi u}{eX} \left[ 1 - \frac{192}{\pi^5} \frac{b}{a} \right] \left( v_E - v_0 \right)
\]

When \( b/a \rightarrow \infty \), \( \zeta_w \) is given by

\[
\zeta_w = \frac{8\pi u}{eX} (v_E - v_0)
\]

Hence, when \( b/a > 2 \), the effect of a finite half-width manifests itself (approximately) as a correction factor \((1 - \frac{192}{\pi^5} \frac{b}{a})/(1 + \frac{384}{\pi^5} \frac{b}{a})\) on the result calculated assuming a parallel-plate velocity distribution. Selected values of the correction factor are given in Table B.1.
Table B.1

Corrections to Eq. [B.14] for Rectangular Cells of Large Aspect Ratio

<table>
<thead>
<tr>
<th>a/b</th>
<th>( \frac{(1 - \frac{192}{\pi^5} \frac{b}{a})}{(1 + \frac{384}{\pi^5} \frac{b}{a})} )</th>
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<tr>
<td>5</td>
<td>0.699</td>
</tr>
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<td>10</td>
<td>0.833</td>
</tr>
<tr>
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<td>0.911</td>
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<tr>
<td>50</td>
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<td>100</td>
<td>0.981</td>
</tr>
<tr>
<td>200</td>
<td>0.991</td>
</tr>
<tr>
<td>∞</td>
<td>1.000</td>
</tr>
</tbody>
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B.2 Potentials Generated by Streaming Currents in Recirculating Systems

Consider the recirculating system drawn schematically in Fig. B.2. The system consists of a parallel-plate test section of material \( t \) and \( N(= n+n') \) flow elements of arbitrary geometry all of material \( a \). One pair of potential measuring electrodes are placed across the test section (\( \Delta E_t \)). A second pair are placed across a portion of the system which includes \( M(= m+m') \) flow elements plus the test section (\( \Delta E_a \)) where \( 0 < M < N \).

The object of the present analysis is to find a relationship for the test section zeta potential, \( \zeta_t \), expressed in terms of the measured quantities \( \Delta E_t, \Delta E_a, \) and \( Q \), the fluid flow rate. Since the geometries of the \( N \) flow elements (excluding the test section) are constant from experiment to experiment but are generally not known, it is hoped that these can be lumped together as constant modifiers in the derived relationship. These modifiers can later be evaluated empirically by measuring \( \Delta E_t \) and \( \Delta E_a \) under conditions of known \( \zeta_t \). The geometry of each test section is measured, but it varies...
Figure B.2. Schematic representation of a complex recirculating system.
slightly from experiment to experiment. Thus, the relationship must account for the test section geometry explicitly as well as for changes in other system parameters such as the fluid dielectric constant $\varepsilon$ and conductivity $\lambda$.

In order to solve the problem, it is necessary to make a number of simplifying assumptions. It is assumed here that the double layer thickness $\kappa^{-1}$ is small relative to the characteristic dimension of any flow element, that $\varepsilon$ and $\mu$ are both constant at their bulk fluid values up to the electrokinetic slip-plane, that surface conductance effects are negligible, and that the fluid flow is laminar and fully developed in every flow element. Under these conditions, Smoluchowski (141) has shown that the streaming current, $I$, generated by a flow $Q$ in a cylindrical channel (radius $R$) is given by

$$ I = \frac{2\varepsilon Q \zeta}{\pi R^2} \quad [B.15] $$

and in a parallel-plate channel (half-width $b$) by

$$ I = \frac{3\varepsilon Q \zeta}{4\pi b^2} \quad [B.16] $$

The conduction current, $I_E$, induced by a potential difference, $\Delta E$, across such channels is given, for a cylindrical channel, by

$$ I_E = \frac{\pi R^2 \lambda \Delta E}{L} \quad [B.17] $$

and for a parallel-plate channel, by

$$ I_E = \frac{2bW \lambda \Delta E}{L} \quad [B.18] $$

where $L$ represents the length of these flow elements. Thus, it is further assumed that for the $N$ flow elements of zeta potential $\zeta_a$, the convection (or streaming) currents are given by
\[ I_i = \alpha_i \varepsilon Q \xi \]  \[ \text{[B.19]} \]

and the conduction currents by

\[ I_{Ei} = \beta_i \lambda \Delta E_i \]  \[ \text{[B.20]} \]

where \( \alpha_i \) and \( \beta_i \) are functions only of the geometry of the \( i^{th} \) element.

For the test section, under the same conditions,

\[ I_t = \frac{3 \varepsilon Q \xi_t}{4\pi b_t^2} \]  \[ \text{[B.21]} \]

and

\[ I_{E_t} = \frac{2b_t W_t \lambda \Delta E_t}{L_t} \]  \[ \text{[B.22]} \]

By carrying out current balances at the \( N \) interior nodal points between each flow element in the system, it becomes possible to relate the potential difference \( \Delta E_i \) generated across each flow element to that of the test section \( \Delta E_t \). The sign conventions used in these operations are as follows:

i) +ve \( Q \) is from left to right,

ii) +ve \( \Delta E \) causes conduction from left to right (i.e. \( E \) decreases from left to right),

iii) \( \xi \) is +ve.

Consider the node between the test section (element \( t \)) and the element \( t-1 \). A current balance gives

\[ I_t + I_{E_t-1} = I_{t-1} + I_{E_t} \]

or

\[ \frac{3\varepsilon \xi_t Q}{4\pi b_t^2} + \beta_{t-1} \lambda \Delta E_{t-1} = \alpha_{t-1} \varepsilon \xi_a Q + \frac{2b_t W_t \lambda \Delta E_t}{L_t} \]
using Eqs. [B.19], [B.20], [B.21], and [B.22]. Thus,

$$\Delta E_{t-1} = \left( \alpha_{t-1} \zeta_a - \frac{3 \zeta_t}{4 \pi b_t^2} \right) \frac{\varepsilon Q}{\lambda \beta_{t-1}} + \frac{2 b_t W_t}{L_t} \frac{\Delta E_t}{\beta_{t-1}}$$ \[[B.23]\]

Now consider the node between elements $t-1$ and $t-2$. A current balance gives

$$I_{t-1} + I_{E_{t-2}} = I_{t-2} + I_{E_{t-1}}$$

or

$$\alpha_{t-1} \varepsilon \zeta_a Q + \beta_{t-2} \lambda \Delta E_{t-2} = \alpha_{t-2} \varepsilon \zeta_a Q + \beta_{t-1} \lambda \Delta E_{t-1}$$

using Eqs. [B.19] and [B.20]. Thus,

$$\Delta E_{t-2} = \left( \alpha_{t-2} - \alpha_{t-1} \right) \frac{\varepsilon \zeta_a Q}{\lambda \beta_{t-2}} + \frac{\beta_{t-1} \lambda \Delta E_{t-1}}{\beta_{t-2}}$$ \[[B.24]\]

Substitution of Eq. [B.23] into Eq. [B.24] yields

$$\Delta E_{t-2} = \left( \alpha_{t-2} \zeta_a - \frac{3 \zeta_t}{4 \pi b_t^2} \right) \frac{\varepsilon Q}{\lambda \beta_{t-2}} + \frac{2 b_t W_t}{L_t} \frac{\Delta E_t}{\beta_{t-2}}$$ \[[B.25]\]

In fact, for any element $i$ ($i \neq t$) it can be proven that

$$\Delta E_i = \left( \alpha_i \zeta_a - \frac{3 \zeta_t}{4 \pi b_t^2} \right) \frac{\varepsilon Q}{\lambda \beta_i} + \frac{2 b_t W_t}{L_t} \frac{\Delta E_t}{\beta_i}$$ \[[B.26]\]

Now, since the flow system is a recirculating one, the first node in the schematic coincides with and in fact is identical to the last one. Thus, both nodes are at the same potential. In other words, the total potential drop around the system must be zero, or

$$\sum_{i=t-n}^{t-1} \Delta E_i + \Delta E_t + \sum_{i=t+1}^{t+n'} \Delta E_i = 0$$

or

$$\sum_{i=t-n}^{t+n'} \Delta E_i + \Delta E_t = 0$$ \[[B.27]\]
Substituting Eq. [B.26] into Eq. [B.27] and solving for $\zeta_t$ yields

$$\zeta_t = \frac{8\pi b_t^3W_t\lambda}{3\varepsilon L_t} \left(1 + \frac{L_t}{2b_tW_t\sigma_1}\right) \frac{\Delta E_t}{Q} + \frac{4\pi b_t^2}{3\sigma_2} \frac{\zeta_a}{\sigma_1} \tag{B.28}$$

where

$$\sigma_1 = \sum_{i=t-n}^{t+m} \frac{1}{\beta_i} \quad \text{and} \quad \sigma_2 = \sum_{i=t-n}^{t+m} \frac{\alpha_i}{\beta_i} \tag{B.29}$$

The purpose of measuring $\Delta E_a$ is to eliminate $\zeta_a$ in Eq. [B.28]. $\Delta E_a$ is given by

$$\Delta E_a = \sum_{i=t-m}^{t+n} \Delta E_{i} + \Delta E_{t} \tag{B.30}$$

Substituting Eq. [B.26] into Eq. [B.30] and solving for $\zeta_a$ yields

$$\zeta_a = \frac{\lambda}{\varepsilon_\sigma} \frac{1}{\sigma_4} \frac{\Delta E_a}{Q} - \frac{2b_tW_t\lambda}{\varepsilon L_t} \left(\frac{\sigma_3}{\sigma_4} + \frac{L_t}{2b_tW_t}\right) \frac{\Delta E_t}{Q} + \frac{3}{4\pi b_t^2} \frac{\sigma_3}{\sigma_4} \frac{\zeta_t}{\zeta} \tag{B.31}$$

where

$$\sigma_3 = \sum_{i=t-m}^{t+m} \frac{1}{\beta_i} \quad \text{and} \quad \sigma_4 = \sum_{i=t-m}^{t+m} \frac{\alpha_i}{\beta_i} \tag{B.32}$$

If Eq. [B.31] is now substituted into Eq. [B.28], the following explicit expression for $\zeta_t$ is obtained:

$$\zeta_t = \frac{8\pi b_t^3W_t\lambda}{3\varepsilon L_t} \frac{\Delta E_t}{Q} + \frac{4\pi b_t^2\lambda}{3\varepsilon} \Sigma_1 \frac{\Delta E_t}{Q} + \frac{4\pi b_t^2\lambda}{3\varepsilon} \Sigma_2 \frac{\Delta E_a}{Q} \tag{B.33}$$

where

$$\Sigma_1 = \frac{\sigma_4 - \sigma_2}{(\sigma_1\sigma_4 - \sigma_2\sigma_3)} \quad \text{and} \quad \Sigma_2 = \frac{\sigma_2}{(\sigma_1\sigma_4 - \sigma_2\sigma_3)} \tag{B.34}$$

Note that when the conduction and convection currents exactly balance in the test section, the potential difference generated is called the streaming...
potential, $\Delta E_{str}$. From Eqs. [B.21] and [B.22], it is easily shown that in this case

$$\zeta_t = \frac{8\pi b_t^3 W_t \lambda}{3\varepsilon L_t} \frac{\Delta E_{str}}{Q} \quad [B.35]$$

Thus, for a recirculating system, it is generally not expected that $\Delta E_t$ and $\Delta E_{str}$ will be equivalent.

Since the various $\sigma$'s are only dependent on the geometries of the individual elements in the system (excluding the test section), $\Sigma_1$ and $\Sigma_2$ are systemic constants which do not vary from experiment to experiment. Thus, once $\Sigma_1$ and $\Sigma_2$ have been evaluated (by some empirical method), the wall $\zeta$-potential may be determined from Eq. [B.33] by measuring the two potential differences, $\Delta E_t$ and $\Delta E_a$, generated in a closed flow system constructed of only two materials.

Eq. [B.28] may be rewritten as

$$\Delta E_t = \frac{eQ}{\lambda \left(1 + \frac{2b_t W_t \sigma_1}{L_t}\right)} \left(\frac{3}{4\pi b_t^2} \sigma_1 \zeta_t - \sigma_2 \zeta_a\right) \quad [B.36]$$

Thus,

$$\frac{d\Delta E_t}{dQ} = \frac{e}{\lambda \left(1 + \frac{2b_t W_t \sigma_1}{L_t}\right)} \left(\frac{3}{4\pi b_t^2} \sigma_1 \zeta_t - \sigma_2 \zeta_a\right) = \text{constant} \quad [B.37]$$

From Eq. [B.33], it can be shown that
\[
\Delta E_a = \frac{3\varepsilon \zeta_t}{4\pi b t^2 \lambda \Sigma_2} - \frac{2b W}{L_t \Sigma_2 + \Sigma_1} \Delta E_t \quad \text{[B.38]}
\]

Thus,
\[
\frac{d\Delta E_a}{dq} = \frac{3\varepsilon \zeta_t}{4\pi b t^2 \lambda \Sigma_2} - \frac{2b W}{L_t \Sigma_2 + \Sigma_1} \frac{d\Delta E_t}{dq} \quad \text{[B.39]}
\]

Substituting from Eq. [B.37] into Eq. [B.39] shows that \(\frac{d\Delta E_a}{dq}\) is also constant. Furthermore, when \(Q = 0\), Eqs. [B.36] and [B.38] can be used to show that \(\Delta E_t = \Delta E_a = 0\). Thus, a plot of experimentally measured values of either \(\Delta E_t\) or \(\Delta E_a\) as a function of \(Q\) should be represented by a straight line passing through the origin.
APPENDIX C

EXPERIMENTAL RESULTS

C.1 Calibrations

C.1.1 Radioactive Particle Concentrations

C.1.1.1 Surface Concentrations of Deposited Particles

Calibration curves relating the concentration of deposited particles with the radioactivity emanating from a test section as measured by the collimated scintillation detector were obtained as follows.

For each batch of radioactive particles produced, suspensions containing 0.1, 0.3, and 1.0 mg. SiO$_2$/ml. were prepared by ultrasonically dispersing 10.0, 30.0, and 100.0 mg., respectively, in 20 ml. of distilled water and then diluting the latter sols to 100 ml. in volumetric flasks. Additional standardized suspensions containing 0.01 and 0.03 mg. SiO$_2$/ml. were prepared by dilution. A test section, whose internal dimensions had been measured at least twice, was filled with distilled water, sealed at both ends (using adhesive tape), and then clamped into position between the entrance and exit sections of the double-loop system. The height of the inlet of the test section (i.e. $x = 0$) was determined using the procedure outlined in Sect. 3.4.3.1. Employing a counting period of 10 minutes, the background radioactivity was measured as a function of distance from the test section inlet ($x = 5, 10, 12.5, 15, 20$ cm.) with the rectangular
collimator and at the longitudinal centre of the test section \(x = 12.5\) cm. with the cylindrical collimator. The test section was then removed from the loop, drained, rinsed with methanol, and then dried by the application of compressed air. Using a glass syringe with a specially-flattened needle, the test section was filled with the calibration suspension of lowest concentration. It was then resealed, repositioned in the loop, and counted again for 10 minutes with both collimators at all of the distances mentioned above. The procedure was repeated for all of the suspension concentrations. In each case, it was necessary to repeat the background count (at all positions) because of the likelihood of the test section becoming contaminated by the previous suspension. [If the suspensions were not well-dispersed, settling of the larger clusters in the test section could alter the local particle concentrations over the length of time taken for a complete calibration cycle (e.g. 6 measurements \(\approx 60\) minutes). The possibility of this occurrence was checked by twice measuring the activity at \(x = 5\) cm., once at the beginning and again at the end of the cycle. The two measured values were always within statistical agreement, indicating that settling was not a significant problem.]

The number concentration of particles in each suspension can be calculated from the mass concentration, knowing the average size and density of the silica spheres. To convert the suspension concentration (particles/ml.) to a surface concentration (particles/cm\(^2\)), it was assumed that the same count rate would be obtained if all the particles in suspension were deposited uniformly on the two walls of the test section. This assumption is quite reasonable for a parallel-plate channel of high aspect ratio. The activity emanating from a given surface concentration was found by subtracting
the background count rate from the count rate obtained with the suspension in place. All of the activities measured were corrected (for decay) to a suitably chosen zero time. The 95% confidence limits on these measurements were obtained by the methods discussed in Sect. C.2.1.4.

The calibration results for the three batches of radioactive particles are presented in Table C.1. By plotting each set of calibration data, it was found that the calibration curve in each instance was best represented by a straight line (see, for example, Fig. C.1) which passed through the origin when plotted using arithmetic co-ordinates. Thus, to simplify data reduction, calibration factors (particles/cm²/corrected net counts/min) were established by finding the slope of the straight line which best fit each set of calibration data. The fit was weighted in inverse proportion to the counting error associated with each activity measurement. The calibration factors thus obtained are also listed in Table C.1.

These results show that the cylindrical collimator is about 10 time more sensitive than the rectangular collimator. It should also be noted that the calibration factors for the rectangular collimator vary somewhat with length. This variation occurs because no amount of shielding will effectively stop all γ-radiation; in fact, the probability of penetration falls off exponentially with increasing shielding thickness. Thus, the position of the detector in relationship to the overall geometry of the radioactive source is of some importance. The maximum count rate (i.e. minimum calibration factor) is obtained at x = 12.5 cm., as might be expected. However, the symmetry of the relationship between calibration factor and distance is skewed somewhat because of the suspension sample port which has been drilled into the top of the counting chamber.
<table>
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<tr>
<th>Series</th>
<th>Surf. Conc. (particles/cm²)</th>
<th>x = 5 cm.</th>
<th>10 cm.</th>
<th>12.5 cm.</th>
<th>15 cm.</th>
<th>20 cm.</th>
<th>12.5 cm.**</th>
</tr>
</thead>
<tbody>
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<td>I</td>
<td>5.96 x 10^6</td>
<td>332 ± 59</td>
<td>465 ± 49</td>
<td>452 ± 44</td>
<td>450 ± 45</td>
<td>396 ± 57</td>
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<td></td>
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<td>3430 ± 70</td>
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<td>5090 ± 63</td>
<td>5000 ± 63</td>
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<td>2.085 x 10^3</td>
<td>1.957 x 10^3</td>
<td>2.087 x 10^3</td>
<td>2.135 x 10^2</td>
<td></td>
</tr>
</tbody>
</table>

**cylindrical collimator

***C.F. = calibration factor (particles/cm²/cpm. corr.)
Figure C.1. Calibration curve relating concentration of deposited particles with measured activity corrected to zero time (0:00/1/11/76) for cylindrical collimator (x = 12.5 cm), series II.
C.1.1.2 Concentration of Radioactive Particles in Suspension

Calibration curves relating the concentration of radioactive particles in suspension to the net activity of a 10 ml. sample of the suspension were obtained in the following manner.

For each batch of radioactive particles produced, suspensions of known concentration were prepared by ultrasonically dispersing preweighed amounts of particles in 100 ml. of distilled water. In some cases, additional standardized suspensions were prepared by dilution. The blank collimator was placed in the counting chamber and the counting stand was positioned some distance away from the test section. A clean, dry 12-ml. glass bottle with screw cap was inserted in front of the detector through the hole provided at the top of the counting chamber. The lead plug was placed in the hole and the empty bottle was counted for 1 min. to obtain the background activity. Using a pipette, 10 ml. of one of the calibration suspensions was transferred to the bottle and the bottle was recounted for 1 min. After cleaning the sample bottle with a brush and flushing it thoroughly with distilled water, the above procedure (including background measurement) was repeated for the other standardized particle suspensions. The same 10 ml. pipette, flushed carefully with distilled water after each transferral, was used for these and all subsequent measurements. Because of their fragility, the sample bottles had to be replaced periodically. However, it was first demonstrated, by measuring the activity of several bottles containing the same radioactive suspension, that switching the sample bottle had no determinable effect on the calibration results.

As before, the number concentration of particles in each calibration suspension was calculated from the mass concentration, knowing the
average size and density of the spheres. The net count rates were corrected for decay to the chosen zero time. The 95% confidence limits of the measured activities were obtained using the methods discussed in Sect. C.2.1.4.

The calibration curves obtained for the three batches of radioactive particles are presented in Figs. C.2, C.3, and C.4. As in the case of the wall concentrations, it was found that the calibration curves (or regions of these curves) for radioactive suspension concentrations were best represented by linear relationships. Thus, to simplify the subsequent analysis, calibration equations were obtained by a least squares fit of the calibration data. These relationships are given in Figs. C.2 and C.3.

C.1.2 Concentration of Non-radioactive Particles in Suspension

A calibration curve relating the concentration of particles in the non-radioactive suspension to the light absorbance of a sample of the suspension was obtained as described below. Since release-rate measurements using non-radioactive particles were carried out only in the last series of deposition runs, just one curve was determined.

As in the case of the radioactive suspension calibrations, suspension of known concentrations of non-radioactive particles were prepared by ultrasonically dispersing preweighed amounts of particles in 100 ml. of distilled water. Samples of the suspensions were then transferred to a 4 cm. path-length glass absorption cell using a 10 ml. pipette. The absorbance of the sample was measured at a wavelength of 400 nm in the Unicam spectrophotometer using an identical 4 cm. cell filled with distilled water as a reference. The resulting calibration curve is given in Fig. C.5.
Figure C.2. Series I. Suspended particle concentration versus corrected activity of 10 ml. sample. Zero time = 0:00/1/10/76.
Figure C.3. Series II. Suspended particle concentration versus corrected activity of 10 ml. sample. Zero time = 0:00/11/11/76.

\[ y = 1.722 \times 10^7 + 7.577 \times 10^2 x \]

\[ y = 4.395 \times 10^6 + 7.389 \times 10^2 x \]
Figure C.4. Series III. Suspended particle concentration versus corrected activity of 10 ml. sample. Zero time = 0:00/1/4/77.
Figure C.5. Series III. Concentration of non-radioactive particles versus absorbance of suspension at 400 nm in a 4 cm cell.
C.1.3 Flow Rate

C.1.3.1 Calibration of 50 ml. Volumetric Cylinder

The 500 ml. volumetric cylinder used for all flow measurements was first calibrated by weighing the amount of water at a known temperature which was required to fill the cylinder to various volume settings. These calibration results are given in Table C.2.

Table C.2
Calibration of 500 ml Volumetric Cylinder

<table>
<thead>
<tr>
<th>Nominal Volume (ml.)</th>
<th>Actual Volume (ml.)</th>
<th>Actual Vol. -50.3 ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>50.3</td>
<td>0.0</td>
</tr>
<tr>
<td>100</td>
<td>100.2</td>
<td>49.9</td>
</tr>
<tr>
<td>150</td>
<td>150.0</td>
<td>99.7</td>
</tr>
<tr>
<td>200</td>
<td>199.7</td>
<td>149.4</td>
</tr>
<tr>
<td>250</td>
<td>249.1</td>
<td>198.8</td>
</tr>
<tr>
<td>300</td>
<td>298.6</td>
<td>248.3</td>
</tr>
<tr>
<td>350</td>
<td>348.5</td>
<td>298.2</td>
</tr>
<tr>
<td>400</td>
<td>398.8</td>
<td>348.4</td>
</tr>
<tr>
<td>450</td>
<td>449.1</td>
<td>398.8</td>
</tr>
<tr>
<td>500</td>
<td>499.8</td>
<td>449.5</td>
</tr>
</tbody>
</table>

C.1.3.2 Flow Rate versus Pressure Drop

Calibration curves relating the circulation flow rate with the change in pressure between the tee in the inlet line to the test section and the pressure port in the entrance section were obtained as follows.

First the flush tank water bath was switched on to adjust the distilled water in the flush tank to the calibration temperature of 25.0 ± 0.1 °C. At the same time, the Datametrics pressure transducing system was switched on and allowed sufficient time to warm up. With valves 5, 10, and 21 open (see Fig. 3.13), the loop pump was switched on and the warmed distilled
water in the flush tank was circulated through the test section to adjust the temperature of the rest of the system to the operating value. After a suitable warm-up period, the pump was switched off and the transducer output was adjusted to zero. The pump speed potentiometer was set to a predetermined level and the pump was again switched on. By opening valve 22 and closing valve 21, the circulating flow was diverted to a precalibrated 500 ml. volumetric cylinder (Sect. C.1.3.1). Using a stopwatch, the time taken for the cylinder to fill to a predetermined volume from the 50 ml. mark was measured. The pump was then shut off and the procedure was repeated (including instrument zeroing) at a number of different potentiometer readings.

The average pressure drop measured for the period in which the flow was timed was obtained from the recorder output. Flow rates were calculated on the basis of the actual volumes of water collected, as determined from Table C.2. The transducer zero setting tended to drift monotonically with time. In order to relieve this problem, a resistor inside the Barocel had to be changed periodically. As this operation affected the response of the instrument, it was necessary to recalibrate the transducer with each resistor change. Thus, the resistor was intentionally changed at the start of each new series of deposition experiments to allow for the maximum possible drift during that series. The three sets of flow calibration curves corresponding to the three series of deposition runs are given as Figs. C.6, C.7, and C.8.

C.1.4 Thermistor and Thermometer Calibrations

The three tank thermistors (monitored by the YSI Telethermometer) and thermometer #2521A were calibrated as follows. The four temperature
Figure C.6. Series I. Flow rate versus measured pressure drop.
Figure C.7. Series II. Flow rate versus measured pressure drop.
Figure C.8. Series III. Flow rate versus measured pressure drop.
sensing devices were placed with the probe of a Hewlett-Packard quartz thermometer in a large Colora constant temperature bath. The three thermistors and the thermometer were arranged in a square pattern with the quartz probe at the centre. All five devices were positioned at the same depth in the bath. To assure homogeneous conditions, the water was circulated using the bath pump. Temperatures were recorded for each instrument as the bath was slowly heated up, time being allowed for equilibrium to be attained at each calibration temperature. The calibration results are given in Table C.3.

C.1.5 Conductivity of NaCl Solutions

A calibration curve relating the concentration of NaCl in solution to the measured conductivity was obtained in the following manner. Solutions of known concentrations of NaCl were made up by dissolving preweighed amounts of NaCl in 1000-ml volumes of distilled and deionized water. The temperature-corrected conductivities of the solution were measured using the Siebold meter. The calibration results are presented in Fig. C.9.

C.1.6 Electrophoresis Apparatus

C.1.6.1 Voltmeter

The supplied voltmeter was calibrated by comparing the voltage reading of the instrument with that of a digital voltmeter (±0.1 V at 100 V full scale, Non Linear Systems Model X-3) at a number of voltage levels applied by a regulated power supply (Anatek Model 50-1.0S). The calibration results are given in Table C.4. The calibration curve is quite non-linear, probably due to imperfections caused in reproducing the instrument scale.
Table C.3
Calibration Results for Three Tank Thermistors and Thermometer #2521A

<table>
<thead>
<tr>
<th>Quartz Thermometer</th>
<th>Thermistor #1 (Active Tank)</th>
<th>Thermistor #2 (Non-active Tank)</th>
<th>Thermistor #3 (Flush Tank)</th>
<th>Thermometer #2521A</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.50</td>
<td>20.30</td>
<td>20.25</td>
<td>20.30</td>
<td>20.84</td>
</tr>
<tr>
<td>21.01</td>
<td>20.85</td>
<td>20.80</td>
<td>20.85</td>
<td>21.34</td>
</tr>
<tr>
<td>21.50</td>
<td>21.35</td>
<td>21.30</td>
<td>21.35</td>
<td>21.82</td>
</tr>
<tr>
<td>22.00</td>
<td>21.90</td>
<td>21.85</td>
<td>21.90</td>
<td>22.32</td>
</tr>
<tr>
<td>22.50</td>
<td>22.35</td>
<td>22.30</td>
<td>22.35</td>
<td>22.80</td>
</tr>
<tr>
<td>23.00</td>
<td>22.85</td>
<td>22.80</td>
<td>22.90</td>
<td>23.29</td>
</tr>
<tr>
<td>23.50</td>
<td>23.40</td>
<td>23.35</td>
<td>23.40</td>
<td>23.77</td>
</tr>
<tr>
<td>24.01</td>
<td>23.95</td>
<td>23.85</td>
<td>23.95</td>
<td>24.27</td>
</tr>
<tr>
<td>24.50</td>
<td>24.40</td>
<td>24.35</td>
<td>24.45</td>
<td>24.75</td>
</tr>
<tr>
<td>25.00</td>
<td>24.90</td>
<td>24.85</td>
<td>24.90</td>
<td>25.25</td>
</tr>
<tr>
<td>25.50</td>
<td>25.40</td>
<td>25.35</td>
<td>25.45</td>
<td>25.74</td>
</tr>
<tr>
<td>26.00</td>
<td>25.90</td>
<td>25.85</td>
<td>25.90</td>
<td>26.23</td>
</tr>
<tr>
<td>27.00</td>
<td>26.90</td>
<td>26.85</td>
<td>26.95</td>
<td>27.22</td>
</tr>
<tr>
<td>27.50</td>
<td>27.45</td>
<td>27.40</td>
<td>27.45</td>
<td>27.73</td>
</tr>
<tr>
<td>28.00</td>
<td>27.95</td>
<td>27.90</td>
<td>27.95</td>
<td>28.23</td>
</tr>
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<td>28.45</td>
<td>28.40</td>
<td>28.45</td>
<td>28.72</td>
</tr>
<tr>
<td>29.00</td>
<td>28.95</td>
<td>28.90</td>
<td>28.95</td>
<td>29.20</td>
</tr>
<tr>
<td>29.50</td>
<td>29.45</td>
<td>29.40</td>
<td>29.45</td>
<td>29.68</td>
</tr>
<tr>
<td>30.00</td>
<td>29.95</td>
<td>29.90</td>
<td>29.95</td>
<td>30.18</td>
</tr>
</tbody>
</table>

all temperatures are in °C
Figure C.9. Concentration of NaCl in solution versus measured conductivity.
To save tedious interpolation procedures, the electrophoresis measurements were usually taken at one of the specifically calibrated voltages (e.g. 50.0 V). The actual voltage could then be obtained from Table C.4.

C.1.6.2 Ammeter

The ammeter supplied with the Rank Bros. instrument was calibrated using the NLS instrument (as an ammeter, ± 5 μA at 5 mA full scale) and the power supply mentioned in Sect. C.1.6.1. The calibration results for the ammeter are given in Table C.5.

Table C.4
Electrophoresis Voltmeter Calibration

<table>
<thead>
<tr>
<th>Volts read</th>
<th>10.0</th>
<th>20.0</th>
<th>30.0</th>
<th>40.0</th>
<th>50.0</th>
<th>60.0</th>
<th>70.0</th>
<th>80.0</th>
<th>90.0</th>
<th>100.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volts actual</td>
<td>10.6</td>
<td>20.9</td>
<td>31.0</td>
<td>41.1</td>
<td>51.0</td>
<td>60.9</td>
<td>71.1</td>
<td>81.0</td>
<td>90.8</td>
<td>100.4</td>
</tr>
</tbody>
</table>

Table C.5
Electrophoresis Ammeter Calibration

<table>
<thead>
<tr>
<th>Amps read</th>
<th>0.05</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amps actual</td>
<td>0.051</td>
<td>0.103</td>
<td>0.202</td>
<td>0.301</td>
<td>0.401</td>
<td>0.504</td>
<td>1.04</td>
<td>2.03</td>
<td>3.02</td>
<td>4.03</td>
<td>5.06</td>
</tr>
</tbody>
</table>

C.1.6.3 Timer

The electrical timer supplied was calibrated against a Heuer stopwatch by letting both run for several 2-minute periods. It was found that the timer was quite precise, but was designed to run on an a.c. current of
50 cycles/sec. Thus, all measured times had to be corrected by multiplying by a factor of 5/6.

C.1.6.4 Eyepiece Graticule

The eyepiece graticule was calibrated by observing a "stage micrometer" (Olympus), a glass slide which, in the present case, is engraved with lines 10 μm apart. Since the working objective is under water when using a cylindrical cell and in air when using a "flat" or rectangular cell, the graticule must be calibrated separately for both configurations.

In the case of the cylindrical cell configuration, the stage micrometer was supported in the cell water bath (filled with distilled water at 25 °C) by means of two brass bars milled to exactly the same length. Since particles in the cylindrical cell are normally observed by means of indirect (refracted) light, it was necessary to position a 45° mirror in front of the condenser to reflect the light beam through the stage micrometer. To yield an estimate of the precision of the measurement, a total of 12 determinations were made, one each for 2, 4, and 6 graticule spacings at each of the four possible rotational configurations of the eyepiece. For the cylindrical cell, it was found that one graticule spacing = 58.78 ± 0.06 μm.

In the case of the flat cell configuration, the stage micrometer was supported in the cell water bath (filled with distilled water at 25 °C) by means of a specially constructed wire support. Again, 12 measurements were taken. For the flat cell, it was found that one graticule spacing = 63.93 ± 0.05 μm.
C.l.6.5 Interelectrode Distance

Each of the four cells supplied with the instrument were engraved with numbers (#1 and #3 - cylindrical, #2 and #4 - flat) to assist in their identification. For each cell, it was necessary to determine the effective inter-electrode distance over which the voltage drop was applied when computing the mobility of a given suspension. If the cell, complete with electrodes, is filled with a solution of known conductivity, \( \lambda \), and is found to have an electrical resistance, \( R \), between electrodes, then the inter-electrode distance, \( I \), is given by \( I = R\lambda A \), where \( A \) is the cross-sectional area at the plane of viewing.

A solution of known conductivity was prepared by carefully dissolving 7.4555 g. of KCl (analytical reagent grade, Fisher Scientific) in 1 litre of distilled and deionized water. This 0.1 N solution of KCl, the cells, the electrodes, and the measuring instrumentation were equilibrated over night in a constant temperature room. The conductivity as a function of temperature for KCl solutions of known concentration is available from standard sources (120).

The interelectrode resistance for each cell was determined as follows. After the solution had been added to the cell, its temperature was measured using thermometer #2521A (calibrated in Sect. C.1.4). The electrodes were then positioned in the cell, and the resistance across the cell was measured using a Beckman Model 16B2 a.c. conductivity bridge operating at 1000 hz. to avoid polarization. For the cylindrical cells, as well as the main electrodes used to apply the electric field, additional wire electrodes were also provided which give a more accurate measurement of the potential gradient. Thus, the resistance between wire electrodes was also
established. Measured results of the product, $\lambda R$, for the four cells are given in Table C.6.

The diameter of each cylindrical cell was determined at the viewing position by using the micrometer focusing adjustment of the electrophoresis microscope. The cell and the cell bath were filled with distilled water and the microscope objective was immersed during these measurements. The thickness of each flat cell was also determined by means of the microscope micrometer. Several thicknesses were measured over the width of the cell and averaged. All measurements were made at the centre of the cell length (the viewing plane). In the case of the flat cells, the bath was filled with distilled water, but the cell remained dry. The width of the flat cell was determined at the viewing plane by means of a travelling microscope. The latter measurement was greatly facilitated by filling the cell with a coloured (KMnO$_4$) solution and placing a strong, diffuse light source behind it. The various dimensions measured and the interelectrode distances calculated for all four cells are shown in Table C.6. The rectangular cell #2 was used for all of the electrophoretic and ex-situ electro-osmotic measurements made in the present investigation, except for run I-1.

C.2 Sample Calculations

C.2.1 Radioactive Measurements

C.2.1.1 Suspension Concentration

If $N$ is the number of counts measured over the time interval $t_c$, then the decay-corrected count rate $r$ may be obtained as

$$r = \frac{N}{at_c} \quad [C.1]$$
<table>
<thead>
<tr>
<th>Cell #</th>
<th>#1 (cyl.)</th>
<th>#2 (flat)</th>
<th>#3 (cyl.)</th>
<th>#4 (flat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda R_{\text{main}}$, cm$^{-1}$</td>
<td>365.2 ± 1.1</td>
<td>71.42 ± 0.04</td>
<td>356.7 ± 0.8</td>
<td>79.61 ± 0.25</td>
</tr>
<tr>
<td>$\lambda R_{\text{wire}}$, cm$^{-1}$</td>
<td>340.1 ± 0.5</td>
<td>-</td>
<td>336.8 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td>width, cm</td>
<td>-</td>
<td>0.987 ± 0.001</td>
<td>-</td>
<td>1.009 ± 0.001</td>
</tr>
<tr>
<td>ht. or dia., cm</td>
<td>0.1823 ± 0.0004</td>
<td>0.1089 ± 0.0001</td>
<td>0.1796 ± 0.0003</td>
<td>0.0948 ± 0.0001</td>
</tr>
<tr>
<td>$A$, cm$^2$</td>
<td>0.02610</td>
<td>0.1075</td>
<td>0.02533</td>
<td>0.0957</td>
</tr>
<tr>
<td>$\ell_{\text{main}}$, cm</td>
<td>9.53</td>
<td>7.68</td>
<td>9.04</td>
<td>7.62</td>
</tr>
<tr>
<td>$\ell_{\text{wire}}$, cm</td>
<td>8.87</td>
<td></td>
<td>8.53</td>
<td></td>
</tr>
</tbody>
</table>
where the decay correction factor $a$ is given by

$$a = e^{-0.693t_D/t_{\frac{1}{2}}} \quad [C.2]$$

t$_D$ being the decay time (days) and $t_{\frac{1}{2}}$ the half-life of the radioactive species [for Co$^{58}$, $t_{\frac{1}{2}} = 71.3$ days (110, p. B-261)]. If $r_s$ is the count rate obtained for the counting bottle including the suspension sample, and $r_b$ the count rate obtained for the counting bottle prior to injecting the sample, then the net count rate $r$ due only to the suspension is

$$r = r_s - r_b \quad [C.3]$$

The concentration of suspended radioactive particles $C_s$ is obtained using the appropriate calibration curve (see Sect. C.1.1.2), which has usually been fitted by a linear relationship. Thus,

$$C_s = mr + b \quad [C.4]$$

where $m$ and $b$ are the slope and intercept, respectively, of the calibration relationship. The 95% confidence limits on $C_s$ are obtained as

$$C_s \pm 1.96m \left( \frac{r_s + r_b}{at_c} \right)^{\frac{1}{2}} \quad [C.5]$$

assuming that the error is due entirely to the statistical nature of the radioactive decay process (see Sect. C.2.1.4).

Consider, for example, run I=11 where

$$N_s = 388693$$

$$N_b = 3056$$
\( t_c = 1.00 \text{ min.} \) for both measurements

\( t_D = 36.60 \text{ days} \)

\[ m = 3.537 \times 10^3 \frac{\text{particles/cm}^3}{\text{cpm}} \]

and \( b = -1.167 \times 10^8 \text{ particles/cm}^3 \)

Using Eq. [C.2],

\[ a = \exp\left(-0.693 \times 36.60 \right) \] \[ = 0.7041 \]

Using Eq. [C.1],

\[ r_s = \frac{388693}{0.7041 \times 1.00} \] \[ = 5.520 \times 10^5 \text{ cpm} \]

and

\[ r_b = \frac{3056}{0.7041 \times 1.00} \] \[ = 4.340 \times 10^3 \text{ cpm} \]

Using Eq. [C.3],

\[ r = 5.520 \times 10^5 - 4.340 \times 10^3 \] \[ = 5.477 \times 10^5 \text{ cpm} \]
Thus, using Eq. [C.4]

\[ C_s = 3.537 \times 10^3 \times 5.477 \times 10^5 - 1.167 \times 10^8 \]

\[ = 1.820 \times 10^9 \text{ particles/cm}^3 \]

The 95% confidence limits on \( C_s \) (using Eq. [C.5]) are

\[ \pm 1.96 \times 3.537 \times 10^3 \times \left( \frac{5.520 \times 10^5 + 4.340 \times 10^3}{0.7041 \times 1.00} \right)^{1/2} \]

\[ = \pm 6.162 \times 10^6 \text{ particles/cm}^3 \]

Thus, the initial concentration of suspended radioactive particles used in Run I-11 is \((1.820 \pm 0.006) \times 10^9 \text{ particles/cm}^3\).

Because of the high sample to background activity ratios usually encountered in the present suspension concentration measurements, the statistical error is almost negligible. Other sources of error such as the bias associated with the calibration curves and problems with replicating the sample volume are probably much more important in this case.

C.2.1.2 Wall Concentrations - Discontinuous Mode

If \( r_{ds}(t) \) is the decay-corrected count rate measured for a test section containing deposited particles using the discontinuous method, and if \( r_{db}(t) \) is the decay-corrected background activity in the presence of a "clean" test section, then the net count rate \( r_d(t) \) due only to the deposited particles is given by

\[ r_d(t) = r_{ds}(t) - r_{db}(t) \]  

[C.6]
The $r_{ds}$ values may be obtained from the counts, $N_d$, measured using the discontinuous mode by applying Eq. [C.1] (Sect. C.2.1.1). The values of $r_{db}$, however, are not generally available. In fact, only the values at the start of a run, $r_{db0}$, (since the test section is initially "clean") and at the end of the run, $r_{dbf}$, (since the "used" test section is replaced by a "clean" one) are known. In general, it was found that the background activity measured at the end of each run increased steadily in every series of experiments. This increase was attributed to the accumulation of particles in the machined entrance and exit sections during each run (see Sect. 3.4.3.1).

Thus, in order to account in some way for the changing background activity, it seems reasonable to assume, as a first approximation, that the values of $r_{db}$ vary linearly with time. Therefore,

$$r_{db}(t) = r_{db0} + \frac{r_{dbf} - r_{db0}}{t_E} t$$

where $t_E$ is the experimental run time.

The concentration of deposited particles $C_w(t)$ is obtained using the appropriate calibration factor $m$ (see Table C.1) as

$$C_w(t) = m r_d(t)$$

[Eq. C.8]

with a 95% confidence interval of (see Sect. C.2.1.4)

$$C_w(t) \pm 1.96 m \left[ \frac{r_{ds}(t) + r_{db}(t)}{a t_c} \right]^{\frac{1}{2}}$$

[Eq. C.9]

where $a$ is the decay correction factor and $t_c$ the time taken to measure each count, as before.
Run I-11 is used here to demonstrate the calculating procedures for both the discontinuous (this section) and continuous (Sect. C.2.1.3) modes of operation, as both types of measurements were carried out for this experiment. For run I-11,

\[ t_c = 10.0 \text{ min. for all measurements} \]
\[ t_E = 360.0 \text{ min.} \]

and \[ m = 1.278 \times 10^3 \frac{\text{particles/cm}^2}{\text{cpm}} \] (cylindrical collimator at 12.5 cm).

The 10-min. discontinuous counts, \( N_d \), measured as a function of time and their associated decay times, \( t_d \), are listed in Table C.7. First, all measured counts were converted to decay-corrected count rates, \( r_{ds} \), using the procedures outlined in Sect. 2.1.1.1, i.e., by employing Eqs. [C.1] and [C.2]. The \( a \) and \( r_{ds} \) values resulting from this procedure are recorded in Table C.7.

From Table C.7, it can be seen that

\[ r_{db0} = 0.430 \times 10^4 \text{ cpm} \]

and \[ r_{dbf} = 0.483 \times 10^4 \text{ cpm} \]

Thus, the various \( r_{db} \) values may be obtained using Eq. [C.7]. For example, at \( t = 60 \text{ min.} \),

\[ r_{db}(60) = 0.430 \times 10^4 + \frac{(0.483 - 0.430) \times 10^4 \times 60}{360.0} \]

\[ = 0.439 \times 10^4 \text{ cpm} \]

These values are also listed in Table C.7. From the known values of \( r_{ds} \) and \( r_{db} \), it is now possible to calculate \( r_d \), \( C_w \), and the 95% confidence
Table C.7
Wall Concentrations - Discontinuous Counts - Run I-II

<table>
<thead>
<tr>
<th>t</th>
<th>N_d</th>
<th>t_D</th>
<th>a</th>
<th>r.ds</th>
<th>r.db</th>
<th>r_d</th>
<th>C_w</th>
<th>±ΔC_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>(min.)</td>
<td>(counts/10 min.)</td>
<td>(days)</td>
<td>(x 10^6 cpm)</td>
<td>(x 10^7 particles/cm^3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>30277</td>
<td>36.62</td>
<td>0.7040</td>
<td>0.430</td>
<td>0.430</td>
<td>0.000</td>
<td>0.000</td>
<td>0.009</td>
</tr>
<tr>
<td>60</td>
<td>89000</td>
<td>36.69</td>
<td>0.7035</td>
<td>1.265</td>
<td>0.439</td>
<td>0.826</td>
<td>1.056</td>
<td>0.012</td>
</tr>
<tr>
<td>120</td>
<td>125867</td>
<td>36.75</td>
<td>0.7031</td>
<td>1.790</td>
<td>0.448</td>
<td>1.342</td>
<td>1.715</td>
<td>0.014</td>
</tr>
<tr>
<td>180</td>
<td>154898</td>
<td>36.81</td>
<td>0.7027</td>
<td>2.204</td>
<td>0.457</td>
<td>1.747</td>
<td>2.233</td>
<td>0.015</td>
</tr>
<tr>
<td>240</td>
<td>177835</td>
<td>36.87</td>
<td>0.7023</td>
<td>2.532</td>
<td>0.466</td>
<td>2.066</td>
<td>2.641</td>
<td>0.016</td>
</tr>
<tr>
<td>300</td>
<td>200438</td>
<td>36.93</td>
<td>0.7019</td>
<td>2.856</td>
<td>0.474</td>
<td>2.782</td>
<td>3.043</td>
<td>0.017</td>
</tr>
<tr>
<td>360</td>
<td>218092</td>
<td>36.98</td>
<td>0.7016</td>
<td>3.109</td>
<td>0.483</td>
<td>2.626</td>
<td>3.355</td>
<td>0.018</td>
</tr>
<tr>
<td>360*</td>
<td>33268</td>
<td>38.97</td>
<td>0.6883</td>
<td>0.483</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*background activity - "clean" test section.
limits on \( C_w \), \( \pm \Delta C_w(t) \), as a function of \( t \). For example, at 60 min., using Eq. [C.6],

\[
\begin{align*}
  r_d(60) &= 1.265 \times 10^4 - 0.439 \times 10^4 \\
  &= 0.826 \times 10^4 \text{ cpm}
\end{align*}
\]

Using Eq. [C.8],

\[
\begin{align*}
  C_w(60) &= 1.278 \times 10^3 \times 0.826 \times 10^4 \\
  &= 1.056 \times 10^7 \text{ particles/cm}^2
\end{align*}
\]

Using Eq. [C.9],

\[
\begin{align*}
  \Delta C_w(60) &= 1.96 \times 1.278 \times 10^3 \times \left[ \frac{1.265 \times 10^4 + 0.430 \times 10^4}{0.7035 \times 10.0} \right]^{\frac{1}{2}} \\
  &= 0.012 \times 10^7 \text{ particles/cm}^2
\end{align*}
\]

The calculated values of \( r_d \), \( C_w \), and \( \Delta C_w \) for the other times are given in Table C.7.

The initial deposition rate is found by determining the polynomial which best fits the values of \( C_w(t) \) and then evaluating its first derivative at \( t = 0 \). For run I-11, it was found that the seven values of \( C_w(t) \) listed in Table C.7 were best represented by a third-order polynomial. From the slope of this relationship at \( t = 0 \), the initial deposition rate, \( J_D^I \), was found to be

\[
J_D^I = 3.73 \times 10^3 \text{ particles/cm}^2\text{-sec.}
\]
C.2.1.3 Wall Concentrations - Continuous Mode

If \( r_{cs}(t) \) is the decay-corrected count rate measured for a test section containing deposited particles using the continuous method, and if \( r_{cb}(t) \) is the decay-corrected background activity, the net count rate \( r_c(t) \) due only to the deposited particles is given by

\[
    r_c(t) = r_{cs}(t) - r_{cb}(t)
\]  

Whereas the \( r_{cs} \) values may be obtained from the continuously measured counts, \( N_c \), the \( r_{cb} \) values, as was the case for the discontinuous counting mode, are not generally available. In the present case, the background is not only that which the counter would detect in the presence of a "clean" test section, but also includes the effect of the suspended particles which are present in the test section throughout the continuous measurement. Furthermore, both types of background change with time as each experiment progresses. While the "clean test section background" steadily increases with time (see Sect. C.2.1.2), the "suspension background" tends to decrease because of deposition in the test section and in other parts of the circulating system. Because the measured rates of deposition on the walls of a test section were always found to decrease with time, it might be expected that the suspension background would follow the same trend. However, the actual suspension concentrations measured during the course of many experiments generally appeared to decline linearly with time, indicating that factors other than deposition in the test section were the dominant source of particle losses. Thus, it will be assumed here as a first approximation that both contributing backgrounds and, hence, the overall background, \( r_{cb} \), vary linearly with time. Therefore,
where $r_{cb_i}$ and $r_{cb_f}$ are the overall background count rates at the start and end, respectively, of the continuous counting interval, and $t_i$ and $t_f$ are the start and end times, respectively, of this interval. [In most experiments operated using the continuous counting mode, all measurements were made in a single interval and, hence, $t_i = 0$ and $t_f = t_E$, the experimental run time. However, in a few experiments, continuous counts were obtained during all or some of the timed intervals associated with a discontinuously operated accumulation run. Eq. [C.11] has therefore been generalized to reflect this latter situation.]

The overall background activities at the start and end of each counting interval may be obtained if it is assumed that the "true" count rate due only to the deposited particles at these times is given by the net activities, $r_d$, calculated using the discontinuous counting procedure (see Sect. C.2.1.2). [Note that even for runs consisting of a single interval, the discontinuous method was used to obtain the final count rate due to deposited particles.] This assumption seems quite a reasonable one under the present circumstances, as the discontinuously measured results are always more reliable than those obtained in the continuous mode, owing to the far lower backgrounds associated with the former measurements. Thus, if $r_{cs_i}$ and $r_{cs_f}$ represent the continuously measured activities at the start and end of the interval, respectively (obtained by extrapolating the $r_{cs}(t)$ curve to $t_i$ and $t_f$, respectively), then

$$r_{cb_i} = r_{cs_i} - r_{d_i}$$  [C.12]
and

\[ r_{cb_f} = r_{cs_f} - r_{d_f} \]  \[C.13\]


\[ r_{cb}(t) = r_{cs_i} - r_{d_i} + \left( r_{cs_f} - r_{d_f} - r_{cs_i} + r_{d_i} \right) \frac{(t - t_i)}{t_f - t_i}, \]

\[ t_i < t < t_f \]  \[C.14\]

The concentration of deposited particles \( C_w(t) \) is then obtained using the appropriate calibration factor \( m \) (see Table C.1) as

\[ C_w(t) = m \cdot r_c(t) \]  \[C.15\]

having a 95% confidence interval of (see Sect. C.2.1.4)

\[ C_w(t) \pm 1.96 \cdot m \cdot \frac{r_{cs}(t) + r_{cb}(t)}{a \cdot t_c} \]  \[C.16\]

where \( a \) is the decay correction factor and \( t_c \) the time taken for each individual count, as before.

Run I-11 is used here to demonstrate the calculating procedure, partly because the \( r_d \) values have already been worked out in the previous section (see Table C.7) but mainly because, by treating only a small but complete segment of an overall curve, it is not necessary to deal with a large number of data points. This example also illustrates the use of the technique in its most generalized form. As it eventually allows the calculation of a deposition rate, the first continuous interval of run I-11 will be considered here. For this interval,
\[ t_c = 10.0 \text{ min. for all measurements} \]
\[ t_i = 0.0 \text{ min.} \]
\[ t_f = 60.0 \text{ min.} \]

\[ r_{d_i} = 0.000 \text{ cpm} \]
\[ r_{d_f} = 0.826 \times 10^4 \text{ cpm} \]

\[ m = 1.278 \times 10^3 \text{ particles/cm}^2 \text{ (cylindrical collimator at 12.5 cm.)} \]

The 10-min. continuous counts, \( N_c \), recorded as a function of time over the first 60-minute interval of run I-11, are tabulated in Table C.8. The operating times \( t \) shown in Table C.8 are taken as the mid-point of each counting period. As well as the time allotted for each count, the counting system requires an additional 0.03925 min. to record each measurement. Thus, for example, the mid-point of the third measurement falls at

\[ t = 5.0 + 2 \times 10.03925 = 25.1 \text{ minutes} \]

From knowledge of the decay time recorded at the start of each continuous counting interval, it then becomes possible to estimate the decay time \( t_D \) for each individual count. These values are also recorded in Table C.8. Thus, by employing the procedures illustrated in Sect. C.2.1.1, i.e. using Eqs. [C.1] and [C.2], the measured counts, \( N_d \), are converted to the decay-corrected counted rates, \( r_{cs} \), shown in Table C.8.

The resulting \( r_{cs} \) values were then fitted by least squares to a second-order polynomial relationship. The fitted expression was extrapolated to 0 and to 60 min. to obtain
Table C.8
Wall Concentrations - Continuous Counts
Run I-11 - First Interval

<table>
<thead>
<tr>
<th>t (min.)</th>
<th>$N_c$ (counts/10 min.)</th>
<th>$t_D$ (days)</th>
<th>$a$</th>
<th>$r_{cs}$ ($x 10^3$ cpm)</th>
<th>$r_{cb}$</th>
<th>$r_c$</th>
<th>$C_w$ ($x 10^7$ particles/cm$^3$)</th>
<th>$\pm \Delta C_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>458614</td>
<td>36.65</td>
<td>0.7038</td>
<td>6.516</td>
<td>6.434</td>
<td>0.082</td>
<td>0.106</td>
<td>0.034</td>
</tr>
<tr>
<td>15.1</td>
<td>470403</td>
<td>36.65</td>
<td>0.7038</td>
<td>6.684</td>
<td>6.398</td>
<td>0.286</td>
<td>0.366</td>
<td>0.034</td>
</tr>
<tr>
<td>25.1</td>
<td>478040</td>
<td>36.66</td>
<td>0.7037</td>
<td>6.793</td>
<td>6.362</td>
<td>0.431</td>
<td>0.551</td>
<td>0.039</td>
</tr>
<tr>
<td>35.1</td>
<td>483388</td>
<td>36.67</td>
<td>0.7036</td>
<td>6.870</td>
<td>6.326</td>
<td>0.544</td>
<td>0.695</td>
<td>0.034</td>
</tr>
<tr>
<td>45.2</td>
<td>490446</td>
<td>36.68</td>
<td>0.7036</td>
<td>6.970</td>
<td>6.290</td>
<td>0.680</td>
<td>0.870</td>
<td>0.034</td>
</tr>
<tr>
<td>55.2</td>
<td>495555</td>
<td>36.68</td>
<td>0.7036</td>
<td>7.044</td>
<td>6.254</td>
<td>0.790</td>
<td>1.009</td>
<td>0.034</td>
</tr>
</tbody>
</table>
\[ r_{cs_1} = 6.452 \times 10^4 \text{ cpm} \]

and

\[ r_{cs_f} = 7.063 \times 10^4 \text{ cpm} \]

Thus, the various \( r_{cb} \) values may be calculated using Eq. [C.14]. For example, at \( t = 25.1 \text{ min.} \),

\[
\begin{align*}
    r_{cb}(25.1) &= (6.452 - 0.000) \times 10^4 \\
    &\quad + \frac{(7.063 - 0.826 - 6.452 + 0.000) \times 10^4 \times 25.1}{60.0} \\
    &= 6.362 \times 10^4 \text{ cpm}
\end{align*}
\]

The \( r_{cb} \) values obtained in this manner are recorded in Table C.8. They show that the change in the "suspension background" with time predominates over the changing "clean test section background" such that the overall background \( r_{cb} \) decreases slightly with time. This predominance of the suspension background was found to occur in most continuously measured runs.

From the known values of \( r_{cs} \) and \( r_{cb} \), it is now possible to calculate \( r_c \), \( C_w \), and the 95% confidence limits on \( C_w \), \( \pm \Delta C_w \), as a function of time. For example, at 25.1 minutes, using Eq. [C.10],

\[
\begin{align*}
    r_c(25.1) &= (6.793 - 6.362) \times 10^4 \\
    &= 0.431 \times 10^4 \text{ cpm}
\end{align*}
\]

Using Eq. [C.15],

\[
\begin{align*}
    C_w(25.1) &= 1.278 \times 10^3 \times 0.431 \times 10^4 \\
    &= 0.551 \times 10^7 \text{ particles/cm}^2
\end{align*}
\]
Using Eq. [C.16],

$$\Delta C_w(25.1) = 1.96 \times 1.278 \times 10^3 \times \left[ \frac{6.793 \times 10^4 + 6.362 \times 10^4}{0.7037 \times 10.0} \right]^{1/2}$$

$$= 0.034 \times 10^7 \text{ particles/cm}^2$$

The other values of $r_c$, $C_w$ and $\Delta C_w$ are included in Table C.8. A comparison of Tables C.7 and C.8 demonstrates that the statistical error associated with the continuous measurements is much greater than those obtained using the discontinuous mode. This phenomenon may be attributed to the much higher backgrounds (caused by the presence of the suspension) encountered in the former measurements (see Sect. C.2.1.4).

As was the case for the discontinuous measurements, the initial deposition rate is found by fitting a polynomial to the calculated values of $C_w(t)$ and then evaluating its first derivative at $t = 0$. A second-order polynomial fit to the data shown in Table C.8 yields

$$J_D' = 4.08 \times 10^3 \text{ particles/cm}^2\text{-sec.}$$

Because the continuously measured data yield more detail about the initial portion of the accumulation curve, the latter value of $J_D'$ was retained for subsequent analysis.

C.2.1.4 Errors in Radioactivity Measurements

Only the error due to the statistical nature of the radioactive decay process will be discussed here. As will be shown below, this error predominates for those wall concentrations measured in the presence of a
high radioactive background. However, there are other factors which may exist that can also lead to experimental inaccuracies, such as improperly flushed lines, bias associated with the calibration curves, and the method used for obtaining time-dependent background count rates (see Sects. C.2.1.2 and C.2.1.3).

Radioactive decay is a random process. Thus, the number of nuclei in a sample of radioactive material that decays in any given time period is not fixed but is quite variable. Because the process is perfectly random, as long as there are a large number of radioactive nuclei present and the half-life, $t_\frac{1}{2}$, of the decay process is sufficiently long, the frequency of count rates, when plotted against all possible count rates, will have a normal or Gaussian distribution (168). The properties of a Gaussian distribution are completely defined by the specification of two parameters, the mean value, $\bar{x}$, (i.e. the value which the measurement is attempting to ascertain), and the standard deviation, $\sigma$ (169). Thus, if $\sigma$ is known, it becomes possible to estimate the reliability of a single measurement $x$. For example, it can be said, with a 95% chance of being correct, that the desired mean count rate $\bar{x}$ lies within the interval $x - 1.96\sigma$, $x + 1.96\sigma$.

For a radioactive decay process, where $N$ is the number of counts measured in a given counting interval $t_c << t_\frac{1}{2}$, as long as $N >> 1$, then the standard deviation may be obtained approximately as (168)

$$\sigma_N \approx N^{\frac{1}{2}}$$ [C.17]

In general, it is of interest to determine the error limits (95% confidence) on a particle concentration (suspension or wall) calculated from the decay-corrected count rates for the sample and the background using a
linear calibration curve. The general relationship for the concentration may be written as

\[ C = m(r_s - r_b) + b \]  \[ \text{[C.18]} \]

where \( r_s \) is the decay-corrected sample count rate, \( r_b \) the decay-corrected background count rate, and \( m \) and \( b \) the slope and intercept, respectively, of the fitted calibration curve. The decay-corrected count rates for the sample and background may be obtained from the originally measured counts, \( N_s \) and \( N_b \), respectively, using Eq. \([C.1]\). Thus,

\[ r_s = \frac{N_s}{a \, t_c}, \quad r_b = \frac{N_b}{a \, t_c} \]  \[ \text{[C.19]} \]

where \( a \) is the decay correction factor given by Eq. \([C.2]\). Eq. \([C.19]\) assumes that the two measurements were taken almost simultaneously (compared to \( t_c \)), using the same counting interval \( t_c \).

In order to obtain the standard deviation of \( C \) on the basis of the count rates, it is necessary to know how error is propagated in complex functions. [Note that the corrected count rates generally have more utility than the uncorrected counts in the present calculations because the latter quantities were not actually measured for many of the background activities used for determining the wall concentrations.] Mickley \textit{et al.} (170, p. 64) have shown that if

\[ y = f(x_1, x_2, \ldots, x_n) \]

then

\[ \sigma_y = \left[ \sum_{i=1}^{n} \left( \frac{\partial y}{\partial x_i} \right)^2 \sigma_{x_i}^2 \right]^{1/2} \]  \[ \text{[C.20]} \]
When Eq. [C.20] is applied to the present problem, it is found from Eq. [C.18] that

$$\sigma_C = m \left( \sigma_s^2 + \sigma_r^2 \right)^{\frac{1}{2}}$$  \hspace{1cm} \text{[C.21]}

Furthermore, since from Eqs. [C.19] and [C.20]

$$\sigma_r_s = \frac{N_r}{a t_c} = \left( \frac{r_s}{a t_c} \right)^{\frac{1}{2}}$$

and

$$\sigma_r_b = \frac{N_b}{a t_c} = \left( \frac{r_b}{a t_c} \right)^{\frac{1}{2}}$$  \hspace{1cm} \text{[C.22]}

Then substituting Eq. [C.22] into Eq. [C.21] yields

$$\sigma_C = m \left( \frac{r_s + r_b}{a t_c} \right)^{\frac{1}{2}}$$  \hspace{1cm} \text{[C.23]}

Thus, the 95% confidence limits on $C$ are $C \pm 1.96 m \left( \frac{r_s + r_b}{a t_c} \right)^{\frac{1}{2}}$.

From Eqs. [C.18] and [C.23], it can be shown that the relative error in $C$ is given by

$$\frac{1.96 \sigma_C}{C} = \frac{1.96 m \left( \frac{r_s + r_b}{a t_c} \right)^{\frac{1}{2}}}{m(r_s - r_b) + b}$$  \hspace{1cm} \text{[C.24]}

Thus, as the background count rate approaches that of the sample, the relative error can become very large.
C.2.2 Electrophoresis and Electro-osmosis Measurements

C.2.2.1 Double Layer Thickness, $1/\kappa$

At higher solution conductivities, where the electrolyte concentration has been adjusted by adding NaCl, NaOH, or HCl, the concentrations of ionic species (primarily Na$^+$ and Cl$^-$) are readily determined by measuring the conductivity of the suspension and using the concentration-conductivity calibration curve given in Fig. C.9. However, at lower conductivities ($\leq 5$ $\mu$mho/cm), these concentrations are not directly obtainable, as both the initial particle dispersion process and the subsequent deposition runs introduce unknown amounts of contaminants into the solution. For the latter case, approximate ion concentrations must be estimated on the basis of a few appropriate assumptions from the suspension pH and conductivity data measured for each run.

What ions are likely to be present in the solution? Initially, the distilled and deionized water used to make the suspension contains only H$^+$ and OH$^-$ ions. During and after the dispersion process, the particles contribute HSiO$_3^-$ ions (dissolution) and NH$_4^+$ ions (desorption) to the solution. Since the suspension is always in contact with air, it is very likely to be saturated with HCO$_3^-$ ions. As each run progresses, traces of chromic acid (Na$^+$, Cr$_2$O$_7^{2-}$, H$^+$, SO$_4^{2-}$ ions) may be leached from the test section and remnants of NaOH (Na$^+$, OH$^-$ ions), left over from the decontamination process, may be leached from other parts of the circulation system. NaOH and HCl (H$^+$, Cl$^-$ ions) are added at the start of each run in order to control the pH. Finally, NaCl (Na$^+$, Cl$^-$) was added in many runs to alter the double layer thickness.

Thus, at low conductivities, contamination of the suspending solution results in a very complex electrolyte. In order to obtain an estimate
of the concentrations of the various ionic species which may be present in this electrolyte, it is necessary to make a number of simplifying assumptions. First, it is assumed that the concentration of each species is low enough that the contribution of their mobilities to the overall conductivity of the solution is additive. Thus (113, p. 333),

\[ \lambda = \sum \frac{N C_i |z_i e_0| u_i}{1000} \]  

where \( \lambda \) is the conductivity of the solution (mho/cm), \( N \) is Avogadro's number, \( C_i \) the concentration of ionic species \( i \) (moles/l.), \( z_i \) the valence of the ion, \( e_0 \) the charge of an electron (coulomb) and \( u_i \) the mobility of the ion (cm\(^2\)/volt-sec). In addition, it is assumed that, except for the dissociation of water, the other incomplete ionization processes (the dissolution of silica, the desorption of ammonia, and the absorption of \( \text{CO}_2 \)) are so slow that it is not necessary to invoke equilibrium arguments for these species. Because the mobilities of all ions other than \( \text{H}^+ \) and \( \text{OH}^- \) are fairly similar, the use of the latter assumption (which greatly simplifies the calculation) does not lead to significant errors in the total counterion (positive ion) concentration.

On the basis of this latter value, the inverse double layer thickness \( \kappa \) can be calculated from Eq. [2.2], which at 25 °C for predominantly univalent counterions, can be rewritten as

\[ \kappa = 0.3286 \times 10^8 \times C^{\frac{3}{2}} \]  

where \( C \) is the counterion concentration in moles/l.
\[ \lambda = 1.29 \times 10^{-6} \text{ mho/cm} \]

\[ \text{pH} = 5.6 \]

Because the pH of the suspension was not adjusted in this run and because the suspension had not yet been circulated around the loop, the only ionic species likely to be present are \( H^+ \), \( OH^- \), \( NH_4^+ \), \( HSiO_3^- \), and \( HCO_3^- \). The mobility of \( HSiO_3^- \) could not be found in the literature and thus it was assumed to have a value similar to that of \( HCO_3^- \). For this reason \( HCO_3^- \) and \( HSiO_3^- \) were lumped together as the single species \( HCO_3^- \) in the calculations.

The relevant ionic mobilities at 25 °C are (113, p. 337)

\[
\begin{align*}
&u_{H^+} = 36.30 \times 10^{-4} \text{ cm}^2/\text{volt-sec} \\
&u_{OH^-} = 20.50 \times 10^{-4} \\
&u_{NH_4^+} = 7.6 \times 10^{-4} \\
&u_{HCO_3^-} = 4.6 \times 10^{-4}
\end{align*}
\]

at pH 5.6,

\[
[H^+] = 10^{-5.6} = 2.512 \times 10^{-6} \text{ moles/l}
\]

Therefore,

\[
[OH^-] = 10^{-14}/[H^+] = 0.004 \times 10^{-6} \text{ moles/l}
\]

If

\[
[NH_4^+] = y \times 10^{-6} \text{ moles/l}
\]

then, to maintain electroneutrality,
\[ [\text{HCO}_3^-] = (y + 2.512 - 0.0004) \times 10^{-6} \]
\[ = (y + 2.508) \times 10^{-6} \text{ moles/l} \]

Thus, substituting the appropriate values into Eq. [C.26],

\[
\frac{6.023 \times 10^{23} \times 1.6023 \times 10^{-19}}{10^3} \\
\times \left[ 2.512 \times 36.30 + 0.004 \times 21.50 + 7.6y \right] \\
+ 4.6(y + 2.508) \times 10^{-4} \times 10^{-6} \\
= 1.29 \times 10^{-6} = \lambda
\]

and solving for \( y \) yields

\[ [\text{NH}_4^+] = 2.529 \times 10^{-6} \text{ moles/l} \]

Therefore

\[ [\text{HCO}_3^-] = (2.529 + 2.508) \times 10^{-6} = 5.037 \times 10^{-6} \text{ moles/l} \]

and the total concentration of counterions

\[ C = [H^+] + [\text{NH}_4^+] \]
\[ = (2.512 + 2.529) \times 10^{-6} \]
\[ = 5.04 \times 10^{-6} \text{ moles/l} \]

Using Eq. [C.27],
\[ \kappa = 0.3286 \times 10^8 \times (5.04 \times 10^{-6})^{\frac{1}{2}} \]

\[ = 7.38 \times 10^4 \text{ cm}^{-1} \]

Of course, as the series of runs progresses, the make-up of the electrolyte changes due to alterations in the degree of ionization of all of the contributing ions listed in the example, due to the introduction of undesired contaminants and due to addition of either NaCl or HCl for pH control. Thus, in addition to the condition of electroneutrality, assumptions about the presence of other ions are required before Eq. [C.26] can be solved for the concentration of the unknown species. Fortunately, the concentration of \( \text{OH}^- \) and \( \text{H}^+ \) ions can be specified from the known pH. Furthermore, the amount of \( \text{Na}^+ \) or \( \text{Cl}^- \) added to adjust the pH was carefully measured. Thus, it was only necessary for assumptions regarding the existence and concentration of the other ions to be made. In general this procedure resulted in a range of \( \kappa \)-values for the suspension used in each run. However, this range was not very large for two reasons: the mobilities of all ionic species (except \( \text{H}^+ \) and \( \text{OH}^- \)) are very similar, and, because of pH adjustment, the measured concentrations of \( \text{Na}^+ \) and \( \text{Cl}^- \) soon predominated over those of the other ions. When a range of \( \kappa \)-values occurred, the midpoint of this range was used in all subsequent calculations.

C.2.2.2 Particle \( \zeta \)-potential from Electrophoretic Mobility

The particle electrophoretic mobility measurements were converted to \( \zeta \)-potentials using the tabulated numerical results of Wiersema, Loeb, and Overbeek (137). The results are given in terms of dimensionless variables and have been tabulated in the form of
\[ E = f(y_0, q_0, m_\pm) \]  

where \( E \), the dimensionless electrophoretic mobility, is given by

\[ E = \frac{6\pi \mu e_0}{e_k T} U \]

\[ = 0.7503 \times 10^4 \, \text{U} \quad \text{at } 25 \, ^\circ\text{C} \]  

\( y_0 \), the dimensionless \( \zeta \)-potential, is given by

\[ y_0 = \frac{e_0 \zeta}{k T} \]

\[ = \frac{\zeta}{25.69} \quad \text{at } 25 \, ^\circ\text{C} \]  

\( q_0 \), the dimensionless double layer thickness, is given by

\[ q_0 = \kappa a \]  

and \( m_+ \) and \( m_- \) are the dimensionless mobilities of the positive and negative ions, respectively, in the solution and are given by

\[ m_\pm = \frac{N e_k T}{6\pi \mu} \frac{z_\pm}{\lambda_0^\pm} \]

\[ = 12.86 \, \lambda_0^\pm \quad \text{at } 25 \, ^\circ\text{C} \text{ for univalent cations and anions} \]

In the above expressions, \( \mu \) is the viscosity of the solution (g/cm·sec), \( e_0 \) the unit of electrostatic charge (statcoulombs), \( e \) the dielectric constant of solution, \( k \) the Boltzmann constant (ergs/°K), \( T \) the absolute temperature (°K), \( U \) the measured electrophoretic mobility (cm²/volt·sec), \( \zeta \) the particle \( \zeta \)-potential (mv), \( \kappa \) the inverse double layer thickness (cm⁻¹), \( a \) the radius of the particle (cm), \( N \) Avogadro's constant, \( z_\pm \) the valence of the cations
and anions, respectively, in solution \((z_\pm = 1\) assumed here) and \(\lambda_0^\pm\) the limiting ionic conductances of these anions and cations \((\text{cm}^2/\text{ohm-equiv.})\). When the electrolyte consists of a mixture of univalent cations and anions, it is assumed that \(m_+\) and \(m_-\) can be calculated as the number averages of the individual \(m_i^\pm\).

Because of the form of the tables, a solution for \(y_0\) cannot be obtained explicitly for known values of \(E\), \(q_0\), and \(m^\pm\). Instead, for a given value of \(q_0\), a curve of \(E\) versus \(y_0\) must be constructed by interpolating the tabulated results presented in Table I of reference (137). Furthermore, since this table gives only the results obtained for \(m^\pm = 0.184\), each of the interpolated \(E\) values must be corrected to correspond to the actual \(m_+\) and \(m_-\). Each corrected value \(E'\) is given by

\[
E' = E + (m_+ - 0.184) \frac{\partial E}{\partial m_+} + (m_- - 0.184) \frac{\partial E}{\partial m_-}
\]

where the values of \(\partial E/\partial m^\pm\) may be interpolated from Table III of reference (137). Thus, finally, from the plotted graph of \(E'\) versus \(y_0\), a value of \(y_0\) corresponding to the experimental value of \(E_{\text{expt}}\) may be extracted.

Consider, for example, run I-1, where

\[
V = 3.812 \times 10^{-4} \frac{\text{cm}^2}{\text{volt}\cdot\text{sec}}
\]

and the concentration of the various ionic species in the solution as well as the double layer thickness have been estimated in Sect. C.2.2.1. Using Eq. [C.29],
Using Eq. [C.31],

\[ q_0 = 7.38 \times 10^4 \times 0.201 \times 10^{-6} = 1.48 \]

The limiting ionic mobilities, \( \lambda_0 \) (113, p. 337), and the individual values of \( m_\pm \) obtained using Eq. [C.32] are listed below for the various ions known to be present in the solution:

<table>
<thead>
<tr>
<th>Ion</th>
<th>( \lambda_0 )</th>
<th>( m_\pm )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^+ )</td>
<td>399.82</td>
<td>0.0368</td>
</tr>
<tr>
<td>( \text{NH}_4^+ )</td>
<td>73.4</td>
<td>0.175</td>
</tr>
<tr>
<td>( \text{OH}^- )</td>
<td>198.0</td>
<td>0.0649</td>
</tr>
<tr>
<td>( \text{HCO}_3^- )</td>
<td>44.43</td>
<td>0.289</td>
</tr>
</tbody>
</table>

Thus, the number average values of \( m_\pm \) are

\[ m_+ = \frac{2.512}{5.041} \times 0.0368 + \frac{2.529}{5.041} \times 0.175 \]

\[ = 0.106 \]

and

\[ m_- = \frac{0.004}{5.041} \times 0.0649 + \frac{5.037}{5.041} \times 0.289 \]

\[ = 0.289 \]

From Table I of reference (137), values of E are obtained by extrapolation for \( q_0 = 1.48, m_\pm = 0.184 \) and for various values of \( y_0 \) (see Table C.9).
Table C.9

$E$ versus $y_0$ - Run I-1

<table>
<thead>
<tr>
<th>$y_0$</th>
<th>$E$</th>
<th>$\partial E/\partial m_+^*$</th>
<th>$\partial E/\partial m_-^*$</th>
<th>$E'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.922</td>
<td>-0.15</td>
<td>-0.33</td>
<td>1.899</td>
</tr>
<tr>
<td>3</td>
<td>2.645</td>
<td>-0.27</td>
<td>-0.65</td>
<td>2.598</td>
</tr>
<tr>
<td>4</td>
<td>3.040</td>
<td>-0.41</td>
<td>-1.12</td>
<td>2.954</td>
</tr>
<tr>
<td>5</td>
<td>3.287</td>
<td>-0.57</td>
<td>-1.79</td>
<td>3.144</td>
</tr>
<tr>
<td>6</td>
<td>3.409</td>
<td>-0.76</td>
<td>-2.71</td>
<td>3.184</td>
</tr>
</tbody>
</table>
[The extrapolation procedure is made much easier if the results of Table I are first plotted.] From Table III of reference (137), values of $\partial E/\partial m_+$ and $\partial E/\partial m_-$ are obtained by extrapolation for $q_0 = 1.48$ and for the same values of $y_0$ (see Table C.9). [Again, the extrapolation procedure is greatly simplified if the results of Table III are first plotted.] The corrected values of $E'$ are then calculated using Eq. [C.33] and the average $m_\pm$ obtained above. The $E'$ versus $y_0$ curve is then plotted. Since $E_{\text{expt}} = 2.860$, the corresponding value of $y_0$ obtained from this plot is $y_0 = 3.68$. Thus, using Eq. [C.30], the $\zeta$-potential of the particles used in run I-1 may be calculated as

$$\zeta = 25.69 \times 3.68$$

$$= 94.5 \text{ mv}$$

From the direction of the particle motion relative to the direction of the applied potential gradient, it is known that the $\zeta$-potential is in fact negative.

C.2.2.3 Errors in Electrophoresis and Electro-osmosis Measurements

There are many potential sources of error in electrophoresis and electro-osmosis measurements. These may be broadly classified into three categories:

i) errors due to locating the measuring levels,

ii) errors due to measuring the electrophoresis time, e.g. depth-of-field errors, effects of Brownian motion, and effects of secondary circulation caused by leakage through electrode chambers, gas evolution, $I^2R$ heating, and radiant heating,
iii) errors due to converting time to electrophoretic mobility, e.g. errors in calibrating the inter-electrode length, the grid spacing, and the voltmeter, and the effects of electrode polarization.

Many of these potential problems can be largely eliminated through proper design of the measuring apparatus. For example, the effects of electrode polarization are minimized by using large potential differences (50-100 V.) applied over relatively long interelectrode distances to achieve the desired electric field gradients. Problems with secondary circulation are reduced by employing a heat filter and immersing the electrophoresis cell in a constant temperature bath. Errors due to locating the stationary levels tend to cancel each other if measurements are made at both levels. Proper location of the mid-plane of the cell is less important because the electro-osmotic velocity profile is almost flat in this region. The various calibration errors can be reduced by repeating the calibration procedure until precise values are obtained.

Thus, the primary source of error in the present measurements may be attributed to the effects of Brownian motion and a finite depth-of-field of the observing system. Together, these two factors lead to a range of possible electrophoresis times which are approximately normally distributed about the desired mean value. The problem, therefore, is to determine the error limits on the resulting particle and wall ζ-potentials which arise when a number of time measurements are taken at each of the prescribed levels, assuming that these times are normally distributed.

The particle ζ-potential, ζ_p, is obtained from the measured electrophoretic mobility, U_{SL} (cm²/volt-sec), obtained at the stationary levels (see Sect. C.2.2.2). The latter quantity, in turn, is determined from the average electrophoretic time measured at the stationary levels t_{SL} (sec), using
where \( n_{SL} \), the number of graticule grid spaces over which the particles were timed, \( l_g \), the length of each grid space (cm), \( l_e \), the interelectrode distance (cm), and \( E \), the applied potential difference (volts). By substituting Eq. [C.34] into Eq. [C.20] (Sect. C.2.1.4), it is possible to show that

\[
\sigma_{U_{SL}} = \frac{n_{SL} l_g l_e \sigma_{t_{SL}}}{E t_{SL}^2}
\]  

where the standard deviation of \( t_{SL} \) is given by (169)

\[
\sigma_{t_{SL}} = \left[ \frac{N_{SL} \sum_{i=1}^{N_{SL}} (t_{SLi} - \bar{t}_{SL})^2}{N_{SL} - 1} \right]^{\frac{1}{2}}
\]  

and \( N_{SL} \) is the total number of measurements made at both stationary levels (i.e. \( N_{SL}/2 \) made at each).

The sample variance, \( \sigma_{U_{SL}} \), does not, on its own, predict how close the sample mean lies to the desired population mean. The statistical parameter which successfully estimates the reliability of the measured \( U_{SL} \) is the confidence limit. For a sample of size \( N_{SL} \), the 95\% confidence limits on \( U_{SL} \) may be obtained as (169)

\[
U_{SL} \pm \left( t_{N_{SL}-1,0.025} \right) \frac{\sigma_{U_{SL}}}{(N_{SL})^{\frac{1}{2}}}
\]  

where \( t_{N-1,0.025} \) is the \( t \)-distribution with \( N-1 \) degrees of freedom for a 95\% probability that \( U_{SL} \) represents the true electrophoretic mobility within
the limits shown. A table of the t-distribution is given by Pearson and Hartley (171). From the range of mobilities given by Eq. [C.37] it is possible to calculate a range of particle $\zeta$-potentials using the techniques described in Sect. C.2.2.2.

Consider, for example, Run I-1. For this run

\[ N_{SL} = 10 \]
\[ \bar{t}_{SL} = 8.27 \text{ sec} \]
\[ \sigma_{t_{SL}} = 4 \]
\[ n_{SL} = 4 \]

\[ E = 71.1 \text{ V} \]

\[ \lambda_g = 5.879 \times 10^{-3} \text{ cm} \]
\[ \lambda_e = 9.53 \text{ cm} \]

Therefore, using Eq. [C.34],

\[ U_{SL} = \frac{4 \times 5.879 \times 10^{-3} \times 9.53}{71.1 \times 8.27} \]
\[ = 3.812 \times 10^{-4} \text{ cm}^2 \text{ volt-sec} \]

Using Eq. [C.35],

\[ \sigma_{U_{SL}} = \frac{4 \times 5.879 \times 10^{-3} \times 9.53 \times 0.336}{71.1 \times (8.27)^2} \]
\[ = 0.155 \times 10^{-4} \text{ cm}^2 \text{ volt-sec} \]

When \( N_{SL} = 10 \), \( t_{N_{SL}-1} = 0.027 = 2.262 \) (172). Thus, the 95% confidence interval on \( U_{SL}, \Delta U_{SL} \), may be found, using Eq. [C.37], as
\[ \Delta U_{SL} = \pm 2.262 \times 0.155 \times 10^{-4} \times 10^{(10)^{\frac{1}{2}}} \]

\[ = \pm 0.111 \times 10^{-4} \frac{\text{cm}^2}{\text{volt-sec}} \]

Using Eq. [C.29] (Sect. C.2.2.2), the 95% confidence limits on \( E, \Delta E \), are obtained as

\[ \Delta E = \pm 0.7503 \times 10^4 \times 0.111 \times 10^{-4} \]

\[ = \pm 0.083 \]

The \( y_0 \) values corresponding to \( E = 2.777 \) and \( 2.943 \) (interpolated from Table C.9) are 3.30 and 3.69, respectively. Thus, from Eq. [C.30], the lower and upper 95% confidence limit on \( \zeta_p \) for run 1-1 can be shown to be equal to -88.6 and -101.2 mv., respectively. In other words, \( \zeta_p = -94.5 \) (+5.9, -6.7) mv. The confidence limits are no longer symmetrically positioned about the mean value because the \( E' \) versus \( y_0 \) curves are not linear.

As was proven in Sec. B.1, the wall \( \zeta \)-potential as determined by a combined electrophoresis-electro-osmosis experiment is given by

\[ \zeta_w = \frac{8\pi \mu}{\varepsilon} \left[ \frac{1 - \frac{192}{\pi^5} \frac{b}{a}}{1 + \frac{384}{\pi^5} \frac{b}{a}} \right] \left( U_{SL} - U_{\frac{1}{2}} \right) \]

\[ = 2.101 \times 10^5 \times (U_{SL} - U_{\frac{1}{2}}) \text{ at } 25 \degree C \text{ for cell #2} \] \[ \text{[C.38]} \]

where \( \zeta_w \) is the wall potential (mv), \( \mu \) the fluid viscosity (g/cm-sec), \( \varepsilon \) the fluid dielectric constant, \( b/a \) the thickness to width ratio (= 0.110 for cell #2), \( U_{SL} \) the electrophoretic mobility measured at the stationary level (cm²/sec-volt) given by Eq. [C.34], and \( U_{\frac{1}{2}} \) the electrophoretic mobility measured at the mid-plane (cm²/sec-volt), given by

\[ U_{\frac{1}{2}} = \frac{n_{\frac{1}{2}}}{\bar{t}_{\frac{1}{2}}} \frac{\lambda g}{E \zeta_{\frac{1}{2}}} \] \[ \text{[C.39]} \]

In the latter expression, \( n_{\frac{1}{2}} \) is the number of grid spaces over which the particles were timed, and \( \bar{t}_{\frac{1}{2}} \) is the average electrophoretic time measured at the mid-plane.
When Eq. [C.39] is substituted in Eq. [C.20] (Sect. C.2.1.4), it can be shown that the standard deviation of \( U_{\frac{1}{2}} \), \( \sigma_{U_{\frac{1}{2}}} \), is obtained as

\[
\sigma_{U_{\frac{1}{2}}} = \frac{n_{\frac{1}{2}}}{E \bar{t}_{\frac{1}{2}}} \exp \left( \sigma_{\bar{t}_{\frac{1}{2}}}^2 \right)
\]  
[C.40]

where \( \sigma_{\bar{t}_{\frac{1}{2}}} \) is given by

\[
\sigma_{\bar{t}_{\frac{1}{2}}} = \left( \sum_{i=1}^{N_{\frac{1}{2}}} \frac{(t_{\frac{1}{2},i} - \bar{t}_{\frac{1}{2}})^2}{N_{\frac{1}{2}} - 1} \right)^{\frac{1}{2}}
\]  
[C.41]

and \( N_{\frac{1}{2}} \) is the number of measurements made at the mid-plane.

If it is assumed that the \( U_{SL} \) and \( U_{\frac{1}{2}} \) values are approximately normally distributed, then the 95% confidence limits on \( \zeta_w \), \( \Delta \zeta_w \), can be obtained as (169).

\[
\Delta \zeta_w = \pm 2.101 \times 10^5 \ t_{M, 0.025} \left[ \frac{\sigma_{U_{SL}}^2}{N_{SL}} + \frac{\sigma_{U_{\frac{1}{2}}}^2}{N_{\frac{1}{2}}} \right]^\frac{1}{2}
\]  
[C.42]

where

\[
\frac{1}{M} = \frac{p^2}{N_{SL}} - \frac{1}{N_{\frac{1}{2}} - 1} + \frac{(1 - p)^2}{N_{\frac{1}{2}} - 1}
\]  
[C.43]

and

\[
P = \frac{\sigma_{U_{SL}}^2 / N_{SL}}{\frac{\sigma_{U_{SL}}^2}{N_{SL}} + \frac{\sigma_{U_{\frac{1}{2}}}^2}{N_{\frac{1}{2}}}}
\]  
[C.44]

Consider, for example, run I-11, where
\[ N_{SL} = 20 \]
\[ n_{SL} = 4 \]
\[ \bar{t}_{SL} = 6.76 \text{ sec} \]
\[ \sigma_{\bar{t}_{SL}} = 0.230 \text{ sec} \]
\[ N_{\frac{1}{2}} = 10 \]
\[ n_{\frac{1}{2}} = 4 \]
\[ \bar{t}_{\frac{1}{2}} = 5.93 \text{ sec} \]
\[ \sigma_{\bar{t}_{\frac{1}{2}}} = 0.315 \text{ sec} \]
\[ E = 71.1 \text{ V} \]
\[ \lambda_g = 6.393 \times 10^{-3} \text{ cm} \] (flat cell #2)
\[ \lambda_e = 7.68 \text{ cm} \] (Sects. C.1.6.4 and C.1.6.5)

Using Eq. \[C.34\],
\[
U_{SL} = \frac{4 \times 6.393 \times 10^{-3} \times 7.68}{71.1 \times 6.76}
\]
\[ = 4.089 \times 10^{-4} \text{ cm/volt-sec} \]

Using Eq. \[C.35\],
\[
\sigma_{U_{SL}} = \frac{4 \times 6.393 \times 10^{-3} \times 7.68 \times 0.230}{71.1 \times (6.76)^2}
\]
\[ = 0.139 \times 10^{-4} \text{ cm}^2/\text{volt-sec} \]
Using Eq. [C.39],

\[ U_\frac{1}{2} = \frac{4 \times 6.393 \times 10^{-3} \times 7.68}{71.1 \times 5.93} \]

\[ = 4.662 \times 10^{-4} \text{ cm}^2/\text{volt-sec} \]

Using Eq. [C.40],

\[ \sigma U_\frac{1}{2} = \frac{4 \times 6.393 \times 10^{-3} \times 7.68 \times 0.315}{71.1 \times (5.93)^2} \]

\[ = 0.248 \times 10^{-4} \text{ cm}^2/\text{volt-sec} \]

Thus, the wall \( \zeta \)-potential can be calculated from Eq. [C.38] as

\[ \zeta_w = 2.101 \times 10^5 \times (4.089 - 4.662) \times 10^{-4} \]

\[ = -12.0 \text{ mv.} \]

Using Eq. [C.44],

\[ p = \frac{(0.139 \times 10^{-4})^2/20}{(0.139 \times 10^{-4})^2} = 0.1357 \]

Using Eq. [C.43],
\[
\frac{1}{M} = \left(\frac{0.1357}{19}\right)^2 + \left(\frac{0.8643}{9}\right)^2
\]

or

\[M = 11.9\]

When \(M = 11.9\), \(t_{M,0.025} = 2.181 (171)\). Thus, the 95% confidence limits on \(\bar{\xi}_w, \Delta \xi_w\), may be found, using Eq. [C.42], as

\[
\Delta \xi_w = \pm 2.101 \times 10^5 \times 2.181 \times \sqrt{\left(\frac{0.139 \times 10^{-4}}{20}\right)^2 + \left(\frac{0.248 \times 10^{-4}}{10}\right)^2}
\]

\[= \pm 3.9 \text{ mv.}\]

C.3 Experimental Data

All of the measured particle deposition results are tabulated on the pages following. As well as the deposited particle concentrations calculated from the accumulation measurements (discontinuous and continuous) and from the release measurements, the tables also include the decay corrected count rates used to initiate these calculations. A listing of all other parameters relevant to each experimental run such as the geometry of the test section, the suspension flow rate, the suspension concentration, the counterion concentration, the solution pH, and the various measured zeta potentials is also given. The symbols used in the tables are defined below.

\(B\) half-thickness of test section (cm)

\(\text{COLL}\) collimator used
  = C cylindrical collimator
  = R rectangular collimator

\(\text{CONCI}\) initial concentration of counterions (moles/l.)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>COND</td>
<td>conductivity of suspension (μ mho/cm)</td>
</tr>
<tr>
<td>CONDI</td>
<td>initial conductivity of suspension (mho/cm)</td>
</tr>
<tr>
<td>CSF</td>
<td>final concentration of suspended particles (particles/cm³)</td>
</tr>
<tr>
<td>CSI</td>
<td>initial concentration of suspended particles (particles/cm³)</td>
</tr>
<tr>
<td>CWC</td>
<td>concentration of deposited particles obtained from continuous accumulation measurements (particles/cm²)</td>
</tr>
<tr>
<td>CWD</td>
<td>concentration of deposited particles obtained from discontinuous accumulation measurements (particles/cm²)</td>
</tr>
<tr>
<td>CWR</td>
<td>concentration of deposited particles obtained from release measurements (particles/cm²)</td>
</tr>
<tr>
<td>DCWC</td>
<td>95% confidence limits on CWC</td>
</tr>
<tr>
<td>DCWD</td>
<td>95% confidence limits on CWD</td>
</tr>
<tr>
<td>DCWR</td>
<td>95% confidence limits on CWR</td>
</tr>
<tr>
<td>DP</td>
<td>average particle diameter (μm)</td>
</tr>
<tr>
<td>E</td>
<td>streaming potential (mv)</td>
</tr>
<tr>
<td>KA</td>
<td>ratio of particle radius to double layer thickness, i.e. Ka</td>
</tr>
<tr>
<td>L</td>
<td>length of test section (cm)</td>
</tr>
<tr>
<td>PHI</td>
<td>initial pH of suspension</td>
</tr>
<tr>
<td>Q</td>
<td>flow rate of suspension (cm³/sec)</td>
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<tr>
<td>QAVG</td>
<td>average flow rate of suspension (cm³/sec)</td>
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<tr>
<td>QI</td>
<td>initial flow rate of suspension (cm³/sec)</td>
</tr>
<tr>
<td>RC</td>
<td>decay corrected count rate obtained from continuous accumulation measurements (cpm)</td>
</tr>
<tr>
<td>RD</td>
<td>decay corrected count rate obtained from discontinuous accumulation measurements (cpm)</td>
</tr>
<tr>
<td>REAVG</td>
<td>average Reynolds numbers of flowing suspension</td>
</tr>
<tr>
<td>REI</td>
<td>initial Reynolds number of flowing suspension</td>
</tr>
<tr>
<td>RR</td>
<td>decay corrected count rate obtained from release measurements (cpm)</td>
</tr>
</tbody>
</table>
SOLN  suspension medium
  = DW essentially distilled water
  = NACL essentially NaCl solution

TEMP  temperature of suspension (°C)

TIME  time (min.)

T/S  test section coating material
  = FORMV Formvar
  = 2VP/S copolymer of 80% 2-vinyl pyridine and 20% styrene

UPI  initial electrophoretic mobility of particles (μm-cm/V-sec)

W  width of test section (cm)

X  longitudinal distance from test section entrance (cm)

ZPI  initial zeta potential of particles (mv)

ZWEI  initial zeta potential of wall obtained by electro-osmosis measurement (mv)
  = NM not measured

ZWS  zeta potential of wall obtained by streaming potential measurement (mv)

ZWSI  initial zeta potential of wall obtained by streaming potential measurement (mv)
  = NM not measured

*  decay corrected background count rate measured with new test section in place
### DISCONTINUOUS COUNTS

<table>
<thead>
<tr>
<th>TIME</th>
<th>RC</th>
<th>CWC</th>
<th>DCWC</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.00</td>
</tr>
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<td>0.00</td>
</tr>
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### ACCUMULATION MEASUREMENTS

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RUN NUMBER I-10

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|----------|--------|---------|---------|----------|-----------|------------|-----------|
| SOLN NACL | 0.102E-02 | COND I 0.115E-03 | PHI 4.30 | DP 0.402 | CSI 0.105E+10 | CSF 0.177E+10 |
| KA 20.09 | UPI 5.281E.145 | ZPI -99.117.2.2.9.6 | ZWEI -14.515.3 | ZWSI NM |

ACCUMULATION MEASUREMENTS

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RUN NUMBER I-9

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| SOLN DW  | 0.460E-04 | COND I 0.589E-05 | PHI 6.60 | DP 0.402 | CSI 0.193E+10 | CSF 0.179E+10 |
| KA 4.48 | UPI 3.583E.052 | ZPI -77.711.3.2.5 | ZWEI -10.7 | ZWSI NM |

ACCUMULATION MEASUREMENTS

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**SOLN NACL** CONC1 0.102E-01 CONC2 0.112E-02 PHI 6.20 DP 0.402 CSI 0.182E+10 CSF 0.165E+10

**CA** 66.70 UPI 4.089(0.065) ZPI -55.2(0.6-1.1) ZWEI -12.0(3.9) ZWSI NM

### ACCUMULATION MEASUREMENTS

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**RELEASE MEASUREMENTS**

**STAGNANT SOLUTION** X 12.5 COLL C

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### RUN NUMBER I-12

**T/S FORMV** 8 0.0436 W 10.26 L 25.32 Q1 12.22 REI 267. OAVG 12.15 REAVG 265. TEMP 25.0

**SOLN NACL** CONC1 0.168E-02 CONC2 0.112E-02 PHI 6.20 DP 0.402 CSI 0.165E+10 CSF 0.161E+10

**KA** 65.40 UPI 4.816(0.067) ZPI -80.4(1.3-1.3) ZWEI -20.7(4.5) ZWSI NM

### ACCUMULATION MEASUREMENTS

**DISCONTINUOUS COUNTS** X 12.5 COLL C

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### RUN NUMBER II-2

- **T/S 2VP/S**: B 0.0426 W 10.24 L 25.37 Q/ 12.97 REI 284. QAVG 13.15 REAVG 284. TEMP 75.0
- **SOLN. DW**: CONC 0.677E-05 CONDI 0.109E-05 PHI 6.00 DP 0.649 CSI 0.797E+08 CSF 0.746E+08
- **KA**: UPI 3.399(0.045) ZPI = 27.1 ZWEI NM ZWSI +15.1
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#### Streaming Potential Measurements

| TIME E O COND ZWS |
|---|---|---|---|
| 120.0 | 22.8 | 12.95 | 2.44 | 11.5 |
| 150.0 | 12.0 | 12.90 | 2.44 | 6.1 |
| 180.0 | 9.6 | 13.03 | 2.41 | 4.8 |

### Accumulation Measurements

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#### Streaming Potential Measurements

<p>| TIME E O COND ZWS |
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| 2.0 | 98.4 | 14.62 | 2.42 | 35.4 |
| 4.0 | 97.8 | 14.62 | 2.42 | 35.2 |
| 8.0 | 90.6 | 14.68 | 2.42 | 32.7 |
| 10.0 | 90.2 | 14.65 | 2.42 | 32.6 |
| 20.0 | 28.8 | 16.55 | 2.42 | 10.4 |
| 32.0 | 70.2 | 16.57 | 2.43 | 25.4 |
| 71.0 | 50.0 | 15.53 | 2.43 | 18.1 |
| 90.0 | 41.0 | 16.60 | 2.44 | 14.9 |
| 120.0 | 32.4 | 16.55 | 2.44 | 11.8 |
| 150.0 | 25.2 | 16.52 | 2.45 | 5.2 |
| 180.0 | 19.0 | 16.63 | 2.45 | 6.9 |</p>
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**DISCONTINUOUS COUNTS**

- **X 5.0 COLL R**
- **X 10.0 COLL R**
- **X 12.5 COLL C**

**CONTINUOUS COUNTS**

- **X 12.5 COLL C**

**STREAMING POTENTIAL MEASUREMENTS**

- **TIME**
- **E**
- **Q**
- **COND**
- **ZWS**
### RUN NUMBER 11-9

**T/S FORM** B 0.0440 W 10.20 L 25.30 C1 12.32 REI 271. QAVG 12.13 REAVG 266. TEMP 25.0

**SOLN DW** CONC1 0.18E-05 CONC1 0.26E-00 PH1 6.60 DP 0.649 CSI 0.832E-08 CSF 0.818E+00

**KA** 4.62 UPI 2.981E+00 ZPI -57.21+1.01-1.31 ZWEI -4.113E+1 ZWSI -34.8

#### ACCUMULATION MEASUREMENTS

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#### STREAMING POTENTIAL MEASUREMENTS

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### RUN NUMBER 11-10

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**SOLN DW** CONC1 0.69E-05 CONC1 0.10E-00 PH1 6.00 DP 0.649 CSI 0.411E+00 CSF 0.388E+00

**KA** 2.73 UPI 3.335E+00 ZPI -74.81+1.01-1.31 ZWEI NM ZWSI -26.8

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**T/S FORM**: B 0.0416 W 10.19 L 25.19 GI 12.50 REI 275. QAVG 12.63 REAVG 276. TEMP 25.0

SCLN DW CONCI 0.399E-04 CONDI 0.407E-05 PHI 6.60 DP 0.649 CSI 0.380E+09 CSF 0.385E+09

KA 8.74 UP1 4.418(0.047) ZPI -113.01 0.16 W 10.19 I. 25.19 GI 12.50 REI 275. OAVG 12.63 REAVG 276. TEMP 25.0

**ACCUMULATION MEASUREMENTS**

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**RUN NUMBER 11-14**

**T/S FORM**: B 0.0420 W 10.26 L 25.25 GI 12.63 REI 276. QAVG 12.63 REAVG 276. TEMP 25.0

SCLN DW CONCI 0.592E-04 CONDI 0.588E-05 PHI 6.80 DP 0.649 CSI 0.379E+09 CSF 0.370E+09

KA 8.20 UP1 4.216(0.066) ZPI -110.71 0.16 W 10.26 I. 25.25 GI 12.63 REI 276. OAVG 12.63 REAVG 276. TEMP 25.0

**ACCUMULATION MEASUREMENTS**

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**T/S FORMV** 0.0391 W 10.21 L 25.36 Q1 12.70 REI 279. OAVG 12.70 REAVG 279. TEMP 25.0

**SOLN NACl** CONCI 0.150E-03 CONDI 0.179E-04 PHI 6.65 DP 0.649 CSI 0.368E+09 CSF 0.354E+09

**KA** 13.06 UPI 4.636(0.088) ZPI -93.614.91 ZWEI -37.814.91 ZWSI -30

#### ACCUMULATION MEASUREMENTS

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**T/S FORMV** 0.0420 W 10.21 L 25.37 Q1 12.62 REI 277. OAVG 12.62 REAVG 277. TEMP 25.0

**SOLN NACl** CONCI 0.146E-03 CONDI 0.174E-04 PHI 6.60 DP 0.649 CSI 0.368E+09 CSF 0.348E+09

**KA** 12.88 UPI 4.342(0.086) ZPI -34.612.9 3.01 ZWEI -41.214.81 ZWSI -25

#### ACCUMULATION MEASUREMENTS

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**T/S FORMV** 0.0395 W 10.18 L 25.30 Q1 12.95 REI 285. OAVG 12.90 REAVG 284. TEMP 25.0

**SOLN NACl** CONCI 0.100E-02 CONDI 0.116E-03 PHI 6.70 DP 0.649 CSI 0.359E+09 CSF 0.334E+09

**KA** 33.70 UPI 6.222(0.207) ZPI 7 ZWEI 35.9110.4 ZWSI NM

#### ACCUMULATION MEASUREMENTS

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**T/S FORMV** B 0.0411 W 10.19 L 25.34 QI 12.93 REI 284. OAVG 12.90 REAVG 244. TEMP 25.0

**SOLN NACL** CONC 0.285E-02 CONDI 0.317E-03 PHI 6.60 DP 0.649 CSI 0.346E-09 CSF 0.329E+09

**KA** 56.90 UPI 5.054E(0.130) ZPI -74.9(1.3, -2.1) ZWEI -15.6(6.8) ZWSI NM

#### ACCUMULATION MEASUREMENTS

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**T/S FORMV** B 0.0419 W 10.22 L 25.32 QI 12.90 REI 283. OAVG 12.99 REAVG 285. TEMP 25.0

**SOLN NACL** CONC 0.900E-02 CONDI 0.102E-02 PHI 6.70 DP 0.649 CSI 0.331E+09 CSF 0.320E+09

**KA** 103.40 UPI 4.53C(0.143) ZPI -61.5(1.2, -2.0) ZWEI -14.1(6.4) ZWSI NM

#### ACCUMULATION MEASUREMENTS

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**T/S FORMV** B 0.0423 W 10.25 L 25.27 QI 12.57 REI 275. OAVG 12.52 REAVG 274. TEMP 25.0

**SOLN NACL** CONC 0.280E-02 CONDI 0.424E-02 PHI 6.70 DP 0.649 CSI 0.293E+09 CSF 0.239E+09

**KA** 178.00 UPI 3.173C(0.103) ZPI -56.0(1.5, -1.3) ZWEI -9.316.17 ZWSI NM

#### ACCUMULATION MEASUREMENTS

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### STEERING POTENTIAL MEASUREMENTS

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#### Release Measurements

#### Flowing Solution

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#### CONTINUOUS COUNTS

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### RELEASE MEASUREMENTS

#### FLOWING SOLUTION

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420.

RUN NUMBER
T/S

I I 1-5

2VP/S

B 0.0436

W 10.22

SOLN N A C L

CONCI

KA

UPI 4 . 1 3 5 I 0 . C 7 3 )

54 . 8 0

ACCUMULATION

0.309E-02

COUNTS

TIME

RD

0.0
360.0
360.0*

0.5065E+04
0.7382E+05
0.6311E+04

CONTINUOUS

1.0
3.1
5 .1
7. 1
9.2
11.2
13.3
15.3
17.3
19.4
21.4
23. 5
25.5
27.5
29.6
31.6
33. 6
35.7
37.7
39. 8
41.8
43.8
45.9
47 . 9
50. 0
52 . 0
54.0
56. 1
58.1
60.2
62.2
64.2
66. 3
68.3
70.4
72.4
74 . 4
76.5
78. 5
80 .6
82. 6
84.6
86.7
88. 7
90.7
92.8
94.8
96.9
98.9

CONDI
ZPI

01

13.65

0.344E-03

REI 2 9 9 .

PHI 6.04

- 6 0 . 4 1 + 1 . 1 , - 1 . C)

OAVG 1 3 . 6 0

DP 0 . 6 0 0
Z WE I

CSI

+24.0(2.61

REAVG 2 9 8 .

0.349E+09
ZWS I

TEMP

CSF

25.0

0.303E+09

NM

MEASUREMENTS

DISCONTINUOUS

TIME

L 25.4 7

CCUNTS

X 12.5

CCLL C
DCWO

TIME

PC

cwc

DCWC

0. 1456E+05
0 . 4 1 0 1 E + 05

100.9'
115.0
125.1
135. 1
145.1
155.2
165.2
175.3
185.3
195.3
205.4
2 15.4
225.5
235.5
245 . 5
255. 6
265.6
285.0
295. 1
305.. 1
315.1
325.2
335.2
345. 3
355.3

0 . 1133E + 06
0 . 1157E+06
0. 1175E+06
0 . 1190E+06
0.12065*06
0.1220E+06
0.1235E+05
0 . 1245E+C6
0 . 1259E+06
0 . 1270E+05
0.1277E+06
0 . 1286E+06
0. 1295E-06
0 . 1302E+06
0 . 1310E+06
0.1318E+06
0 . 1326E+06
0 . 1336E+06
0 . 1343E+C6
0 . 1350E+06
0 . 135 5 5*06
0 . 1365E+06
0 . 1364E+06
0. 1369E*C6
0 . 1378E+06

0 . 7 9 0 4 5 +07
0.8485E+07
0 . 8923E+07
0 . 9284E+07
0.9670E*07
0.1002E+08
0 . 1038E+08
0.1066E-08
0 . I 1005 +08
0 . 1 127E +08
0 . 1 146E + 08
0. U7IE+08
0 . I 194E+08
0 . 1214E + 0 8
0 . 1236E+08
0.1258E+08
0 . 1 2 7 9 5 +08
0 . I 310E+08
0. 133IE+08
0 . I349E+08
0 . 13655+08
0 . 1 391E+08
0 . 1 394E +08
0 . 1410E+08
0 . 1 433E+08

C.1409E+06
0.6337E*05
0.6364E+05
0.6384E+05
0.6407E+05
0.6427E+05
0.6447E+05
0.6462E+05
0. 6 4 8 1 E + 05
0.6494E+05
C.6502E+05
0.6514E+05
0.6524E+05
0 . 6 5 3 2 E + 05
0.6542E+05
0.6552E+05
0. 6561E+05
0.6571E+05
0 . 6 5 7 9 E + 05
C.6586E+05
.0.6592E+05
0.6604E+05
0.6600E+05
0.6605E+05
C. 6 6 1 5 E + 0 5

CWO
0.0
0.1441E+08

X

12.5

COLL C

RC

CWC

DCWC

0.7871E+05
0.8004E+05
0.8045E+05
0 . 6 1 7 5 E + 05
0.821RE+05
0.8369E+05
0.8439E+05
0.8508E+05
0.8614E+05
C. 8665E + 05
0.877IE+05
0. 8883E-05
0 . 8 9 9 0 F +05
0.9055E+05
0.91C4E+05
0.9209E+05
0.9303E-05
0.9347E+05
0.9445E+05
C . 9 5 6 7 E + C5
0.S622E+05
0.9741E+05
C.5763E+05
0.9842E+05
0.9913E-05
C.9579E+05
0.1004E+06
0.1C09E-06
0.1022E+06
0.L024E+06
0 . 1 C 3 2 E + 06
0.1036E+06
0.1043E-06
0.1051E+05
0.1059E+06
0.1C66E+06
0.1068E+06
0. 1071E-06
0.1C81E+06
0.1073E+06
0.1C34E+C6
0.1093E+06
0.1095E+06
0.1I02E+06
0.Ill1E+06
0 . I U 2 E + 05
0 . 1120E + 0 6
0.1122E+06
0. U 2 7 E + 0 6

0.5746E+05
0.3514E+06
0 . 4 4 8 4 E +06
0.7367E+06
0.8370E+06
0 . 1 168E+07
0 . 1328E + 07
0.1485E+07
0 .1 720E+07
0 . 1839E + 07
0.2076E+07
0.2324E+07
0.2561E+07
0.2711E+07
0 . 2824E+07
0.3057E+07
0.3267E+07
0 . 3 372E + 0 7
0 . 3 59 I E + 0 7
C.3859E-07
0.3986E+07
0 . 4 2 5 1E+07
0. 4307E+07
0.4487E+07
0 . 4 6 4 7E+07
0.4797E+07
0.4939E+07
. 5 04 8 E + 0 7
.5330E+07
•5403E+07
.5563E+07
.5 659E+07
.5835E-07
0 . 6 0 0 3 E + 07
0 .6 191F-0 7
0.6343E+07
0.6391E+07
0.64805-07
0 . 6 6 9 5 E + 07
0 . 6 64 7E+0 7
0.6787E-07
0.6972E+07
0.70335+07
0.7183E+07
0.7392E+07
O.7432E+07
0 . 7 6 U E + 07
0.7658E+07
0.7781E-07

0 . 1283E+06
0 . 1 2 8 8 E + 06
0 . 1289E+06
0 . 1295E + 06
0. 1296E+06
0 . 1302E+06
C. 1 3 0 5 E + 06
C.1307E+06

0.1311E+06
0. 1313E + 06
0.1317E+06
0 . 1321E + 06
0. 13265+06
0.1328E-06
0 . 1 3 3 0 E + 06
0.1334E+06
0 . 1 3 3 7E+06
0 . 1 3 3 9 E + 06
0.1342E+06
0 . 1347E+06
0. 1349F+06
0.1353E+C6
0 . 1 3 5 4 E + 06
C.1357E+C6
,1360E+06
.1362E+06
,1364E+06
,1366E+06
1371E+C6
0.1371E-06
0.1374E+06
0.1375E+06
0.1378E+06
0.1301E+06
0. 1 384E+06
0.1386E+06
0.1337E+C6
0.1388E+06
0.1391E+06
0 . H 9 0 E + 0O
0.1392E+06
C. 1 3 9 5 F + 0 6
0.1396E+06
C.1393E+06
C.1402E+06

0.1402F-06
0 . 1 4 0 5 E + 06

0.1405E+06
0.1407E+06

RELEASE

MEASUREMENTS

FLOWING

SOLUTION

TIME

RR

365.0
375.1
385. 1
395.1
405.2
415.2

0 . 7404E+05
0 . 74135+05
0. 7396E-C5
0 . 7391E+05
0.7398E+05.
0 . 74035+05

FLOWING
TIME
425.2
435 .3
445.3
455.3
465.4
475. 4
485.5
495.5
505. 5
515.6
997.5

SUSPENSION

X

COLL C
DCWR

CWR
0.
0.
0.
0.
0.
0.

14465+08
1 4 4 8 E +08
1444E+08
1443E+08
14455+08
1446E+08

X 12.5

0.
0.
0.
0.
0.
0.
0.
0.
0.
0.
0.

0 . 4112E+05
0 . 4115E+05
0.4110E+05
C. 4 1 0 9 E + C 5
0 . 411 I E + 0 5
0. 4112E+05

COLL C

CWR

RR
0 . 7 4 1 3 E + 05
0.7410E+05
0.73945-05
0.74045+05
0.74015+05
C. 7 4 0 7 E - C 5
0.7389E+05
0.7399E+05
0. 73975-05
0.74O3E+O5
0.7389E+05

12.5

14485+08
14475+08
1 4 4 4 5+0 8
1446F + 08
1 4 4 5 6 +08
144 7 E - 0 8
1443E+08
1445E +08
144 5E+0 8
1 4 4 6 E +08
144 3 E - 0 8

DCWR
0.4116E+05
0 . 4116E + 05
0.4112E*05
0.4114E+05
0 . 4 1 1 4 E + 05
0.4115E+05
C.411IE+05
0.4114E+05
0.4113E+05
C . 4 1 1 5 E + 05
0.4118E+05


## Accumulation Measurements

### Discontinuous Counts

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### Continuous Counts

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<td>0.317E+06</td>
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<tr>
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## Release Measurements

### Flowing Solution

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<td>0.311E+05</td>
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<tr>
<td>375.1</td>
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<td>0.656E+07</td>
<td>0.311E+05</td>
</tr>
<tr>
<td>385.1</td>
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<td>0.656E+07</td>
<td>0.311E+05</td>
</tr>
<tr>
<td>395.1</td>
<td>0.391E+05</td>
<td>0.656E+07</td>
<td>0.311E+05</td>
</tr>
<tr>
<td>415.1</td>
<td>0.391E+05</td>
<td>0.656E+07</td>
<td>0.311E+05</td>
</tr>
<tr>
<td>435.1</td>
<td>0.391E+05</td>
<td>0.656E+07</td>
<td>0.311E+05</td>
</tr>
<tr>
<td>455.1</td>
<td>0.391E+05</td>
<td>0.656E+07</td>
<td>0.311E+05</td>
</tr>
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<td>0.656E+07</td>
<td>0.311E+05</td>
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<td>0.656E+07</td>
<td>0.311E+05</td>
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<td>535.1</td>
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<td>0.311E+05</td>
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<td>555.1</td>
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## Temperature

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## Other Measurements

- RUN NUMBER 111-6
- FS FORM W 0.040A 10.92 25.28 01 13.60 REF 297.
- OAVG 13.60 REAVG 293.
- TEMP 25.0
- SOLN NACL CECI 0.281E-02 CONDI 0.314E-03 PHI 6.00 DP 0.600 CSI 0.404E+09 CSF 0.315E+09
- KA 52.30 WPI 1.29(0.067) ZPI -59.3(1.0)-13.1 ZWEI 10.013.2 ZWSI NH
### Accumulation Measurements

#### Discontinuous Counts

<table>
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<tr>
<th>TIME</th>
<th>RC</th>
<th>CWC</th>
<th>DCWC</th>
</tr>
</thead>
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<tr>
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<tr>
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<tr>
<td>60.0*</td>
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<td>0.101E+05</td>
<td>0.130E+06</td>
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</tbody>
</table>

#### Continuous Counts

<table>
<thead>
<tr>
<th>TIME</th>
<th>RC</th>
<th>CWC</th>
<th>DCWC</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.873E+05</td>
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<tr>
<td>3.1</td>
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#### Release Measurements

#### Flowing Solution

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### RUN NUMBER III-11

**T/S FORMV** 8 0.0422 W 10.21 L 25.33 QI 13.15 REI 288. QAVG 12.97 REAVG 285. TEMP 25.0

**SOLN NACL** CONC 0.257E-02 COND1 0.287E-03 PHI 7.00 DP 0.600 CSI 0.2205E+09 CSF 0.192E+09

**KA** 50.00 UPI 4.131(1.18) ZPI -58.3(1.1) ZWEI -18.4(4.5) ZWSI NN

**ACCUMULATION MEASUREMENTS**

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**FLOWING SOLUTION**

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**T/S FORMV** 8 0.0427 W 10.21 L 25.37 QI 13.15 REI 288. QAVG 13.12 REAVG 288. TEMP 25.0

**SOLN NACL** CONC 0.262E-02 COND1 0.296E-03 PHI 6.02 DP 0.600 CSI 0.192E+09 CSF 0.141E+09

**KA** 50.70 UPI 3.898(0.051) ZPI -54.6(0.7) ZWEI -16.2(1.3) ZWSI NN

**ACCUMULATION MEASUREMENTS**

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**SOLN NACL** CONC 0.261E-02 COND1 0.291E-03 PHI 7.99 DP 0.600 CSI 0.184E+09 CSF 0.147E+09

**KA** 50.40 UPI 4.413(1.67) ZPI -62.5(1.1) ZWEI -22.5(6.5) ZWSI NN

**ACCUMULATION MEASUREMENTS**

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**Accumulation Measurements**

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**Accumulation Measurements**

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**Accumulation Measurements**

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#### Flowing Solution

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### Accumulation Measurements

**Discontinuous Counts**

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<td>0.0</td>
<td>0.2387E+05</td>
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<td>0.2513E+05</td>
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**Release Measurements**

**Flowing Solution**

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**Run Number III-18**

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**CONTINUOUS COUNTS X 12.5 COLLC**

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APPENDIX D

COMPUTER PROGRAMS
D.1 Evaluation of Extended Graetz Solutions

D.1.1 GPCK - Parallel-Plate Channel


- SHL = 4*DR, LOCAL SH BASED ON C0
- SHAV = 4*(1-CHI)/(1+GAMMA), OVERALL SH BASED ON C0
- SHL = 4*UR/CM, LOCAL SH BASED ON CM
- SHAV = 4*(GAMMA/M-13*GAMMA), OVERALL SH BASED ON CM
- EFL = 11-CM,-1-CM, OVERALL COLLECTION EFFICIENCY COMPARING TO A CHANNEL WITH K = INFINITY
- EFL = (1+CMZ)/(1+CM), LOCAL COLLECTION EFFICIENCY COMPARED TO CHANNEL WITH K = INFINITY

WHERE C0 IS THE INLET CONCENTRATION, GAMMA THE DIMENSIONLESS LUNGTITUDE DISTANCE, AND DR AND CM ARE THE DIMENSIONLESS DEPOSITION RATE AND MEAN CONCENTRATION OBTAINED FOR THE SPECIAL CASE K = INFINITY. THIS, IN ORDER TO USE THE PROGRAM, IT IS NECESSARY TO READ IN (ON UNIT 7) ALL OF THE EIGENVALUES AND COEFFICIENTS FOR THE K = INFINITY CASE, THESE ARE EVALUATED IN A SEPARATE PROGRAM WHICH MAY BE OBTAINED FROM THE PRESENT ONE BY DELETING ALL TERMS WITH A (-1) IN THE DENOMINATOR, THE PARAMETERS DR, CM, SHL, SHAV, SHAV, EFL, AND EFL ARE CALCULATED AND TABULATED FOR VARIOUS VALUES OF GAMMA IN THE RANGE 1E+02 TO 1E+07.

DATA INPUT (ONE CARD FOR EACH K-VALUE)

- COLUMN FORMAT NAME PURPOSE
  1 5 15 IFLAG CONTROL FLAG
  1 5 15 IFLAG CONTROL FLAG
  2 =0 END OF DATA FILE
  3 =1 OUTPUT EIGENVALUES AND COEFF.
  4 =2 OUTPUT DI, CM, SH, EF ONLY
  5 6-10 15 NT NUMBER OF EXACT TERMS IN SERIES
  6 11-15 15 NMAX TOTAL NUMBER OF TERMS IN SERIES
  7 16-30 015-5 A K-VALUE
  8 IMPLICIT REAL*4(A-H,O-Z)
  9 DIMENSION EIGEN(100001),DI(100001),DI(100001)
  10 DIMENSION EIGEN(100001),DO(100001),DO(100001)
  11 COMMON A,NT
  12 1 READ(5,2) IFLAG,NT,NMAX,A
  13 2 FORMAT(IS5,I5,5)
  14 DD27 I=1,NTX4
  15 READ(26) EIGEN(I),DO(I),DO(I)
  16 26 FORMAT(1X,5D23.16)
  17 27 CONTINUE
  18 28 REWRITE(0,4)
  19 WRITE(16,3)
  20 3 FORMAT(1I)
  21 WRITE(0,4)
  22 FORMAT(1X,53HPARALLEL GRAETZ PROBLEM - CONSTANT SURFACE RESISTANCE
  23 /1/)
  24 IF(FLAG.EQ.0) GO TO 22
  25 WRITE(16,5)
  26 5 FORMAT(1X,36HEIGENVALUES AND COEFFICIENTS FOR K =F13.5/7)
  27 WRITE(16,6)
  28 6 FORMAT(7X,1HN,6X,9HLAMBD(A),3X,4HE(1),12X,4HE(2),12X,4HE(3)
  29 GO TO 9
  30 WRITE(16,8)A,NT,NMAX
  31 FORMAT(1X,3H,9K =F13.5,10X,44NT =15,12X,4NMAX =15)
  32 8 =1
  33 DELX=0,10 00
  34 9 =1
  35 10 FOLD=FOLD+DELX
  36 11 XNEW=XOLD+DELX
  37 12 FN=W,FM,W+DELX
  38 13 FN=NEW+FM
  39 14 IF(FM.LT.0.001 GO TO 12
  40 15 FOLD=FM
  41 16 =11

29
**DOUBLE PRECISION FUNCTION FIX(N,A,N,T)**

**IMPLICIT REAL*8A-H,0-Z)**

**IF(IN.GT.NT) GO TO 5**
DOUGLE PECISION FUNCTION DF(X,N,A,N,T)

IMPLICIT REAL*8(A-H,0-Z)

COMMON A, NT

IF(N.GT.NT) GO TO 4

U=-0.2D Ol*A/(X*DEXP(-0.5D 00*X)*3FI X,L,A,N,T)  )

U=O. ID 01

S=O.OD  00

J = l

U=(+J-0.3D 01-X)*X*U/(2*J*(2*J-ll)

ADD=U*(2*J-X)

S=S+ADD

IF(IOABSIADD).LT.0.10-05) GO TO 2

IFIJ.GT.10000)  GO TO 3

J = J-1

GO TO 1

D2=0.150  01*D2/X*X)

RETURN

END

SUBROUTINE C0EFF(X,L,D1,02,03)

IMPLICIT REAL*8(A-H,0-Z)

COMMON A, NT

IF(L.GT.NT) GO TO 8

D1=-0.20  Ol*A/(X*DEXP(-0.5D 00*X)*3FI X,L,A,N,T)  )

U=O. ID 01

S=O.OD  00

J = l

U=(+J-0.3D 01-X)*X*U/(2*J*(2*J-ll)

ADD=U*(2*J-X)

S=S+ADD

IF(IOABSIADD).LT.0.10-05) GO TO 2

IFIJ.GT.10000)  GO TO 3

J = J-1

GO TO 1

D2=0.150  01*D2/X*X)

RETURN

END

DOUBLE PRECISION FUNCTION F(X,N,A,N,T)

IMPLICIT REAL*8(A-H,0-Z)

IF(N.GT.NT) GO TO 4

U=0.10  01

V=-0.50  00

S=O.OD  00

J = l

U=(4*J-0.3D 0l-X)*X*U/(2*J*(2*J-ll)

V=V-O.LD  Ol/(4*J-0.30  Ol-X)

AOO=U*((J/X-VI*IA-2*J-XI-0.10 01)

S=S+ADD

IF(DABS!ADD).LT.0.10-05) GO TO 2

IFIJ.GT.10000)  GO TO 3

J = J+1

GO TO 1

F=O.50  00*1 X-A) -3. ID 0 1»S

RETURN

END

SUBROUTINE C0EFF(X,L,D1,02,03)

IMPLICIT REAL*8(A-H,0-Z)

COMMON A, NT

IF(L.GT.NT) GO TO 8

D1=-0.20  Ol*A/(X*DEXP(-0.5D 00*X)*3FI X,L,A,N,T)  )

U=O. ID 01

S=O.OD  00

J = l

U=(+J-0.3D 01-X)*X*U/(2*J*(2*J-ll)

ADD=U*(2*J-X)

S=S+ADD

IF(IOABSIADD).LT.0.10-05) GO TO 2

IFIJ.GT.10000)  GO TO 3

J = J-1

GO TO 1

D2=0.150  01*D2/X*X)

RETURN

END
GEGR evaluates the extended Graetz solution for a cylindrical channel. First, the eigenvalues, \( \lambda_{n} \), are obtained as the roots of Eq. (1A.151). Then, the coefficients, \( D_{n}, E_{n} \), and \( F_{n} \), are calculated using Eqs. (1A.149), (1A.147), and (1A.201). From the eigenvalues and coefficients, series solutions (truncated to \( N_{\text{MAX}} \) terms) are constructed for the dimensionless deposition rate, \( \Omega \), and the dimensionless mean suspension concentration, \( C_{\text{M}} \), using Eqs. (1A.241) and (1A.241) for the dimensionless mean suspension concentration, \( C_{\text{M}} \), using Eqs. (1A.231) and (1A.221). Finally, \( \Omega \) and \( C_{\text{M}} \) are employed in evaluating the following Sherwood numbers, \( \text{SH} \), and collection efficiencies, \( \text{EF} \):

\[
\text{SH}_{\text{OL}} = 2\Omega \text{DR}_{\text{L}} \\
\text{SH}_{\text{AV}} = \frac{\text{ALOG}_{1} C_{\text{M}}}{2\Gamma}, \text{OVERALL SH BASED ON CM} \\
\text{SH}_{\text{OL}} = \frac{2\Omega}{C_{\text{M}}}, \text{LOCAL SH BASED ON CM} \\
\text{SH}_{\text{AV}} = \frac{-\text{ALOG}_{1} C_{\text{M}}}{2\Gamma}, \text{OVERALL SH BASED ON CM} \\
\text{EF}_{\text{OL}} = \frac{(\Omega \text{CM}_{\infty})}{(\Omega \text{CM}_{\infty})}, \text{OVERALL COLLECTION EFFICIENCY COMPARED TO A CHANNEL WITH} \ K \ = \ \infty \\
\text{EF}_{\text{OL}} = \frac{(\Omega \text{CM}_{\infty})}{(\Omega \text{CM}_{\infty})}, \text{LOCAL COLLECTION EFFICIENCY COMPARED TO CHANNEL WITH} \ K \ = \ \infty \\
\]

WHERE \( \text{CM} \) IS THE INLET CONCENTRATION, \( \Gamma \) THE DIMENSIONLESS LONGITUDINAL DISTANCE, \( \Omega \text{DR}_{\text{L}} \) AND \( \text{CM}_{\infty} \) ARE THE DIMENSIONLESS DEPOSITION RATE AND MEAN CONCENTRATION OBTAINED FOR THE SPECIAL CASE \( K = \ \infty \). Thus, in order to use the program, it is necessary to read in (on unit 7) all of the eigenvalues and coefficients for the \( K = \ \infty \) case. These are evaluated in a separate program which may be obtained from the present one by deleting all terms with a \( (\sqrt{K}) \) in the denominator. The parameters \( \Omega \), \( \text{CM} \), \( \text{SH}_{\text{OL}} \), \( \text{SH}_{\text{AV}} \), \( \text{EF}_{\text{OL}} \), and \( \text{EF}_{\text{OL}} \) are calculated and tabulated for various values of \( \Gamma \) in the range \( \text{1E+G2} \) to \( \text{1E-07} \).

DATA INPUT (ONE CARD FOR EACH \( K \)-VALUE)

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<td>NT</td>
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</tr>
<tr>
<td>11-15</td>
<td>I5</td>
<td>NMAX</td>
<td>TOTAL NUMBER OF TERMS IN SERIES</td>
</tr>
<tr>
<td>16-30</td>
<td>O15</td>
<td>A</td>
<td>A K-VALUE</td>
</tr>
</tbody>
</table>

IMPLICIT REAL*8(A-H.O-Z)
DIMENSION EIGEN(10000),DZ(10000),EZ(10000)
COMMON A,NT
READ(5,2) IFLAG,NT,NMAX,A
FORMAT(3I5,D15.5)
DO 2 1=1,NMAX
READ(7,26) EIGEN(II),DZ(II),EZ(II)
CONTINUE
REWIND 7
IF(IFLAG.EQ.0) GO TO 22
GAM=0.1D 03
TGAM=0.1D 03
DELGAM=0.1D 03
NUM=1
WRITE(6,3) A
FORMAT(1X,9H COMMON A,NT)
READ(5,2) IFLAG,NT,NMAX,A
FORMAT(7X,LHN,6X,9HLAMBDA(N),8X,4HC(N),12X,4HD(N),12X,4HE(N)/)
GO TO 9
WRITE(6,8) A,NT,NMAX
FORMAT(1X,3H EIGENVALUES AND COEFFICIENTS FOR K =.F13.5//)
WRITE(5,6) A
FORMAT(7X,1HN,6X,9HLAMBDA(N),8X,4HC(N),12X,4HD(N),12X,4HE(N)/)
GO TO 9
WRITE(6,8) A,NT,NMAX
FORMAT(1X,3H EIGENVALUES AND COEFFICIENTS FOR K =.F13.5//)
WRITE(5,6) A
FORMAT(7X,1HN,6X,9HLAMBDA(N),8X,4HC(N),12X,4HD(N),12X,4HE(N)/)
GO TO 9
WRITE(6,8) A,NT,NMAX
FORMAT(1X,3H EIGENVALUES AND COEFFICIENTS FOR K =.F13.5//)
WRITE(5,6) A
FORMAT(7X,1HN,6X,9HLAMBDA(N),8X,4HC(N),12X,4HD(N),12X,4HE(N)/)
GO TO 9
WRITE(6,8) A,NT,NMAX
FORMAT(1X,3H EIGENVALUES AND COEFFICIENTS FOR K =.F13.5//)
WRITE(5,6) A
FORMAT(7X,1HN,6X,9HLAMBDA(N),8X,4HC(N),12X,4HD(N),12X,4HE(N)/)
GO TO 9
WRITE(6,8) A,NT,NMAX
FORMAT(1X,3H EIGENVALUES AND COEFFICIENTS FOR K =.F13.5//)
WRITE(5,6) A
FORMAT(7X,1HN,6X,9HLAMBDA(N),8X,4HC(N),12X,4HD(N),12X,4HE(N)/)
GO TO 9
WRITE(6,8) A,NT,NMAX
FORMAT(1X,3H EIGENVALUES AND COEFFICIENTS FOR K =.F13.5//)
WRITE(5,6) A
FORMAT(7X,1HN,6X,9HLAMBDA(N),8X,4HC(N),12X,4HD(N),12X,4HE(N)/)
GO TO 9
WRITE(6,8) A,NT,NMAX
FORMAT(1X,3H EIGENVALUES AND COEFFICIENTS FOR K =.F13.5//)
CALL COEFF(X,N,51,52,53)
CALL EIGEN(N,X)
CALL COEF1(X,N,51,52,53)
CALL EIGEN2(N,X)
COSTRUCT SERIES SOLUTION FOR DR AND CM
OR=0.0000
CM=0.0000
CMZ=0.0000
EX=DEXP(-EIGEN*I) *EIGEN(I) *GAM)
EXZ=DEXP(-EIGENZ(I) *EIGENZ(I) *GAM)
DR = OR-D(I) *EX
DRZ=DRZ-DZ(I) *EXZ
CM = CM-EI(I) *EX
CMZ = CMZ-ZE(I) *EXZ
CONTINUE
EVALUATE SHERWOOD NUMBERS AND COLLECTION EFFICIENCIES
SHOL=0.2001*DR
SHOAV=0.2001*CM
IF (SHOAV.LT.0.0000) GO TO 3J
SHL=0.2001*OR/CM
SHAV=-LOG(CM)/0.2001*GAM)
GO TO 31
EFC=(OR-CM)/0.0001-CMZ)
BS=DRZ*CM
IFI8S-LE.0.0000) GO TO 32
EFL=DR*CMZ/IRONZ*CM)
GO TO 33
GAM=0.2001*TGAM
NUM=NUM+1
GO TO 19
GAM=0.4001*TGAM
NUM=NUM-1
GO TO 19
GAM= TGAM
NUM=1
GO TO 19
DOUBLE PRECISION FUNCTION FIX(N,A,N,NT)
IMPLICIT REAL*(A-H,O-Z)
IF (N.GT.NT) GO TO 5
A=A*0.1000
B=A*0.0000
J=1
END
434.

179 1 U=(4*J-0.20 01-X)*X*U/(4*J*J)
180 AND=(A+2)*X-1*U
181 S=S+ADD
182 IF(DABS(AAND1.LT.O.10-05)) GO TO 2
183 IF(J.GT.10000) GO TO 3
184 J=J+1
185 GO TO 1
186 2 F=A-X-S
187 GO TO 6
188 3 F=0.00 00
189 GO TO 6
190 5 P=0.3141592653589792 01
191 R1=PI/0.40 01
192 B2=PI/0.30 01
193 B3=0.20 01*B2
194 B4=0.8946146367929449 00
195 B5=0.8217003877099470 00
196 B6=0.3333333333333333 00
197 F=84*10.60 00*A-0.10 01*DSIN(B1*X-B3)*X**(-B6)-B5/A1*
198 DSIN(B1*X-B2)*X**B6
199 6 RETURN
200 END
201 C
202 DOUBLE PRECISION FUNCTION DFIX N, A, NT
203 IMPLICIT REAL*8(A-H,O-Z)
204 IF(N.GT.NT) GO TO 4
205 U=0.1D 01
206 V=-0.5D 00
207 S=0.00 00
208 J=1
209 1 U=(4*J-0.20 01-X)*X*U/(4*J*J)
210 V=V-0.1D 01/(4*J-0.20 01-X)
211 ADD=U*((J/X)+V)*(A+2*J-X-0.1D 01)
212 S=S+ADD
213 IF(DABS(AOD1).LT.O.10-05) GO TO 2
214 IF(J.GT.10000) GO TO 3
215 J=J+1
216 GO TO 1
217 2 DF=0.5D 00*(X-A)-0.10 01*S
218 GO TO 5
219 3 DF=0.00 00
220 GO TO 5
221 4 P=0.3141592653589792 01
222 B1=PI/0.40 01
223 B2=PI/0.30 01
224 B3=0.20 01*B2
225 B4=0.8946146367929449 00
226 B5=0.8217003877099470 00
227 B6=0.3333333333333333 00
228 PI=0.3141592653589792 01
229 B1=PI/0.40 01
230 B2=PI/0.30 01
231 B3=0.20 01*B2
232 B4=0.8946146367929449 00
233 B5=0.8217003877099470 00
234 B6=0.3333333333333333 00
235 D1=-0.2D 01/X*UFI X,N,A,NT))
236 02=01*(0.6l) 00*B4*0SIN(B 1*X-B3)*X**I-B6)-B5/A1*
237 DSIN(B1*X-B2)*X**B6
238 3 RETURN
239 END
240 C
241 SUBROUTINE COEFF(X,N,D1,D2,03)
242 IMPLICIT REAL*8(A-H,O-Z)
243 COMMON A,NT
244 IF(N.GT.NT) GO TO 8
245 01=-0.2D 01*A/X*DEXP(-0.50 00*X)*D2X,N,A,NT))
246 U=0.10 01
247 S=0.00 00
248 J=1
249 4 U=(4*J-0.20 01-X)*X*U/(4*J*J)
250 ADD=U*(2*J-X)
251 S=S+ADD
252 IF(DABS(AOD1).LT.O.10-05) GO TO 2
253 IF(J.GT.10000) GO TO 3
254 J=J+1
255 GO TO 1
256 2 D2=O1*DEXP(-0.50 00*X)*D2X,N,A,NT))
257 GO TO 4
258 3 D2=0.00 00
259 4 D3=-0.40 01*D2X,N,A,NT))
260 GO TO 9
261 8 P=0.3141592653589792 01
262 B1=PI/0.40 01
263 B2=PI/0.30 01
264 R3=0.20 01*B2
265 B5=0.8217003877099470 00
266 B6=0.3333333333333333 00
267 D1=0.20 01/X*UFI X,N,A,NT))
268 D2=01*(0.6l) 00*405IN(B1*X-B3)*X**I-B6)-B5*DSIN(B1*X-B2)*X**B6
269 D3=0.40 01*D2X,N,A,NT))
270 9 RETURN
271 END
D.2 Calculation of K-values

D.2.1 K1 - Eq. (2.4)

1. K1 calculates the dimensionless surface reaction rate constant, X, from Eq. (4.14). The required integration is carried out using Simpson's rule over several (N1) intervals. The first interval starts at H01, and has N steps of size DELH1. The next N1-1 intervals start where the last one ended and each has N steps of size DELH2. The integrated result after each interval is tabulated. The calculation is repeated for several values of the Hamaker constant, Ah, in the range 1.2E-13 to 1.0E-13. The overall interaction energy, F1HI, is the sum of the electrical double layer energy given by Eq. (2.11) and the retarded van der Waals energy given by Eq. (2.6).

2. Data input (three cards per run):

   CARD COLUMN FORMAT NAME PURPOSE

   1 1-8 2A4 RUN1, RUN2 Run number
   2 2-7 F7.4 BB Test section half-thickness (cm)
   3 3-8 2A4 RUN1, RUN2 Run number
   4 4-9 1E8.1 HO Lower integration limit (cm)
   5 5-8 1E8.1 DELH1 Step-size, first interval (cm)
   6 6-11 1E8.1 DELH2 Step-size, next intervals (cm)
   7 7-12 1E8.1 DELH3 Step-size, next intervals (cm)
   8 8-13 1E8.1 DELH4 Step-size, next intervals (cm)

   Common:
   C1, C2, A1, A2, A3, 4/4, 4/5, A6, A7, A8, AP, CAPA, AH

   Integer:
   RUN1, RUN2

   9 READ(5,1) RUN1, RUN2
   10 FORMAT(2A4)
   11 READ(5,2) BB, AP, CAPA, ZP, ZW
   12 FORMAT(F7.4, E10.3, F7.2, F7.1, F7.1)
   13 IF(BB.EQ.0.) GO TO 16
   14 AH=0.1E-12
   15 0E=0.2E-13
   16 DATA BK, T/0.133E-15, 298.2/
   17 DINF=5.953*BK*T/AP
   18 READ(5,3) N, NI, HO, DELH1, DELH2
   19 FORMAT(2I4, 3E8.1)
   20 WRITE(6,4) RUN1, RUN2
   21 WRITE(6,5) ZP, ZW, CAPA, BB, AP
   22 FORMAT(1X, E6.1, 3X, E6.1, 3X, E7.2, 3X, E6.2)
   23 WRITE(6,6) AH
   24 FORMAT(1X, 20HINTERVAL, 3X, 10H, 6HAPRIME/)
   25 ALPHAIMP = AH
   26 C1 = 0.435 6E-09*AP*ZP*ZW
   27 C2 = 0.2178*AP*ZP*ZW

   Common:
   C1, C2, A1, A2, A3, 4/4, 4/5, 4/6, 4/7, A6, A7, A8, AP, CAPA, AH

   Integer:
   RUN1, RUN2

   28 READ(5,4) RUN1, RUN2
   29 FORMAT(2A4)
   30 READ(5,5) BB, AP, CAPA, ZP, ZW
   31 FORMAT(F7.4, E10.3, F7.2, F7.1, F7.1)
   32 IF(BB.EQ.0.) GO TO 16
   33 AH=0.1E-12
   34 0E=0.2E-13
   35 DATA BK, T/0.133E-15, 298.2/
   36 DINF=5.953*BK*T/AP
   37 READ(5,6) N, NI, HO, DELH1, DELH2
   38 FORMAT(2I4, 3E8.1)
   39 WRITE(6,7) RUN1, RUN2
   40 WRITE(6,8) ZP, ZW, CAPA, BB, AP
   41 FORMAT(1X, E6.1, 3X, E6.1, 3X, E7.2, 3X, E6.2)
   42 WRITE(6,9) AH
   43 FORMAT(1X, 20HINTERVAL, 3X, 10H, 6HAPRIME/)
   44 ALPHAIMP = AH
   45 C1 = 0.435 6E-09*AP*ZP*ZW
   46 C2 = 0.2178*AP*ZP*ZW

   Common:
   C1, C2, A1, A2, A3, 4/4, 4/5, 4/6, 4/7, A6, A7, A8, AP, CAPA, AH

   Integer:
   RUN1, RUN2

   47 WRITE(6,10) RUN1, RUN2
   48 FORMAT(2A4)
   49 READ(5,6) BB, AP, CAPA, ZP, ZW
   50 FORMAT(F7.4, E10.3, F7.2, F7.1, F7.1)
   51 IF(BB.EQ.0.) GO TO 16
   52 AH=0.1E-12
   53 0E=0.2E-13
   54 DATA BK, T/0.133E-15, 298.2/
   55 DINF=5.953*BK*T/AP
   56 READ(5,6) N, NI, HO, DELH1, DELH2
   57 FORMAT(2I4, 3E8.1)
   58 WRITE(6,7) RUN1, RUN2
   59 WRITE(6,8) ZP, ZW, CAPA, BB, AP
   60 FORMAT(1X, E6.1, 3X, E6.1, 3X, E7.2, 3X, E6.2)
   61 WRITE(6,9) AH
   62 FORMAT(1X, 20HINTERVAL, 3X, 10H, 6HAPRIME/)
   63 ALPHAIMP = AH
   64 C1 = 0.435 6E-09*AP*ZP*ZW
   65 C2 = 0.2178*AP*ZP*ZW

   Common:
   C1, C2, A1, A2, A3, 4/4, 4/5, 4/6, 4/7, A6, A7, A8, AP, CAPA, AH

   Integer:
   RUN1, RUN2

   66 WRITE(6,10) RUN1, RUN2
   67 FORMAT(2A4)
   68 READ(5,6) BB, AP, CAPA, ZP, ZW
   69 FORMAT(F7.4, E10.3, F7.2, F7.1, F7.1)
   70 IF(BB.EQ.0.) GO TO 16
   71 AH=0.1E-12
   72 0E=0.2E-13
   73 DATA BK, T/0.133E-15, 298.2/
   74 DINF=5.953*BK*T/AP
   75 READ(5,6) N, NI, HO, DELH1, DELH2
   76 FORMAT(2I4, 3E8.1)
   77 WRITE(6,7) RUN1, RUN2
   78 WRITE(6,8) ZP, ZW, CAPA, BB, AP
   79 FORMAT(1X, E6.1, 3X, E6.1, 3X, E7.2, 3X, E6.2)
   80 WRITE(6,9) AH
   81 FORMAT(1X, 20HINTERVAL, 3X, 10H, 6HAPRIME/)
   82 ALPHAIMP = AH
   83 C1 = 0.435 6E-09*AP*ZP*ZW
   84 C2 = 0.2178*AP*ZP*ZW

   Common:
   C1, C2, A1, A2, A3, 4/4, 4/5, 4/6, 4/7, A6, A7, A8, AP, CAPA, AH

   Integer:
   RUN1, RUN2

   85 WRITE(6,10) RUN1, RUN2
   86 FORMAT(2A4)
436.

11 CONTINUE
44 AK=9/SUM
45 AKP=DOINF*AK/BB
46 WRITE(6,121) INT,AK,AKP
97 FORMAT(3X,13.4X,E10.3X,13.4X,E10.3)
98 IF(INT.NE.0)GO TO 13
99 DELH=DELH2
100 INT=INT+1
101 GO TO 10
102 IF(AH.LT.0.3E-13) GO TO 14
103 AH=AH-DELAH
104 GO TO 7
106 GO TO 15
107 ENO
108 C
109 FUNCTION F(H)
110 COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
111 E=EXP(-CAP*H)
113 F1=C1ALOG((1.+E)/(1.-E))
114 F2=C2ALOG((1.-E)
115 DUM1=A1*(H**3+H-2.*AP**2)*(A2*(H+AP)/H**3+AP)**2)
116 DUM2=A3*(P-H**3)*4.*AP-P-H)
117 DUM3=A3*(P-H**3)*(P-H)**2)
118 DUM4=A5/(1-P-H)**2-AP**2)+(A2*(H+AP)/H**3+AP)**2)
119 DUM5=A5*(P-H)**2-AP**2)+(A2*(H+AP)/H**3+AP)**2)
120 DUM6=A5*(P-H)**2-AP**2)+(A2*(H+AP)/H**3+AP)**2)
121 DUM7=A5*(P-H)**2-AP**2)+(A2*(H+AP)/H**3+AP)**2)
122 DUM8=A5*(P-H)**2-AP**2)+(A2*(H+AP)/H**3+AP)**2)
123 DUM9=A5*(P-H)**2-AP**2)+(A2*(H+AP)/H**3+AP)**2)
124 F=F1+F2-2.*AH*0UM1
125 RETURN
126 ENO
129 C
130 FUNCTION ALPHA(H)
131 IF(H.LT.10.)GO TO 1
132 ALPHA=1.3333333*S*SUM
133 RETURN
134 END
135 COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
136 E=EXP(-CAP*H)
138 X=ALOG(HN+SQR(HH+H+1.1))
139 S=SINH(X)
140 S2=SINH(S)
141 2 NN=NN+1
142 NNP=NN+1
143 NN3=NN+1
144 ANP=NN+1
145 ANP=NN+0.5
146 ANP=NN+0.5
147 NNP=3*SINH(NNP)*X)
148 S=3*SINH(X)
149 NNP=3*SINH(NNP)*X)
150 TNEW=R*(S**2+(SNP*SNP)/14.*SH**2
151 INNP*INNP+55)**1.1)
152 SUM=SUM+TNEW
153 OLD=TNEW
154 IF(AUSDIFF.LT.0.4E-2) GO TO 3
155 TNEW=OLD
156 N=N+1
157 GO TO 2
158 3 ALPHA=1.3333333*S*SUM
159 RETURN
160 END

0.2.2 K2 - Eq. [2.62]
PRESENTED SEPARATELY AS FFP AND FS, RESP. THE CALCULATION IS RE¬
PEATED FOR SEVERAL VALUES OF THE HAMAKER CONSTANT, AH, IN THE
RANGE 0.2E-13 TO 1.0E-11, THE ELECTRICAL DOUBLE LAYER INTERACTION
ENERGY IS GIVEN BY EQ. (2.11), THE RETARDED VAN DER WAALs ENERGY BY
BY EQ.(2.12), ALPHAI BY EQ.(2.14).
DATA INPUT (TWO CARDS PER RUN)
CARD COLUMN FORMAT NAME PURPOSE
1 1-8 2A4 NRUN1,NRUN2 RUN NUMBER
2 2 2-7 F7.4 BB TEST SECTION HALF-THICKNESS (CM)
3 2-7 F7.2 CAPA KAPP*AP
4 8-17 E10.3 AP PARTICLE RADIUS (CM)
5 13-24 F7.2 ZP PARTICLE ZETA POTENTIAL (MV)
6 25-31 F7.1 ZW WALL ZETA POTENTIAL (MV)
7 32-38 F7.1 ZW WALL ZETA POTENTIAL (MV)

COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
REAL MP,KFP,KFS
READ(15,2) NRUN1,NRUN2
READ(11,3) BB,AP,CAP,AP,ZW
FORMAT(T2 A4)
READ(10,4) MP, KFP, KS
FORMAT(A)
READ(11,5) NRUN1,NRUN2
FORMAT(A)
READ(10,6) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(11,7) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(10,8) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(11,9) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(10,10) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(11,11) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(10,12) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(11,13) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(10,14) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(11,15) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(10,16) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(11,17) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(10,18) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(11,19) BB,AP,CAP,AP,ZW
FORMAT(A)
READ(10,20) BB,AP,CAP,AP,ZW
IF(BB.LE.0.0) GO TO 16
DATA BK.T/0.138E-15.298./
AH=0.1E-12
0ELAH=0.2E-13
XO=0.2E-07
DELX=0.1E-07
MP=9.215*AP**3
DINF=5.958*BK*T/AP
CAP=CAPA/AP
C1=0.435 6E-09*AP*ZP*ZW
C2=0.2178E-09*AP*(ZP*ZP+ZW*ZW)
EL=0.1E-04
A = 1.0
B=0.8796/EL
C=0.3899*EL
D=0.05167*EL*EL
P = 0.4775«EL
A3=(-A/I4.*P**4+B/13.*P**3)*C/15.*P**5)-0/
(6.*P**61/12.
A4=-A/( 12.*P**3l+H/(6.*P*P)«-C/(20-*P«*4l-0/( .iO.*P*»5l  )/3.
A5=A/12.
A6=8/6.
A7=C/(60.*P**31
A8=D/(360.*P**4I
WRITE!6,4  1
4 FORMAT(1H13)
WRITE(6,4) NRUN1,NRUN2
FORMAT(A)
WRITE(6,5) NRUN1,NRUN2
FORMAT(A)
WRITE(6,6) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,7) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,8) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,9) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,10) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,11) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,12) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,13) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,14) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,15) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,16) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,17) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,18) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,19) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,20) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,21) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,22) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,23) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,24) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,25) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,26) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,27) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,28) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,29) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,30) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,31) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,32) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,33) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,34) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,35) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,36) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,37) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,38) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,39) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,40) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,41) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,42) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,43) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,44) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,45) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,46) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,47) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,48) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,49) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,50) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,51) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,52) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,53) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,54) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,55) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,56) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,57) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,58) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,59) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,60) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,61) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,62) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,63) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,64) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,65) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,66) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,67) BB,AP,CAP,AP,ZW
FORMAT(A)
WRITE(6,68) BB,AP,CAP,AP,ZW
FORMA
FUNCTION FIH
COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
C=EXP(-CAP*H)
E2=EXP(-2.*CAP*H)
F1=1.+E/(1.-E)
F2=2.*ALOG(E)-E2
DUM1=ALOG(E**2+2.*AP**2)+2.*CAP*H/(H+AP)+10**(-2.*CAP*H)**3
IF(F1.GE.P) GO TO 1
DUM2=A1*(1.-E)**3*(1.+E-2.*AP**2)/((H**3)**(H+2.*AP)**3)
DUM3=ALOG(f/H)+10**(-2.*CAP*H)**3
DUM4=H**3*(CAP*P)**3
DUM5=AP+2.*AP**2
DUM6=DUM1+DUM2+DUM3*DUM4+DUM5+DUM6+DUM7
1 = F=F1+F2-2.*APDUM1
RETURN
END
FUNCTION DFIH
COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
E=EXP(-CAP*H)
E2=EXP(-2.*CAP*H)
DF1=-2.*CAP*E/(1.-E**2)
DF2=2.*CAP*E2/(1.-E**2)
DUM1=-4.*A1*(H-AP)/H**3/(H+2.*AP)**4
DUM2=4.*A3*(P-H)**3/(H**4*(H+2.*AP)**4)
DUM3=-6.*A4*(P-H)/H**3/(H+2.*AP)**4
DUM4=A5*(-1./H-1./P+2.*AP)/H**3/(H+2.*AP)**4
DUM5=A6*(2.*AP)/(H*H)*2./H-2.*AP/H**3
DUM6=A7*(6.*P**3)/(H**4)-24.*AP*P**4/H**5)
DUM7=A8*(6.*P**4)/(H**5)
DUM1+DUM2+DUM3+DUM4+DUM5+DUM6+DUM7
1 = DF=DF1+DF2-2.*APDUM1
RETURN
END
FUNCTION D2FIH
COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
E=EXP(-CAP*H)
E2=EXP(-2.*CAP*H)
D2F1=2.*CAP*CAP*E*(1.+E2)/(1.-E2)**2
D2F2=-4.*CAP*CAP*E2/(1.-E2)**2
DUM3=ALOG(P/H)+10**(-2.*CAP*H)**3
DUM4=H**3*(CAP*P)**3
DUM5=AP+2.*AP**2
DUM6=DUM1+DUM2+DUM3+DUM4+DUM5+DUM6+DUM7
1 = D2F=D2F1+D2F2-2.*APDUM1
RETURN
END
FUNCTION ALPHAIH
COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
C=EXP(-CAP*H)
E2=EXP(-2.*CAP*H)
DUM3=ALOG(P/H)**2*(H+AP)**3
DUM4=A5*(1.+E)**3*(1.+E-2.*AP**2)/((H**3)**(H+2.*AP)**3)
DUM5=AP+2.*AP**2
DUM6=DUM1+DUM2+DUM3+DUM4+DUM5+DUM6+DUM7
1 = D2F=D2F1+D2F2-2.*APDUM1
RETURN
END
FUNCTION FLIN
COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
C=EXP(-CAP*H)
E2=EXP(-2.*CAP*H)
DUM3=ALOG(P/H)**2*(H+AP)**3
DUM4=A5*(1.+E)**3*(1.+E-2.*AP**2)/((H**3)**(H+2.*AP)**3)
DUM5=AP+2.*AP**2
DUM6=DUM1+DUM2+DUM3+DUM4+DUM5+DUM6+DUM7
1 = D2F=D2F1+D2F2-2.*APDUM1
RETURN
END
FUNCTION ALPHAIH
COMMON C1,C2,A1,A2,A3,A4,A5,A6,A7,A8,P,AP,CAP,AH
C=EXP(-CAP*H)
E2=EXP(-2.*CAP*H)
DUM3=ALOG(P/H)**2*(H+AP)**3
DUM4=A5*(1.+E)**3*(1.+E-2.*AP**2)/((H**3)**(H+2.*AP)**3)
DUM5=AP+2.*AP**2
DUM6=DUM1+DUM2+DUM3+DUM4+DUM5+DUM6+DUM7
1 = D2F=D2F1+D2F2-2.*APDUM1
RETURN
END
SUM = SUM + NEW
DIFF = NEW - TOLD
IF (ABS (DIFF) LT 0.1E-03) GO TO 3
TOLD = NEW
N = N + 1
GO TO 2
ALPHA = 1.33333333 * SUM
RETURN
END