THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

A METHOD FOR DETERMINING LIQUID-JUNCTION ELECTROMOTIVE FORCE BY CONTACT POTENTIAL MEASUREMENTS

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

BY
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Norman, Oklahoma
1959

A METHOD FOR DETERMINING LIQUID-JUNCTION ELECTROMOTIVE FORCE BY CONTACT POTENTIAL MEASUREMENTS

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ACKNOWLEDGEMENTS

It is with pleasure that I declare my indebtedness to the late Professor William Schriever who initially suggested that we make an attempt at measuring phase-boundary potential differences. His friendly interest and encouragement, specifically in the earlier portion of the research, were of considerable benefit. In particular, it should be mentioned that the idea of using a liquid-quadrant electrometer is due to Professor Schriever.

To Professor J. Rud Nielsen goes my gratitude for his interest in the latter stages of the research and for his concern in seeing that the apparatus not fall into desuetude after this work is terminated.

To the physics shop and, especially, Mr. Jim Hood go my thanks and commendation for a job well and patiently done. Mr. Hood's care and concern over many months is manifest in the good mechanical performance of the final apparatus.

Finally and most personally, I wish to record my heartfelt gratitude for the myriad ways in which my wife, Elvira, has been of help during the years of this research. Without her assistance this work would not have been carried out.

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CHAPTER I

HISTORICAL INTRODUCTION

The chronicle of attempts at determining individual phase-boundary potential differences is a long and tortuous comedy of errors without a satisfying ending. Even today, after more than a century of work on this question, no single potential difference is known to within reasonable certainty.

In the pages of this chapter we shall outline the main courses of thought concerning this formidable problem. This discourse will, naturally, not be exhaustive and some of it can be found elsewhere[1] with detailed references which are omitted here. Furthermore, we shall reserve the precise conceptual picture for the next chapter which will give a modern interpretation of the problem. Here we shall be content to use terms loosely in their historical context.

The beginning of thought about phase-boundary potentials is coincident with the beginning of electrochemistry. About 1800 Volta discovered his celebrated "pile" and immediately began to conjecture

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[1] J. A. V. Butler, Electrical Phenomena at Interfaces (Methuen and Co., London, 1951).

concerning its seat of electrical energy which he tentatively put at the metal-metal contact. Volta was led to this postulate by his discovery of what has come to be called the Volta effect--the contact charging of unlike metals. He found that whenever two dissimilar pieces of metal are put into contact and then separated, they bear opposite electric charges. Thus, it seemed to him that the observed electromotive force of an electrochemical cell should be due largely to the metal-metal contact.

By 1870 quantitative methods of measuring the Volta effect had been developed. Kelvin made the opposite pairs of quadrants of his quadrant electrometer out of unlike metals and thus determined the contact potential difference between them. (A similar, though much more complicated, method using liquid quadrants is described in Chapter VI.) F. W. Kohlrausch used a null method in which an adjustable potentiometer is connected across two parallel plates of unlike metals. At balance, no deflection of a quadrant electrometer occurs when the plates are touched and separated. The potentiometric potential difference is then equal and opposite to the contact potential difference. It was Kelvin, however, who, in later decades, refined this technique to a relatively high degree of precision. The metal-metal contact potential difference was investigated for many metal pairs and was usually found to be of the order of a few volts and to be markedly dependent of the state of the surface. In particular, oxidation and adsorption of water vapor were found to have a most pronounced effect. In some cases even the sign of the potential difference could be changed by burnishing or heating in air. In summary: the various experimental methods are capable, if suitable precautions are taken, of unambiguously measuring the contact potential difference between two surfaces-- the difficulty arises only when an attempt is made to measure the contact potential difference between pure phases.

Up till the last two decades, it was believed that a measurement of the contact potential difference between absolutely clean metals in vacuum would be ipso facto a measurement of the potential difference at the metal-metal contact. That this is not so (due to metal-vacuum potential jumps) seems to be at present universally conceded by those few workers who are nowadays concerned with such matters. (We shall discuss this question more thoroughly in the next chapter.) Apart from this, needless to say, the problem of obtaining pure metal surfaces is exceedingly difficult. Duplication of results among workers using the same as well as different techniques has been poor until very recently when modern ultra-high vacuum techniques were brought to bear on the problem.[1] Even now most contact potential measurements between presumably pure metals are uncertain to within roughly eighty millivolts or more.

For several succeeding decades the study of contact potential difference lay relatively dormant until awakened in the early part of this century by the thorough and refined investigations of thermionic and photoelectric electron emmission conducted largely by Richardson and Millikan. These new and totally different techniques rediscovered the phenomenon and its attendant dependence on surface conditions. It was also found that the contact potential difference between two metal surfaces is equal to the difference of their work functions. (This is only approximately true due to the fact that a photoelectric measurement is weighted toward that exposed crystal face which has the smallest work

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[1] J. C. Riviere, Proc. Roy. Soc. 70B, 676 (1957).

function while the Kelvin method of measuring contact potential difference measures the statistical average over all exposed crystal faces.)

In 1916, using the new work function data, Langmuir showed that the contact potential difference between two metals is very roughly equal to the emf of an electrochemical cell composed of the same two metals dipping into normal solutions of their salts. This he took to be a strong indication of the essential correctness of Volta's original hypothesis. Butler[1] and Gurney and Fowler[2] seized upon this idea and incorporated it in their kinetic classical and (later) quantum mechanical explanation of electrode potentials. Their treatment, which analyzes the electrode potential into parts contributed by the metallic work function, sublimation energy of the metal atom, ionization energy of the metal ion, and hydration energy of the ion, has entirely supplanted the vague and inconsistent "solution pressure" hypothesis of Nernst.[3] Strangely enough though, even the kinetic picture of electrode processes does not, as we shall see later, answer the old question regarding the seat of the emf.

Thus far, we have dealt with only one side of the celebrated controversy concerning the seat of emf in electrochemical cells which has persisted from the early nineteenth century. By the middle of the nineteenth century two coherent and vociferous schools of thought had emerged. The so-called "physical" school, led by Pellat, Ayrton, and Perry, held that the observed metal-metal contact potential difference is the prime contributor to the observed emf and, indeed, is also the cause of the

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[1] J. A. V. Butler, Phil. Mag. 48, 927 (1924).

[2] Gurney and Fowler, Proc. Roy. Soc. (London), 136A, 378 (1932).

[3] W. H. Nernst, z. physikal. Chem. 4, 129 (1899).

electrode reactions. The "chemical" school, led by Fabroni, Lodge, and Nernst held that the observed contact potential difference is caused by surface impurities (however small) and that the real contributors to the cell emf are the metal-electrolyte interfaces where the chemical reactions take place. Lodge was led to his attempt to explain away the pure-metal Volta effect by the fact that the order of metals in the Volta contact series was very much the same as the order of their heats of oxidation. He thus supposed that each metal had a differential attraction for oxygen, causing a potential difference to be set up. This hypothesis was not shown to be untenable until the development of modern vacuum technique--the time for the adsorption of a monomolecular layer of gaseous impurities may now be longer than an hour.

Of the several undeniable facts which early militated against Volta's hypothesis, perhaps the most forceful resulted from the enunciation of the principle of the conservation of energy by Mayer, Kelvin, and Helmholtz and its subsequent application to the electrochemical cell. No changes of any kind except the very small liberation or absorption of Peltier heat (equivalent to at most a few millivolts of emf) could be detected at the metal-metal junction while chemical changes were readily apparent at the metal-solution junctions. Kelvin found reasonable agreement between the thermochemically measured heats of reaction of the supposed electrode reactions and the electrical energy developed by the electrochemical cell. (Actually, as was shown later by Helmholtz and Gibbs, it is the free energy of the chemical reactions which appears as the electrical energy in a reversible cell.) Thus, the seat of energy in the cell could unambiguously be placed at the electrodes. It was then natural and convenient to assume that the seat of emf is also almost entirely at the two electrodes since the heat evolved at the metal-metal junction is almost negligible. Another fact which was used to support the "chemical" hypothesis was that if the electrolyte in an electrochemical cell be replaced by any metal, the circuit of three metals does not exhibit a measurable emf. A third fact much used in the controversy is that the emf of an electrochemical cell is markedly dependent on the concentration of the metal ions in the solutions and on the kind of solvent. Indeed, even the sense of the emf can sometimes be reversed by merely changing the kind of anion.

During the later part of the nineteenth century, and well into the twentieth, the "chemical" school reigned supreme and the controversy was subdued until the discovery of the photoelectric effect indirectly resuscitated the debate. It should be clear that neither school of thought had an "air-tight" argument. The "physical" school had but one major point--the undeniably large contact potential differences observed between metals and their rough parallel with the electrochemical series. This argument loses its impact if it is conceded that a contact potential measurement does not ipso facto determine the potential difference at the metal-metal junction but determines the sum of it and those at the two metal-vacuum boundaries. These latter two potentials then become a part of the electrode potentials as was adumbrated in the aforementioned work of Butler, Gurney, and Fowler. Such considerations explain in part the rough parallel between cell emfs and contact potential differences. On the other hand, the "chemical" hypothesis is rendered weaker by the realization that the seats of energy and the seats of electrostatic potential are not necessarily coincident. This will be made clearer by the concepts of the next chapter.

During the 1930 decade, a number of serious attempts (largely by Gurney and Butler) were made at reconciling the two divergent views. Unfortunately, these endeavors are almost entirely vitiated because of misconceptions regarding the nature of electrostatic potential in condensed phases. For example, Gurney in his very interesting and original book Ions in Solution[1] considered the contact potential difference to exist solely at the metal-metal contact. This vitiates many important aspects of his treatment of electrochemical cells.

From the standpoint of general knowledge in the field of electrochemistry, the present situation regarding phase-boundary potentials is no less confused. An examination of most of the textbooks and some of the review articles on physical chemistry and electrochemistry written in the last three decades shows that they can usually be grouped into two classes concerning their treatments of phase-boundary potentials. The larger group totally ignores the metal-metal junction and thus implies that the cell emf is composed of the two electrode emfs and the (small) solution-solution emf. The smaller group mentions the Volta effect and assumes that the full contact potential difference exists at the metal-metal junction. This then implies that the standard electrode potentials tacitly contain the metals' work functions as well as the electrode emf. Neither viewpoint is totally consistent.

At this point it might not be amiss to mention a few of the reasons why the problem of interphase (including the solution-solution emf)

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[1] R. W. Gurney, Ions in Solution (Cambridge Univ. Press, London, 1936).

potentials has commanded so much attention for the past century. Naturally, the quest is of interest per se as knowledge for its own sake. Beyond this though it is really the central problem of electrochemistry which, if solved, would put the discipline on a considerably firmer theoretical foundation. Accurate knowledge of a single electrode emf and/or a solution-solution (liquid junction) emf would enable calculations to be made (for the first time in most cases) of

a) activities of single ionic species in solution,
b) heats of hydration of single ionic species,
c) partial molar entropies of single ionic species,
d) chemical potentials of single ionic species, and
e) accurate, consistent pH.

Needless to say, the utility of such knowledge would ramify throughout most branches of electrochemistry.

Further considerations along these lines as well as discussions concerning the invariably unsuccessful experimental and theoretical methods of determining single phase-boundary potentials must be postponed until after the concepts have been rendered more exact. Suffice it to say for now that, as might have been anticipated from acquaintance with other historical controversies, both schools of thought are partially wrong and both partially right. We shall see that, also as usual, the outcome of the issue depends in part on the definitions used. But, in spite of all that has been done, no man can yet claim knowledge of the magnitudes of these elusive potential differences in the electrochemical cell.

CHAPTER II

THE CONCEPT OF INTERPHASE POTENTIALS

Definitions

By the word "phase" we shall mean a region containing matter which is macroscopically homogeneous in all significant physical and chemical properties (especially density, temperature, and chemical composition). At thermodynamic equilibrium, all regions of a phase (even "insulators" if enough time is allowed) are macroscopically at the same potential. Since gases are not normally equipotential, the word "phase" as used in this treatment will refer only to a condensed state of aggregation. Adding the requirement of equilibrium regardless of mensurationally significant elapsed time demands that only conducting phases be considered. For concreteness then, the term "phase" will refer to homogeneous metallic conductors, semi-conductors, or ionic liquid solutions.

By a phase boundary we shall mean the transition region between two phases or between one phase and a gas or vacuum. This transition region is usually of atomic dimensions although (for example, between two aqueous solutions) it need not be.

From these restrictive definitions it follows that at thermodynamic equilibrium macroscopic differences of potential can only exist at phase boundaries. Thus, in the electrochemical cell, we are justified in assigning a potential difference to each of the three or more phase boundaries. Indeed, there is good reason to believe that wherever two unlike phases of any kind come into contact, a difference of potential arises.

Several more or less distinct probable causes of phase-boundary potentials can be enumerated:[1]

a) Transfer of ions and/or electrons across the boundary.

b) Unequal adsorption of ions of opposite charge.

c) Adsorption and preferential orientation of dipolar molecules.

d) Deformation of polarizable atoms or molecules in the unsymmetric non-Coulombic force field at the boundary.

Undoubtedly in many cases each "cause" can depend on the others so that the concept of independent causes is debatable. In particular, (a) is likely to be influenced by (c). In any case it is safe to aver that any real phase-boundary possesses a tremendously complicated structure.

In this section we shall put forth a scheme of phase-boundary potentials which was, in slightly different form, originated by Lange[2] and has since been elaborated by Parsons[3] in a review-type treatment of the subject. However, the scheme given here is perhaps more similar to that given by Strehlow[4] than to the others. It distinguishes six "potentials" between a phase and vacuum--three purely Coulombic and three non-Coulombic.

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[1] R. Parsons, "Equilibrium Properties of Electrified Interphases," Modern Aspects of Electrochemistry, ed. by J. O'M. Bockris (Butterworths Scientific Publications, London, 1954).

[2] E. Lange, Wien-Harms Handb. exp. Phys. 12, 2, 267 (1933).

[3] Parsons, op. cit.

[4] H. Strehlow, z. Elektrochem. 56, 119, (1952).

The electrochemical potential $\bar{\mu}_i^{\alpha}$ of constituent particle i in phase α is the (non-gravitational) work required to carry the particle from field-free infinity through vacuum, through the phase boundary, and into the bulk of the phase.

The chemical potential μ_i^{α} of constituent particle i in phase α is the (non-Coulombic, non-gravitational) work required to carry the particle from field-free infinity through vacuum, through the phase boundary, and into the bulk of the phase.

The real potential ρ_i^{α} of constituent particle i in phase α is the (non-gravitational) work required to carry the particle from field-free infinity through vacuum, through the phase boundary, and into the bulk of the phase when the phase has no net electrostatic charge (therefore when $\psi = 0$).

The Volta potential ψ^{α} of phase α is the Coulombic part of the total work required to carry a particle bearing unit positive charge from field-free infinity to a point "just outside" the phase.

The Galvani potential φ^{α} of phase α is the Coulombic part of the total work required to carry a particle bearing unit positive charge from field-free infinity to a point inside the bulk of the phase.

The surface potential χ_{φ}^{α} of phase α is the Coulombic part of the total work required to carry a particle bearing unit positive charge from a point "just outside" the phase to a point inside the bulk of the phase.

By a point "just outside" a phase we mean a point far enough removed from the phase boundary so that all short-range (that is, all non-inverse-square) forces between the test particle at the point and the atoms of the boundary are vanishingly small, but not so far that the spacial fall-off of electrostatic potential becomes appreciable. These two limitations require that "just outside" mean between roughly 10^{-5} cm and 10^{-1} cm from the boundary for phases of normal laboratory dimensions. A detailed analysis for the case of a spherical phase of one centimeter radius is given by Parsons.[1] The limitation imposed by spacial fall-off could be obviated by defining the Volta potential as the electrostatic potential at a point inside a cavity within the phase and more than 10^{-5} cm distant from the cavity walls. However, this prescription has no direct relation to experiment.

The six potentials are by no means independent. It is easy to arrive at the following basic relations among them:

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i e \varphi^\alpha$$
$$\varphi^\alpha = \psi^\alpha + \chi^\alpha$$
$$\rho_i^\alpha = \mu_i^\alpha + z_i e \chi^\alpha$$
$$\rho_i^\alpha = \bar{\mu}_i^\alpha - z_i e \psi^\alpha.$$

In these equations z_i, which may be positive or negative, is the number of electronic charges carried by the particle and e is the magnitude of the electronic charge. The real potential ρ_e^M of an electron in a

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[1] Parsons, op. cit.

metal is the negative value of the work function ω^M of the metal. The Volta potential of a phase is due to its net electrostatic charge and to its electrostatic capacitance. It thus corresponds to the electrostatic potential of ordinary electrostatic theory.

These potentials, which are defined here from a particle standpoint, can also be looked upon as partial free energies in the thermodynamic sense. Indeed, it is the latter view which has priority in the case of μ and $\bar{\mu}$ which were defined originally by Gibbs[1] and Guggenheim[2] respectively.

Contact Potential Difference and the Electrochemical Cell

For a system of phases sharing a common neutral constituent j in thermodynamic equilibrium at constant temperature and pressure, Gibbs[3] was able to show that

$$\mu_j^\alpha = \mu_j^\beta = \mu_j^\gamma = \dots$$

By applying exactly analogous reasoning to phases sharing a common charged constituent i Guggenheim[4] was able to show that

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta = \bar{\mu}_i^\gamma = \dots$$

This is a formally powerful theorem in the field of phase-boundary potentials. Thus, at equilibrium between two conducting phases, we have

$$\mu_i^\alpha + z_i e \varphi^\alpha = \mu_i^\beta + z_i e \varphi^\beta$$

where i is the potential-determining ion, that is, the charged particle that moves across the phase boundary. Or, $\varphi^\alpha - \varphi^\beta = (\mu_i^\beta - \mu_i^\alpha)/z_i e$.

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[1] *The Collected Works of J. Williard Gibbs* (Longmans, Green, and Co., New York, 1928).

[2] E. A. Guggenheim, J. Phys. Chem. 33, 842 (1929); 34, 1540 (1930).

[3] Gibbs, *op. cit.*

[4] Guggenheim, *op. cit.*

From Earnshaw's theorem of electrostatics it is known that no configuration of electric charges can be stable if the only forces acting are electrostatic. Thus, a Coulombic phase-boundary potential difference can only be sustained if non-Coulombic forces are operative. In this sense $\Delta\mu$ can be regarded as the (non-Coulombic) electromotive force which causes and maintains the Coulombic potential difference $\Delta\varphi$. Under non-equilibrium conditions, it is $-\nabla\bar{\mu}$ that is the "driving force" acting on a charged particle. At equilibrium,

$$\nabla\bar{\mu} = 0 = \nabla\mu + z_i e \nabla\varphi$$

and the equilibrium interphase distribution of charged particles is governed by the equality of the two opposed "driving forces" $-\nabla\mu$ and $-\nabla\varphi$. $-\nabla\mu$ acts on the particle through its non-Coulombic aspects while $-\nabla\varphi$ acts on its electric charge.

After Lange,[1] we define the contact potential difference between two phases to be the Volta potential difference between the phases when they are in direct contact. For the special case of two phases in which the charge carriers are electrons only, it is simple to show that the contact potential difference is equal to the work function difference. At equilibrium, $\bar{\mu}_e^a = \bar{\mu}_e^b$ but $\bar{\mu}_e = \rho_e + (-1) e \psi$. Thus, $\rho_e^a - e\psi^a = \rho_e^b - e\psi^b$ or, $\psi^a - \psi^b = (\rho_e^a - \rho_e^b)/e$. Now, by its definition, the real potential ρ is the negative value of the work function ω. Thus, we have $\psi^a - \psi^b = (\omega^b - \omega^a)/e$. The contact potential difference between a metal and a solution of its

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[1] Lange, *op. cit.*

ions is more complicated because the charge carriers are electrons in one phase and ions in the other. For this case it can be shown[1] that $\psi^M - \psi^S = (\mu_a^M - \rho_i^S)/z_i e + \omega^M/e$ where μ_a^M refers to the chemical potential of the neutral atom in the metal and ρ_i^S denotes the real potential of the metal ion in solution. Because of the aura of confusion which has so long enveloped the subject, it should again be emphasized that the contact potential difference between two phases does not exist solely at their common boundary and that a Volta potential difference is not necessarily a contact potential difference.

It is also easy to show that, as is found experimentally, the insertion of a third electronic conductor between two others does not affect the contact potential difference between the latter two if thermodynamic equilibrium is maintained throughout. For example, let c be inserted between a and b. Then, we have $\bar{\mu}_e^a = \bar{\mu}_e^c$ and $\bar{\mu}_e^c = \bar{\mu}_e^b$, whence $\bar{\mu}_e^a = \bar{\mu}_e^b$ as before. Thus, no electronically conducting impurities (such as metallic oxides) *at the junction* between two metals can affect the contact potential difference between the metals. This is obviously not true for ionic conductors such as electrolytes. Therefore, so long as moisture is excluded, any method of joining metallic conductors is proper in an electrostatic circuit.

The following paragraph constitutes a very brief excursion into the physics of metals which, while not entirely necessary, may well be useful for purposes of illustration.

The Fermi energy level of "free" electrons in a metallic lattice is that energy at which an allowed state has an equal probability of

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[1] Parsons, *op. cit.*

being occupied or empty. Thus the Fermi energy, referred to field-free infinity, is the electrochemical potential of the metal since it requires on the average the negative value of this energy to remove electrons from the metal. According to the simple Sommerfeld wave-mechanical model, at 0° K (and to a good approximation at room temperature) only energy levels having a "kinetic" energy less than the critical energy, $\epsilon = \frac{h^2}{8m_e}\left(\frac{3n}{\pi}\right)^{2/3}$ where n is the number of free electrons per unit volume, are completely filled by electrons. All levels of higher energy are always vacant. However, in addition to this "kinetic" energy, the electrons also possess a mean potential energy with respect to the lattice of positive ions.[1] This "inner potential" η, as it is referred to in electron diffraction studies where it is the experimentally determinable refractive potential, is also a part of the total electron energy with respect to infinity. Thus, $\bar{\mu}_e = \eta + \epsilon$, which is determinable, or, $\mu_e - e\varphi = \eta + \epsilon$. Further resolution is impossible. Again, as always, while $\bar{\mu}$ can usually be determined, its Coulombic and non-Coulombic components cannot be resolved. The only partition that has been accomplished here is to divide the electrochemical potential of an electron in a metal into potential energy and kinetic energy terms--or, in perhaps more meaningful language, into energies of interaction with the local lattice and with the potential well constituted by the metal as a whole.

From previous definitions we can write the following relation for the work function of a metal: $\omega = -\rho_e = e\chi_\varphi - \mu_e$. That the surface potential of a metal is not negligible is shown by the

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[1] *Ibid.*

variation among the experimentally determined work functions of different faces of the same metallic crystal. For example, photoelectric measurements of the 111 and 100 faces of a copper crystal give[1] 4.89 ev and 5.64 ev respectively. For tungsten, thermionic measurements on five different crystal faces give[2] 4.39, 4.69, 4.39, 4.56, and 4.68 ev. Since μ_e is defined for the bulk of the crystal, this variation is attributed[3] to the variation in χ_φ. From this it can also be inferred that the Volta potential of a crystal depends on which plane is exposed. Thus, too, a Kelvin-type metal-metal contact potential difference is an average over the exposed crystal faces of the elementary surface crystals.

The surface potential of a pure metal is presumably due to the asymmetry of the force fields at the surface which polarizes the electron distribution. Several exploratory attempts[4,5,6] have been made at calculating the metallic surface potential from simple models using wave-mechanics. The numerical values thus obtained are little more than order-of-magnitude approximations but they are consistent in giving negative values in the neighborhood of a few tenths of a volt. This means that the equivalent surface double layer is oriented with its positive side facing vacuum. Rough calculations of the magnitude of the Galvani potential difference across a metal-metal junction have also been attempted[7]

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[1] N. Underwood, Phys. Rev. 47, 502 (1935).

[2] M. Nichols, Phys. Rev. 57, 297 (1940).

[3] Parsons, op. cit. [4] J. Bardeen, Phys. Rev. 49, 653 (1936).

[5] Huang and Wyllie, Proc. Phys. Soc. 62A, 180 (1949).

[6] R. Smoluchowski, Phys. Rev. 60, 661 (1941).

[7] Lange and Nagel, z. Elektrochemie 42, 50 (1936).

showing that it is likewise of the order of a few tenths of a volt.

So far, we have not considered methods for measuring these potentials. The discussion of practical methods of measuring Volta potential differences will be reserved for a later chapter. Here we shall describe the simplest method conceivable which, while correct in principle, is too insensitive in practice. In this method the two phases--for concreteness call them metals--are made into plane parallel plates separated by a narrow gap and joined by a wire connecting their non-opposed sides. Now the Volta potential of a phase is determined by its net charge and electrostatic capacitance. Thus, in this case the most direct method of measurement is to measure the force of attraction between the plates and, from it and the geometry, to calculate the potential difference. Then, by definition, $\psi^a - \psi^b \equiv (\varphi^a - \chi_\varphi^a) - (\varphi^b - \chi_\varphi^b) = \varphi^a - \varphi^b + \chi_\varphi^b - \chi_\varphi^a$, which relates the internal Coulombic potential difference $\Delta\varphi$ at the metal-metal junction to the external Coulombic potential difference $\Delta\psi$ across the vacuum gap between the metals. The phase-boundary potential difference is $\Delta\varphi$ while the contact potential difference is $\Delta\psi$. Unfortunately, $\Delta\psi$ is the only purely Coulombic potential difference capable of measurement.

If metals a and b dip into solutions α and β of their ions respectively, the cell thus formed can be represented by the schema, $a|\alpha|\beta|b|a'$, which implies that the emf of the cell is to be measured between two pieces of the metal a. (The prime merely signifies electrical separateness.) The Volta potential difference of the cell measured across the gap in metal a is

$$\psi^a - \psi^{a'} \equiv (\psi^a - \varphi^a) + (\varphi^a - \varphi^\alpha) + (\varphi^\alpha - \varphi^\beta) + (\varphi^\beta - \varphi^b) + (\varphi^b - \varphi^{a'}) + (\varphi^{a'} - \psi^{a'}),$$

or,

$$ {}^{a}\Delta^{a'}\psi = -\chi_{\varphi}^{a} + {}^{a}\Delta^{\alpha}\varphi + {}^{\alpha}\Delta^{\beta}\varphi + {}^{\beta}\Delta^{b}\varphi + {}^{b}\Delta^{a}\varphi + \chi_{\varphi}^{a'}. $$

But $\chi_{\varphi}^{a'} = \chi_{\varphi}^{a}$ and therefore*

$$ {}^{a}\Delta^{a'}\psi = {}^{a}\Delta^{a'}\varphi = {}^{a}\Delta^{\alpha}\varphi + {}^{\alpha}\Delta^{\beta}\varphi + {}^{\beta}\Delta^{b}\varphi + {}^{b}\Delta^{a}\varphi . $$

Thus, the Volta potential difference and the Galvani potential difference of the cell are equal and are composed of the four phase-boundary Galvani potential jumps. In more common notation, $E = E_{a\alpha} + E_{\alpha\beta} + E_{\beta b} + E_{ba}$. In textbooks on electrochemistry E_{ba} is usually denied existence. Even when it is recognized, it is put equal to the metal-metal contact potential difference. This is wrong unless (as is never done) all of the other E's are also defined as contact potential differences since it is true that $\Delta\psi = \Delta\varphi = {}^{a}\Delta^{\alpha}\psi + {}^{\alpha}\Delta^{\beta}\psi + {}^{\beta}\Delta^{b}\psi + {}^{b}\Delta^{a}\psi$. However, even if this should be done, a serious inconsistency would remain since contact potential differences are not the thermodynamically valid electrode potential differences used in the development of electrochemistry.

Since the measured emf of an electrochemical cell can be regarded either as the sum of the Galvani potential differences or as the sum of the contact potential differences, the historical controversy as seen in retrospect was in part due to the lack of precise definitions. In brief, it arose partly because of a lack of appreciation of the importance of distinguishing between the inner potential and the outer potential of a

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*There is no need to make the assumption of identical surface potentials, which is probably not realized in practice anyway because of different amounts of surface impurities on the two surfaces. With the assumption of time constancy of the surfaces, the determination of $\Delta\psi$ of the cell can still be effected by measuring $\Delta\psi$ with both pieces of metal a connected metallically and subtracting this value from the measured $\Delta\psi$ of the cell.

phase. Perhaps most of the blame lies with the discipline of electrostatics which in effect regards electricity as a continuum or fluid separate from matter. As will now be shown, the essence of the difficulty arises from the fact that any electric charge is inextricably linked with a material particle which experiences other interactions than the purely Coulombic.

Conceptual Difficulties

Heretofore, the scheme of potentials has been dealt with largely as pure formalism--little attempt has been made to relate the potentials to physical reality. In the definitions it was tacitly assumed that the work of transporting a charged particle into condensed matter can be partitioned into a Coulombic and a non-Coulombic part. Yet it is from this very dichotomy that all of the conceptual difficulties arise. For example, the Volta potential difference is the only Coulombic potential difference that can be measured. Nonetheless, as has been mentioned previously, if $\bar{\mu}$ could be partitioned into μ and φ , then $\Delta\mu$ and $\Delta \varphi$ across the junction could be obtained and $\Delta \chi$ could be calculated from $\Delta \psi$ and $\Delta \varphi$. However, this Coulombic versus non-Coulombic inseparability prevents our knowing anything but $\Delta \psi$.

What then is this thing called non-Coulombic? It is widely recognized that forces of attraction and repulsion exist between uncharged particles. Phenomena such as sublimation energy and surface tension demonstrate the existence of non-Coulombic attractive forces between the particles of condensed phases. The condensation of inert gases shows that non-Coulombic attractive forces exist even between atoms possessing no permanent dipolar or higher multipolar moments. Compressibility measurements performed on crystals of known lattice structure can determine the space-dependency of the repulsive force. With respect to energy, perhaps the homopolar valence bond is the most impressive. These non-Coulombic forces can be differentiated from the inverse-square forces by naming them "short-range forces" since their space-dependency is given by a higher inverse power of the distance.

The main categories of non-nuclear short-range forces are van der Waals, spin-spin, and homopolar valence forces. The category of van der Waals forces includes all permutations of the possible interactions among permanent and induced multipoles as well as the non-specific London dispersion (fluctuating dipole) force which exists between atoms possessing no permanent multipolar moments. Several of the van der Waals forces vary approximately as the inverse seventh power of the distance. Thus, they are negligible beyond ten Ångstrom units. The London dispersion interaction is distinguishable from the homopolar valence bond by the fact that it does not depend on the symmetry of the interaction wave-function, is thus independent of spin, is non-saturable in forming aggregates, and is smaller by almost two orders of magnitude. Of the several van der Waals interactions, the London dispersion is the most energetic except for the case of molecules (like water) with extremely large permanent moments.

The short-range forces, especially those not involving permanent dipoles, are often called "chemical" forces. However, with the possible exception of the spin-spin interactions, they can all be reduced to electrical (or electromagnetic) interactions although the form of the non-multipolar interactions is governed by quantum mechanical rules.

Since a Galvani potential difference is always established by the motion of charged particles or the orientation of multipoles, in this work we shall not be directly concerned with the homopolar bond. On the other hand--for example in solvation--van der Waals forces play predominant roles in determining the chemical potential of the charge-carriers. In the case of electrons in metals it is unlikely that van der Waals forces play any part; however here spin interactions combine with Coulombic interactions to determine the electrochemical potential of the charge-carriers.

The electrostatic potential difference between two points in a vacuum or within a single phase is a meaningful concept since the time-average force experienced by a charge-carrier is only Coulombic as is shown by the following treatment of non-equilibrium conditions in a phase. The total time-average force on the charge-carrier is given by the gradient of its electrochemical potential as is implied in the definition of the latter. Now $\nabla\bar{\mu} = \nabla\mu + ze\nabla\varphi$. In a vacuum or a gas far from its critical point, μ which is due to short-range interactions, is zero over a time-average. In a homogeneous condensed phase $\nabla\mu$ is zero macroscopically, that is, as a space-average. If we assume that in a statistical mechanical sense temporal and spacial averages are equivalent, then $\nabla\mu$ is zero as a time-average also. Thus, $\nabla\bar{\mu} = ze\nabla\varphi$. At thermodynamic equilibrium, $\nabla\varphi$ becomes zero macroscopically. In the practically important case of a current in a conducting phase, the electrochemical potential difference across the phase is identical with the "IR drop." It is noteworthy that it is the tremendously large charge-to-mass ratio of charge-carriers which permitted the above partition of $\nabla\bar{\mu}$ into $\nabla\mu$ and $\nabla\varphi$ in a condensed phase. To be sure, the redistribution of charge-carriers required to provide a $\Delta\varphi$ across a phase does cause a slight change in $\Delta\mu$ but usually this is less than roughly one part in 10^9 as can be shown by a simple calculation.

What has been done in the previous pages is, for the most part, to furnish a foundation for the comprehension of the following statement: no operational significance can be attached to the concept of the Galvani potential difference between two points in different phases. In essence, the reason for this is that in different phases charge-carriers experience different local electrical (or electromagnetic) environments. Naturally, this is true a fortiori for the case of a metal and an electrolyte in which the charge-carriers are different.

For concreteness, let us consider the case of water and benzene in contact when each contains dissolved hydrogen chloride. The HCl will be completely dissociated in water but only partially in benzene. There is good reason to believe that the solvation energy of the ions--which is a measure of the van der Waals interaction between the charge-carriers and the solvent--is drastically different in the two solvents. This is borne out by measurements on the solvation of electrolytes in different solvents. (The solvation energy of individual ions cannot be measured.) In water, which is strongly polar, considerable attraction and orientation of the water molecules around an ion exists. This leads to a large ionic solvation energy. In benzene the solvation energy is smaller because no orientation can exist since the molecules possess no permanent dipole moment.

At equilibrium between the water and the benzene, since the electrochemical potentials are equal, no net work is required to transport an ion from one to the other. By definition the Galvani potential difference between water and benzene is the Coulombic work required to carry a unit positive charge via any path from a point within the water to a point within the benzene. Thus, at equilibrium, a Galvani potential difference must exist at the phase boundary if non-Coulombic work is done in carrying an ion across the boundary. Since the other arguments indicate that non-Coulombic work is done in transporting an ion across the phase boundary, the existence of a phase-boundary Galvani potential difference is established. It is regrettable that a determination of this potential has, Tantalus-like, remained beyond our reach.

While the conceptual difficulty with interphase potentials was recognized by Gibbs,[1] it was Guggenheim[2] who first made a thorough study of the problem. By considering the types of possible thermodynamic systems he was able to show that, in every case, it is the sum of the chemical potential and the Galvani potential of a conducting phase which appears in the thermodynamic equations. Thus, there is no hope of *thermodynamically* resolving the electrochemical potential into its Coulombic and non-Coulombic components. For the future there remains a possibility of effecting the resolution by means of improved knowledge of the molecular architecture of condensed matter. But, at present, there is no possibility of measuring and little possibility of calculating the phase-boundary Galvani potentials within the electrochemical cell with any reasonable accuracy although theoretical work, mostly in the Soviet Union, toward this end is currently in full swing. The calculations are complicated and beyond the scope of this cursory survey. Suffice it to say that they are usually based on calculated single ion solvation energies, work functions, calculated metal surface potentials, the calculated surface potential of water, Volta potential measurements, and the like.

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[1] Gibbs, *op. cit.*

[2] Guggenheim, *op. cit.*

In Chapter V we shall describe how Volta potential measurements combined with a non-thermodynamic experimental result can effect a measurement of the Galvani potential difference between two aqueous solutions. If this method proves to be valid, it will provide the first experimental evaluation of a single Galvani potential difference. While not intrinsically as important as an evaluation of a metal-solution Galvani potential difference, it can nonetheless provide crucial data on such fundamentally important constructs as single ionic activities and energies of hydration which are measures of the ion-ion and ion-water interaction energies.

To close this brief treatment of the concept of interphase potentials, we shall now consider two methods--one theoretical and one empirical--which have been proposed for determining Galvani potentials.

Latimer, Pitzer, and Slansky[1] calculated the "absolute electrode potential" of the calomel half-cell reaction

$$\mathrm{Hg\ (l.) + Cl^- \ (aq.) = Hg\ Cl\ (s.) + e^- \ (in\ Hg)}$$

by regarding its Gibbs free energy as the sum of five artificially introduced sub-reaction free-energies involving the sodium ion.

$$\mathrm{Na^+ \ (g.) = Na^+ \ (aq.)} \qquad \Delta F_a = -\ 89.7\ \mathrm{kcal.}$$

$$\mathrm{Na\ (g.) = Na^+ \ (g.) + e^- \ (g.)} \qquad \Delta F_b = 118.1\ \mathrm{kcal.}$$

$$\mathrm{Na\ (s.) = Na\ (g.)} \qquad \Delta F_c = 18.7\ \mathrm{kcal.}$$

$$\mathrm{Hg\ (l.) + Na^+ (aq.) + Cl^- (aq.) = Hg\ Cl\ (s.) + Na\ (s.)} \qquad \Delta F_d = 68.8\ \mathrm{kcal.}$$

$$\mathrm{e^- \ (g.) = e^- \ (in\ Hg)} \qquad \Delta F_e = 104.5\ \mathrm{kcal.}$$

$$\mathrm{Hg\ (l.) + Cl^- \ (aq.) = Hg\ Cl\ (s.) + e^- \ (in\ Hg)} \qquad \Delta F = 11.4\ \mathrm{kcal.}$$

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

$$E = -\frac{\Delta F}{\mathfrak{F}} = -0.5.\ \text{volt}.$$

ΔF_e is the work-function for mercury. The ΔF_b, ΔF_c, and ΔF_d terms are from the measured ionization energy, sublimation energy, reaction energy and solution energy. The hydration energy ΔF_a is by far the least certain of the set. It was calculated from electrostatic theory with three parameters: the effective hydration radius of the sodium ion, the dielectric constant of the solvent in the immediate vicinity of the sodium ion, and the temperature coefficient of this dielectric constant. The numerical values of these parameters are much in doubt as is also the validity of the calculation of ΔF_a. The uncertainty of the final result is made evident by the fact that an uncertainty of 10 kcal in ΔF_a represents an uncertainty of 0.43 volt in E.

While several criticisms have been directed at the calculation with regard to its numerical uncertainty, the method is believed[1] to be correct in principle. However, this validity in principle seems dubious if one asserts that the calculated E is the electrode Galvani potential difference as is usually implied. For what is calculated is certainly not just the Coulombic part of the total energy required to carry a charge from the solution into the mercury but is the free energy of three reversible processes each of which requires a specific non-Coulombic energy. And, if this calculated "absolute potential" is not the Galvani potential difference, there is some question as to what thermodynamic significance it may have.

The first systematic attempts at measuring a phase-boundary

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[1] R. E. Wood, "Absolute Half-Cell Potentials," Electrochemical Constants, (National Bureau of Standards Circular 524, 1953).

potential occurred in the latter part of the nineteenth century and grew out of Lippmann's classic study[1] of the relation between the applied electrical potential difference between mercury and an aqueous electrolytic solution and the observed surface tension of the mercury-solution interface. Lippmann found that the graph of the surface tension versus applied potential is very roughly parabolic so that at some applied potential, the surface tension goes through a maximum. The theory of this effect was investigated by Lippmann and was elaborated and put on a firm thermodynamic foundation by Gibbs.[2] The theory predicts that the maximum in the surface tension occurs when the mercury-solution interface is uncharged--that is when no double-layer due to ionic separation exists at the interface. Many workers concluded that the electrostatic potential difference between the mercury and the solution therefore must be zero at the electrocapillary maximum and set about using this "null electrode" as a means of determining the electrode potentials of other electrodes. Scores of experiments over a span of half a century were performed on this null electrode system. The usual set-up used was to form a cell composed of the mercury-solution interface and a calomel electrode. The choice of the latter electrode has the advantage that essentially the only metal in the cell is mercury, thus precluding any metal-metal ambiguities. In general, the solution in contact with the mercury is not identical with the potassium chloride solution of the calomel electrode and therefore a solution-solution diffusion emf is set up. Since the maximum uncertainty (as will be shown in the next chapter) caused by this emf is around five millivolts, it will be regarded as negligible in what follows.

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[1] G. Lippmann, Ann. Chem. Phys. 5, 494 (1875). [2] Gibbs, op. cit.

Thus, if indeed the Lippmann electrocapillary electrode behaves as a null electrode, a measurement of the cell emf when the surface tension of the mercury-solution interface is at its maximum gives the much-desired Galvani potential difference of the calomel electrode. However, much to the detriment of the foundation of electrochemistry, the situation is not that simple. The foremost ambiguity is that putting different electrolytic solutions in contact with the mercury causes the emf of the cell to vary by roughly 0.4 volt.[1] This variation is attributed to preferential ion adsorption. Thus, not all solutions in contact with mercury at the electrocapillary maximum form null electrodes and there is no indisputable way of telling which, if any, do.

A theoretical objection of devastating consequence is that the absence of net charge on the mercury-solution interface does not necessarily imply that the Galvani potential difference across the interface is zero. This is because the thermodynamic derivation ignores the possibility of surface potentials at the mercury and solution boundaries. Theoretical calculations of doubtful accuracy show that the surface potential of mercury is about − 0.2 volt while that of water is about − 0.4 volt. The present consensus, contrasted with the long prevailing one, is that the electrocapillary electrometer does not, even approximately, furnish a method of determining a phase-boundary potential difference.

More than a score of attempts have been made at finding a null electrode by other empirical devices. These will not be described here because, in every case, more ambiguities in results and a greater number

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[1] D. C. Grahame, Chem. Rev. <u>41</u>, 441 (1947).

of difficulties in interpretation exist than in the case of the electrocapillary electrometer. These experiments usually involve two unlike metals. As a basis for comparison, the supposed null electrode in each case is used to measure the "absolute electrode potential" of the calomel electrode. These "absolute electrode potentials," as determined by the several methods, vary over a range of about one volt. Moreover, the tabulations comparing the results given in several treatments of the subject are incorrect in that either no correction is made for the metal-metal Galvani potential difference or else the whole contact potential difference is assumed in its stead.

CHAPTER III

THE LIQUID-JUNCTION POTENTIAL DIFFERENCE

Up till now our consideration has been directed toward the general problem of the potentials of condensed phases with special emphasis on the metal-metal and metal-solution boundaries. Since it has been shown that the main potential difference of interest at these two boundaries--the Galvani potential--is, at least at present, indeterminable; we now turn toward the lesser problem of the liquid-junction potential difference. While the general remarks of the preceding chapter concerning interphase potentials are also applicable to the case of two homosolvent solutions, the calculation of the potential difference for dilute solutions is on somewhat firmer ground because no change of charge-carrier and little change in the microscopic environment of an ion exists between the two phases. Moreover, there is some hope of determining the homosolvent liquid-junction potential difference experimentally in the case of moderately dilute solutions. The remainder of this dissertation is dedicated to that hope.

The importance of homosolvent liquid-junction electromotive forces to the field of electrochemistry is rather great. In practical work, solution-solution boundaries are perhaps most troublesome in pH measurements where lack of knowledge of liquid-junction emf precludes the possibility of even defining pH rationally. In many measurements involving "standard electrode potentials," it is the liquid junction which largely limits the accuracy. In more fundamental work, the problem of determining the activity coefficients of individual ions outside the concentration range of the Debye-Hückel limiting-law is inextricably bound up with the problem of determining the emf of a liquid junction.

In physiology too, the lack of knowledge of liquid-junction emf's is often an impediment to unambiguous measurements. For example, in the determination of the potential difference across the bounding membrane of a cell, a microtube of KCl solution is inserted into the cell and a second capillary of KCl solution of the same concentration is put into contact with the extra-cellular fluid. Identical metallic electrodes are placed in the two identical KCl solutions to form an electrochemical cell the emf of which can be measured. This measured emf is the sum of three liquid-junction potential differences:

KCl | intracellular fluid | extracellular fluid | KCl

of which one is the desired cell-membrane potential difference. While arguments are given to the effect that the emf's at the KCl boundaries are fairly small, nonetheless, the justification for equating the measured emf with the cell-membrane emf is limited since the accuracy is perhaps only twenty per cent.

The Concept of Activity

Whenever a solute is dissolved in a solvent to form a solution, the properties of the latter differ from those of the pure solvent. The relative change from the properties of the pure solvent due to the presence of the solute may be calculated by equating the chemical potentials in the two states in thermodynamic equilibrium if the chemical potentials are taken to depend logarithmically on the mole fraction of solute or solvent present in each phase, as Gibbs showed they must in ideal solutions. For ideal solutions the chemical potential of constituent i in phase α is given by $\mu_i^\alpha = \mu_{oi}^\alpha + RT \ln X_i^\alpha$, (1) where μ_{oi}^α is the arbitrarily defined chemical potential of the standard state and X_i^α is the mole fraction of i in phase α.

As an example, let us derive the Nernst distribution law for the partition of a common uncharged solute (monomeric in both phases) between two immiscible solvents. At equilibrium, the chemical potentials of the solute are equal: $\mu_i^\alpha = \mu_i^\beta$ that is,

$$\mu_{oi}^\alpha + RT \ln X_i^\alpha = \mu_{oi}^\beta + RT \ln X_i^\beta,$$

$$\text{or,} \quad \ln X_i^\beta / X_i^\alpha = (\mu_{oi}^\alpha - \mu_{oi}^\beta)/RT.$$

Thus X_i^β / X_i^α is a constant at a given temperature. Likewise, all colligative properties of dilute solutions can be derived. When one of the phases involved is a vapor, the mole fraction becomes the partial pressure.

At high or even moderate concentrations the above procedure is no longer verified. The concentration at which marked departure from "ideality" first occurs varies tremendously with the kind of solute and the kind of solvent. For solutions of non-electrolytes in water concentrations above $x = 10^{-2}$ may behave ideally while in the case of electrolytes even concentrations below $x = 10^{-6}$ often exhibit signs of non-ideal behavior. For ideal behavior, the average mutual energy of interaction between the solute particles must be small compared with kT. For non-electrolytes, the inter-particle forces are short-range forces and a high concentration is required to give a relatively large time-average interaction energy. The Coulombic forces between the ions of dissolved electrolytes, on the other hand, are long-range and cause relatively large time-average interaction energies even at very low concentrations.

The concept of activity is introduced to make the form of the laws for dilute solutions invariant as the concentration increases beyond the limits of ideal behavior. Therefore, it is a construct which furnishes no new physical insight but is a great aid in simplifying both thought and its mathematical expression. Thus, for the general case, we write:

$$\mu_i^\alpha = \mu_{oi}^\alpha + RT \ln a_i^\alpha \qquad (2)$$

in which the activity replaces the mole fraction. Thus the Nernst Distribution Law becomes, for all concentrations: a_i^β / a_i^α = constant at a given temperature. Usually, the thermodynamic equations are developed in terms of concentrations and then the activities are substituted as an afterthought.

As an aid in comparing the degree of non-ideality of solutions, the concept of activity coefficient is introduced. The defining relation between the activity, the activity coefficient f and the mole fraction is simply a = fx. Precisely, f is the so-called rational activity coefficient. If the concentration is expressed in molarity (moles of solute per liter of solution), then we write $a = f_c c$ where f_c is the molar activity coefficient. Furthermore, if the concentration is expressed in molality (moles of solute per 1000 grams of solvent), we then write $a = f_m m$ where f_m is the molal activity coefficient. In cases of extreme dilution $a \rightarrow x$ and thus $f_x \rightarrow 1$. But f_c and f_m do not approach unity at extreme dilution. To obviate this they are "normalized" by complicated expressions[1] and the resulting "practical" activity coefficients

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[1] A. J. Rutgers, Physical Chemistry (Interscience Publishers Inc., New York, 1954), p. 379.

f_c' and f_m' do then approach unity at extreme dilution. It is these "practical" activity coefficients which are most frequently used. Fortunately, at the low concentrations considered in this work, molarity and molality are always equal to within a tenth of one per cent.

Thus, the departure of the activity coefficient of a solute from unity serves as a measure of the time-average energy of interaction between the molecules or ions of the solute. In the case of a "strong" electrolyte--which is the only one that will concern us--the molecules are essentially fully dissociated in common aqueous solutions, and the interionic interactions are usually predominantly Coulombic. In this instance the two or more species of ions are regarded as separate solutes which are interrelated by the requirement that any macroscopic region of the solution be electrically neutral. Therefore, the total chemical potential of the solute is the sum of the individual ionic chemical potentials. For a binary electrolyte,

$$\mu_i = \mu_+ + \mu_- = \mu_{0+} + \mu_{0-} + RT(\ln a_+ + \ln a_-),$$

or, we can write: $\mu_i = \mu_{0\pm} + RT \ln a_+ a_-$,

where $\mu_{0\pm} \equiv \mu_{0+} + \mu_{0-}$. Now, it is found that all measurements--whether they be of colligative properties or the emf of a cell--made on systems involving electrolytic solutions yield only values of μ_i with reference to the standard state. Thus, from an operational point of view a_+ and a_- are inseparable and their product is raised to the status of an entity by defining the "mean activity" $a_\pm$ as $a_\pm \equiv \sqrt{a_+ a_-}$.

For a binary electrolyte, we write in compact form:

$$\mu_i = \mu_{0\pm} + 2RT \ln a_\pm .$$

But, also $a_\pm \equiv f_\pm c = \sqrt{f_+ f_-}\, c$, where $f_\pm$ is the mean activity coefficient. $\Delta\mu_i$ and therefore $\Delta f_\pm$ between two solutions are unambiguously determinable. If the assumption is made (as is borne out by theory and experiment) that $f_\pm \rightarrow 1$ as $c \rightarrow 0$, then $f_\pm$ for a given solution is determinable as a function of concentration.

In order to demonstrate some of the relationships between activity and emf, we shall now discuss the concentration cell composed of two identical metallic electrodes dipping into two solutions of their ions at different concentrations. For concreteness, let the electrolytes be silver nitrate in water at concentrations C_1 and C_2 respectively: $M \mid S_1\ (C_1) \mid S_2\ (C_2) \mid M'$. At the metal-solution interfaces, it is the Ag^+ ion which is the potential-determining ion and therefore, at equilibrium, $\overline{\mu}_+^{M} = \overline{\mu}_+^{S_1}$ and $\overline{\mu}_+^{M'} = \overline{\mu}_+^{S_2}$. We have from the first equation,

$$\mu_{0+}^{M} + RT \ln a_+^{M} + e\varphi^{M} = \mu_{0+}^{S_1} + RT \ln a_+^{S_1} + e\varphi^{S_1}.$$

Thus,

$$e(\varphi^{M} - \varphi^{S_1}) = \mu_{0+}^{S_1} - \mu_{0+}^{M} + RT \ln \frac{a_+^{S_1}}{a_+^{M}}.$$

Similarly, the second equation gives

$$e(\varphi^{M'} - \varphi^{S_2}) = \mu_{0+}^{S_2} - \mu_{0+}^{M} + RT \ln \frac{a_+^{S_2}}{a_+^{M}}.$$

Now the cell emf E is given by

$$E \equiv (\varphi^{M} - \varphi^{S_1}) + (\varphi^{S_1} - \varphi^{S_2}) + (\varphi^{S_2} - \varphi^{M'}).$$

Substituting, the above values for the metal-solution Galvani potential differences and replacing the electronic charge by the faraday in order to obtain a molar equation, we obtain

$$E = E_j + \frac{RT}{\mathcal{F}} \ln \frac{a_+^{S_1}}{a_+^{S_2}} \qquad (3)$$

where E_j is the Galvani potential difference across the liquid junction. This equation makes the experimental interdependency between the liquid-junction emf and the single-ion activity very clear. If one were measured, the other could be determined. In the next section it will be shown that any accurate theoretical calculation of the liquid-junction emf also depends on knowledge of the single-ion activities.

It is interesting to attempt a calculation of the diffusion emf of the concentration junction by assuming thermodynamic equilibrium and equating the electrochemical potentials of both ions which carry charge across the junction. For the above illustration we would have for the equilibrium of the silver ion, $\bar{\mu}_+^{S_1} = \bar{\mu}_+^{S_2}$, or,

$$\mu_{0+}^{S_1} + RT \ln a_+^{S_1} + \mathcal{F} \varphi^{S_1} = \mu_{0+}^{S_2} + RT \ln a_+^{S_2} + \mathcal{F} \varphi^{S_2}.$$

Whence,

$$\varphi^{S_1} - \varphi^{S_2} = + \frac{RT}{\mathcal{F}} \ln \frac{a_+^{S_2}}{a_+^{S_1}} .$$

Similarly, from the equilibrium of the nitrate ion,

$$\varphi^{S_1} - \varphi^{S_2} = - \frac{RT}{\mathcal{F}} \ln \frac{a_-^{S_2}}{a_-^{S_1}} .$$

Now these two equations are incompatible in general and only become compatible when the solutions become identical, in which case $E_j = 0$. This shows that, as would certainly be expected from the irreversibility of the diffusion process, two different homosolvent solutions can never be in thermodynamic equilibrium.

The Concentration Junction

A concentration junction is formed between two homosolvent, homosolute electrolytic solutions. Contrasted with that of the homosolvent, heterosolute junction, the emf of the concentration junction is more reproducible, varies considerably less with time, and is better understood theoretically. It is thus eminently suited for exploratory investigations directed toward establishing a new experimental method and, indeed, is so utilized in the experiments to be described in later chapters. In spite of its greater inherent difficulties, however, the heterosolute junction continues to receive much attention due to its larger practical importance in pH measurements, standard electrode measurements, and cell membrane emf measurements.

In this chapter and, indeed, throughout the remainder of this work, our considerations will largely be restricted to binary, uni-univalent electrolytes in aqueous solution. These are the electrolytes which have received the preponderant share of theoretical and experimental investigation over a span of a century. Generalization of the equations to cover more complicated electrolytes is straightforward but usually complicated and, furthermore, adds nothing new in principle.

Let us, for concreteness, consider the concentration junction between two HCl solutions. The free diffusion coefficient of the H^+ ion is about five times greater than that of the Cl^- ion. Thus, at the instant of contact between the two solutions, while both the H^+ ions and the Cl^- ions diffuse toward the less concentrated solution, the H^+ ions "outrun" the Cl^- ions and therefore the more dilute solution acquires a net negative charge. The Coulombic potential difference thus set up across the junction causes a field strength in a sense which will retard the diffusion of the H^+ ions and enhance the diffusion of the Cl^- ions. The H^+ ions continue to outrun the Cl^- ions at an ever decreasing pace until, finally, the resulting field strength causes the rates of diffusion to equalize. Thus, a stationary state of diffusion is set up in which the flux of positive ions toward the more dilute solution just equals the flux of negative ions in the same sense and the electrolyte thenceforth diffuses as a whole. In this stationary state the Galvani potential difference between the solutions remains constant for durations as long as several days, as is shown experimentally, if no appreciable net current is allowed to flow across the junction.

A purely kinetic derivation of the emf of a concentration junction will now be made which is slightly similar to the hybrid kinetic-thermodynamic derivation given by Kortüm and Bockris.[1] In this derivation the key assumption is that the ions of the solute possess diffusion and mobility properties which are related in the same manner as those of ideal gases. In the derivation proper, no allowance is made for interionic effects.

The net particle current densities, J_+ and J_- of positive and negative ions due to both free diffusion and the influence of electric field strength are expressed by

$$J_+ = -D_+ \nabla n_+ - n_+ U_+ \nabla \varphi$$

and

$$J_- = -D_- \nabla n_- + n_- U_- \nabla \varphi$$

where $n \equiv$ number of ions per unit volume, $D \equiv$ diffusion coefficient, and $U \equiv$ mobility (speed per unit field strength). Now, due to the tremendously large charge-to-mass ratio of ions, even the most intense space charge is caused by relatively few excess ions so that in any macroscopic volume $n_+ = n_- \equiv n$ with amazing exactness. The insertion of this equality into the above equations and specialization to a plane boundary yields:

$$J_+ = -D_+ \frac{dn}{dx} - n\, U_+ \frac{d\varphi}{dx}$$

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[1] Kortüm and Bockris, Textbook of Electrochemistry (Elsevier Publishing Co., New York, 1951), p. 270.

and $$J_- = -D_- \frac{dn}{dx} + n U_- \frac{d\varphi}{dx} .$$

When the stationary state is attained, $J_+ = J_-$ and thus

$$\frac{d\varphi}{dx} = -\frac{D_+ - D_-}{U_+ + U_-} \frac{1}{n} \frac{dn}{dx} \qquad (4)$$

which is a generally valid equation for uni-univalent electrolytes. Assuming that $D = \frac{kT}{e} U$, as is shown in the kinetic theory of gases, and that $\frac{U_+ - U_-}{U_+ + U_-}$ is concentration-independent, we can perform a simple integration and obtain

$$\varphi^{\alpha} - \varphi^{\beta} = -\frac{kT}{e} \frac{U_+ - U_-}{U_+ + U_-} \ln \frac{n^{\alpha}}{n^{\beta}}$$

which, expressed in molar quantities, becomes

$$\varphi^{\alpha} - \varphi^{\beta} = -\frac{RT}{\mathcal{F}} \frac{U_+ - U_-}{U_+ + U_-} \ln \frac{C^{\alpha}}{C^{\beta}} . \qquad (5)$$

This equation was originally derived by Nernst[1] from a thermodynamic argument. As it stands, the equation is capable of only crude accuracy because interionic effects have been neglected. These Coulombic effects are quite important even at 10^{-4} N--that is, even at the lowest concentration that can conveniently be studied experimentally.

In order to generalize somewhat the expression for the emf of a concentration junction, we return to the differential equation (4) and make allowance for interionic effects by use of the Debye-Hückel theory. Instead of the concentration we put $a = fC$ where $f = e^{-A\sqrt{C}}$ is the

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[1] W. H. Nernst, z. physik. Chem. 4, 129 (1889).

form of the activity coefficient given by the Debye-Hückel limiting-law and A is a constant (the same for all univalent ions) calculable from the Debye-Hückel theory. Also from the Debye-Hückel limiting-law, the expression for the variation of mobility with concentration is $U = U_\infty - (aU_\infty + b)\sqrt{C}$ where U_∞, a, and b are constants determinable from measurements and from the Debye-Hückel theory. With these substitutions, the differential equation takes the form:

$$d\varphi = -\frac{RT}{\mathfrak{F}}\,\frac{k_1 - k_2\sqrt{C}}{k_3 - k_4\sqrt{C}}\left(\frac{1}{C} - \frac{A}{2\sqrt{C}}\right) dC \tag{6}$$

in which the k's are complicated constants involving a and b and the ionic mobilities at infinite dilution, U_∞. Integration combined with the approximation of replacing ln (1 + y) by y, yields

$$\varphi^\alpha - \varphi^\beta = -\frac{RT}{\mathfrak{F}}\,\frac{U_{\infty+} - U_{\infty-}}{U_{\infty+} + U_{\infty-}}\left[\ln\frac{C^\alpha}{C^\beta} - B\left(\sqrt{C^\alpha} - \sqrt{C^\beta}\right)\right] \tag{7}$$

where

$$B \equiv A - \frac{2k_4}{k_3}\left(1 - \frac{k_2/k_4}{k_1/k_3}\right).$$

Expressed in common logarithms and specialized to 25°C (the standard temperature for electrochemical measurements), the equation becomes

$$\varphi^\alpha - \varphi^\beta = -0.05915\,\frac{U_{\infty+} - U_{\infty-}}{U_{\infty+} + U_{\infty-}}\left[\log\frac{C^\alpha}{C^\beta} - B'\left(\sqrt{C^\alpha} - \sqrt{C^\beta}\right)\right] \tag{7'}$$

where $B' \equiv \frac{B}{2.303}$. This equation for binary electrolytes can be regarded as correct within the range of validity of the Debye-Hückel limiting law--that is, up to concentrations of about 0.005 N for uni-univalent electrolytes. To a fair approximation (say within about three per cent), it probably is valid up to 0.02 N. The coefficient B is a slowly varying function of temperature and valence as well as of $U_{\infty +}$, $U_{\infty -}$, and the Debye-Hückel constants. It may be either positive or negative. For the three most thoroughly studied electrolytes, HCl, KCl, and NaCl, B' takes on the values 0.383, 0.160, and 0.097, respectively, at 25°C. Thus, for NaCl, the Nernst equation (5) is approximately correct. For multiple-valent electrolytes, the departure from the Nernst equation is usually extreme.

The mobility U of an ion constituent in an electrolyte is not determined directly but is calculated from the transference number t, the equivalent conductance Λ and the faraday $\mathcal{F}$ (which are experimentally determinable) by the relations,

$$U_+ = \frac{t_+ \Lambda}{\mathcal{F}} \text{ or, } U_- = \frac{t_- \Lambda}{\mathcal{F}} .$$

The transference number of an ion is that fraction of the total current which the ion constituent carries. Thus, $t_+ + t_- = 1$.

Since $$\frac{t_+}{t_-} = \frac{U_+}{U_-} \quad \text{and} \quad t_+ - t_- = \frac{U_+ - U_-}{U_+ + U_-} ,$$

the mobility factor in the concentration junction equation may be written

$$\frac{U_{\infty +} - U_{\infty -}}{U_{\infty +} + U_{\infty -}} = 2t_{\infty +} - 1 .$$

The cation transference number at infinite dilution $t_{\infty +}$ is, of course, obtained by extrapolation from experimental measurements.

We have seen that a thermodynamic calculation utilizing the equality of the electrochemical potentials across a liquid junction is impossible since the two solutions forming the junction are not in thermodynamic equilibrium. It may, however, be of some interest to give here a quasi-thermodynamic derivation which appears in different guises in most of the textbooks on the subject. This derivation has, at least, the merit of giving an answer in agreement with the kinetic derivation given above.

The passage of one faraday of charge across the junction results in the displacement of $\frac{t_+}{z_+}$ mole of cations and $\frac{t_-}{z_-}$ mole of anions in opposite senses across that junction. If an infinitesimal layer of the junction is considered, the total ionic concentration will be C at one plane and C + dC at the other. Therefore, the "reaction" due to the passage of charge may (with specialization to the HCl junction for concreteness) be written as

$$\frac{t_+}{z_+} H^+(C) + \frac{t_-}{z_-} Cl^-(C + dC) \longrightarrow \frac{t_+}{z_+} H^+(C + dC) + \frac{t_-}{z_-} Cl^-(C) .$$

A basic assumption is now introduced: the Gibbs free energy of the system is a minimum with respect to the changes brought about by the passage of charge. From thermodynamics we appropriate the relation

$$dG = VdP - SdT + \sum_i \bar{\mu}_i dn_i$$

in which the electrochemical potentials are here written in place of the commonly used chemical potentials. Equating dG to zero under conditions of constant temperature and pressure enables us to write for the above "reaction,"

$$\frac{t_+}{z_+} \bar{\mu}_+^{C} + \frac{t_-}{z_-} \bar{\mu}_-^{C+dC} = \frac{t_+}{z_+} \bar{\mu}_+^{C+dC} + \frac{t_-}{z_-} \bar{\mu}_-^{C}$$

or,

$$\frac{t_+}{z_+} d\bar{\mu}_+ = -\frac{t_-}{z_-} d\bar{\mu}_- .$$

Or, $\frac{t_+}{z_+} d(\mu_{o+} + RT \ln a_+ + z_+\mathcal{F}\varphi) = -\frac{t_-}{z_-} d(\mu_{o-} + RT \ln a_- + z\mathcal{F}\varphi)$.

Insertion of the uni-univalent values $z_+ = 1$ and $z_- = -1$ gives:

$$RTt_+d \ln a_+ + \mathcal{F}t_+d\varphi = RTt_-d \ln a_- - \mathcal{F}t_-d\varphi$$

or,
$$-\frac{\mathcal{F}}{RT} d\varphi = t_+d \ln a_+ - t_-d \ln a_- \qquad (8)$$

which may be integrated to give

$$-\frac{\mathcal{F}}{RT}(\varphi^\alpha - \varphi^\beta) = \int_\beta^\alpha t_+d \ln a_+ - \int_\beta^\alpha t_-d \ln a_- \qquad (8')$$

when the limits of integration are logarithms of the activities at the respective ionic concentrations in the bulk of the two solutions. Idealization to the case in which the transport numbers are independent of concentration gives

$$-\frac{\mathcal{F}}{RT}(\varphi^\alpha - \varphi^\beta) = t_+\ln\frac{a_+^\alpha}{a_+^\beta} - t_-\ln\frac{a_-^\alpha}{a_-^\beta}. \qquad (9)$$

If the limiting-law result that $a_+ = a_- \equiv a$ is used,

$$\varphi^\alpha - \varphi^\beta = -\frac{RT}{\mathcal{F}}(2t_+ - 1)\ln\frac{a^\alpha}{a^\beta} \qquad (10)$$

which is the Nernst equation with activities written for concentrations. Indeed if, as was originally done historically, we had defined the chemical potential to be an explicit function of concentration instead of activity, the original Nernst equation would have been obtained.

As before, the treatment can be somewhat generalized by inserting the Debye-Hückel limiting-law concentration dependency of t_+ and a into the differential equation (8). Integration then gives an equation which can be shown to be identical with equation (7). However, it is either the Nernst equation or the Nernst equation written with activities which appears in textbooks. Frequently, the assumption that $a_+ = a_-$ is not made explicit in the derivation.

We now undertake to compare four methods of calculating the emf of a concentration junction utilizing the above equations with various degrees of empiricism introduced at different stages. A tabulation of the four sets of results for aqueous HCl concentration junctions at 25°C will be given. HCl was chosen because it forms perhaps the most common concentration junctions, the relevant constants are known to high accuracy because of the large amount of work done with this electrolyte, and the discrepancies should be relatively large because of its large B factor and relatively large E_j.

Method I utilizes the equation

$$E_j = -0.05915(2t_{\infty+} - 1)\left[\log \frac{C^{\alpha}}{C^{\beta}} - B'(\sqrt{C^{\alpha}} - \sqrt{C^{\beta}})\right]$$

which should be correct within the range of validity of the Debye-Hückel limiting-law and accurate to within one millivolt or so up to about 0.03 N. It is the most purely theoretical of the four methods.

Method II utilizes the equation

$$E_j = -0.05915\left[t_+^{av} \log \frac{a_+^{\alpha}}{a_+^{\beta}} - t_-^{av} \log \frac{a_-^{\alpha}}{a_-^{\beta}}\right]$$

in which the <u>average</u> values of the empirically determined transference numbers at C^{α} and C^{β} are used. Furthermore, the single-ion activity coefficients are <u>calculated</u> from the <u>extended</u> Debye-Hückel theory and thus are probably accurate up to 0.07 N. (In this range the Debye-Hückel theory has indirectly been verified by measuring $f_{\pm}$ and comparing it with $\sqrt{f_+ f_-}$ calculated from the theory.)

Method III utilizes the modified Nernst equation

$$E_j = -0.05915\,(2t_+^{av} - 1)\log\frac{a_\pm^{\alpha}}{a_\pm^{\beta}}$$

in which t_+^{av} is the average cation transference number as above and the mean activity coefficients are the "best values" gleaned from the results of several different experimental methods.

Method IV utilizes Methods I and Methods II in their respective unique ranges of validity. Where both solutions forming the junction are less than 0.01 N, the exact limiting-law equation of Method I is the method of choice since Method II does not precisely take the concentration-dependence of the transference numbers into account. On the other hand, where both concentrations are greater than about 0.01 N, Method II becomes the method of choice by default. Method II should be reasonably exact up to about 0.1 N if the two concentrations are nearly equal because the transference numbers are fairly slow functions of the concentration. (Since Method III assumes the equality of the ionic activity coefficients and does not adequately take the variation of t with concentration into account, it has nothing to recommend it a priori in any concentration range. It is included here for purposes of comparison since it is the method of computing E_j given in most textbooks.) For cases in which one of the concentrations lies well within the limiting-law range and one lies without, it is difficult to choose between Methods I and II. In these cases we use Method IV which mathematically divides the junction in question into two junctions: $C^{\alpha} \mid C^{\gamma} \mid C^{\beta}$ in which C^{γ} is given the somewhat arbitrary value of 0.01 N. For concreteness, if we wish to calculate E_j for $C^{\alpha} = 0.001$ N and $C^{\beta} = 0.05$ N, we use Method I to calculate

0.001 N | 0.01 N and Method II to calculate 0.01 N | 0.05 N. The sum of the two calculations is then E_j for 0.001 N | 0.05 N by Method IV.

Table 1 gives a comparison of values of E_j calculated by the four methods for various HCl concentration junctions in water at 25°C. The four sets of values obtained using the diverse methods--which, of course, employ different specializations of the same basic equation--are not much disparate except for cases in which one concentration is very low and the other is relatively high. It is interesting to note that Method III, while theoretically suspect, is vindicated a posteriori by the fact that its E_j values lie between those of Method I and Method II. Whether this would also be true in the case of other electrolytes has not been determined here. Another surprising observation is that the tabulated values of Method II can be rather accurately represented by the equation,

$$E_j = -0.05915\,(2t_{\infty +} - 1) \log \frac{C^{\alpha}}{C^{\beta}}$$

which is even simpler than the Nernst equation. Thus, according to either Method I or Method II, a circuit of three or more HCl solutions would--analogous to a circuit of metals--give zero emf.

The behavior of transference number with respect to concentration differs markedly among electrolytes--for HCl t_+ increases with C, for KCl t_+ is almost independent of C, for NaCl t_+ decreases with C. In these cases t_+ is rather accurately given by the limiting-law up to almost 0.01 N. By way of contrast, the concentration variations of f_+ or f_- calculated from the extended Debye-Hückel law are roughly parallel for different electrolytes up to about 0.1 N. The fact that, at concentrations above about 0.01 N, specific differences between ions of the same

TABLE 1

VALUES OF E_j IN MILLIVOLTS CALCULATED BY FOUR METHODS AS DESCRIBED IN THE TEXT FOR AQUEOUS HCl CONCENTRATION JUNCTIONS AT 25 DEGREES C.
(THE CONCENTRATIONS ARE IN MOLES PER LITER)

Junction Solutions		Method of Calculation			
$\hat{C}^{\alpha}$	$\hat{C}^{\beta}$	I	II	III	IV
0.0001	0.001	37.6	37.8	37.7	. . .
0.0001	0.005	63.5	64.1	63.9	. . .
0.0001	0.01	74.5	76.1	75.2	. . .
0.0001	0.1	109.3	113.8	112.3	112.8
0.001	0.002	11.2	11.3	11.2	. . .
0.001	0.005	25.9	26.1	26.0	. . .
0.001	0.01	36.9	37.5	37.3	. . .
0.001	0.02	47.7	48.9	48.2	48.2
0.001	0.05	61.6	64.0	62.9	63.1
0.001	0.1	71.7	75.5	74.0	74.5
0.002	0.005	14.7	15.0	14.8	. . .
0.002	0.01	25.7	26.2	25.9	. . .
0.002	0.02	36.5	37.5	37.0	37.0
0.002	0.05	50.4	52.5	51.5	51.9
0.002	0.1	60.4	63.9	62.5	63.3
0.005	0.01	11.0	11.3	11.2	. . .
0.005	0.02	21.8	22.6	22.3	22.3
0.005	0.05	35.7	37.5	36.8	37.2
0.005	0.1	45.7	49.0	48.0	48.6
0.01	0.02	10.8	11.3	11.1	. . .
0.01	0.05	24.7	26.2	25.5	. . .
0.01	0.1	34.8	37.6	36.7	. . .
0.02	0.05	13.9	14.8	14.6	. . .
0.02	0.1	24.0	26.4	25.5	. . .
0.05	0.1	10.1	11.6	11.1	. . .

valency type appear is an indication that interionic interactions also involve non-Coulombic forces.

Ideally, it should be possible to obtain precise values of E_j at any higher concentration for which the differential equation (8) is valid by inserting the empirical values of the transference numbers and the calculated values of the single-ion activity coefficients into the equation and using numerical integration. Unfortunately, the amount of labor required for each junction would be large. Furthermore, such an undertaking will remain of doubtful merit until methods of determining single-ion activity coefficients empirically beyond the limiting-law range are developed.

The Heterosolute Junction

Contrasted with the concentration junction, the heterosolute junction poses more experimental and theoretical difficulties. It is found experimentally that its emf usually varies with time and also with how the junction is formed. The method of formation which yields time invariance as well as the greatest reproducibility is the so-called "flowing junction" in which the two solutions flow toward a common, stationary boundary at a rate of at least ten drops a minute.* Since, in the experimental work to be described later, the non-salt-bridge heterosolute junction has not been studied, its treatment here will be cursory.

The first recorded attempt at calculating the emf of a heterosolute junction was made by Planck[1] who achieved a kinetic derivation with

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*An ambiguity in the flowing-junction method (in the case of very dilute solutions) that is often overlooked is caused by the concomitant streaming potential difference which is difficult to separate from the intrinsic junction emf.

[1] M. Planck, Ann. physik (3), 39, 161 (1890); (3), 40, 561 (1890).

with the aid of the following postulates:

a) The properties of the solvent are unchanged throughout the junction.

b) The mobility of the ions is constant throughout the junction.

c) The laws of ideal solutions are obeyed. (That is, the single-ion activities equal the ion concentrations.)

d) The junction is of the constrained diffusion type. (Ions may diffuse freely between the parallel planes A and B but to the left of A and the right of B the concentrations of the original solutions remain unaltered.)

Not only is the derivation quite involved, but the general final expression for the emf is transcendental. For the case of the homosolute junction, Planck's equation reduces to the previously derived Nernst equation (5). There is another case in which the final result is especially simple--that in which both solutions have the same concentration and one ion in common. Here, for two uni-univalent electrolytes sharing, for example, a common anion, Planck obtains

$$E_j = -\frac{RT}{\mathcal{F}} \ln \frac{U_{1+} + U_-}{U_{2+} + U_-} .$$

Henderson[1] was able to give a somewhat simpler derivation by starting with the equation

$$d\varphi = -\frac{RT}{\mathcal{F}} \sum_i \frac{t_i}{z_i} d \ln a_i$$

which is a generalization of the quasi-thermodynamic equation (8) derived

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[1] P. Henderson, z. physik. Chem. 59, 118 (1907); 63, 325 (1908).

previously. His assumptions are identical with those of Planck save that the assumption of a "constrained diffusion" junction is replaced by a "continuous mixture" junction in which the concentration of each ionic species is assumed to vary linearly from the bulk of one solution to the bulk of the other. The general final equation is different from that of Planck and is somewhat simpler. However, for the special cases mentioned above, it reduces to the same expressions.

For the junction HCl (0.1 N) | KCl (0.1 N) both the Planck and the Henderson treatments predict $E_j = 26.8$ mv. For the junction HCl (0.1 N) | KCl (0.01 N) Planck's equation predicts 52.7 mv while Henderson's predicts 57.3 mv. In many cases the disparity is greater than fifteen per cent.

In both the Planck and Henderson treatments the assumptions were made in order to achieve an analytical integration--not because they are the most physically reasonable. In order to reduce the amount of arbitrariness, MacInnes[1] gives a graphical method utilizing the assumption of a free diffusion boundary and using experimentally determined mean activity coefficients and concentration-dependent transference numbers. Thus, most of the simplifying assumptions of the analytical treatments are rendered unnecessary. Nonetheless, a questionable element remains in that it is necessary to assume that the two electrolytes diffuse independently. Apart from this, moreover, the graphical method is limited, at the present time, to the junction HCl (0.1 N) | KCl (0.1 N) since data of the requisite precision and completeness are lacking for other junctions. For

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[1] D. A. MacInnes, The Principles of Electrochemistry (Reinhold Publishing Corp., New York, 1939), pp. 237-243.

this junction graphical integration[1] predicts 28.2 mv for a free diffusion boundary and 28.6 mv for a mixture boundary.

If, as is often done, it is assumed that the activity of the chloride ion at a given concentration is independent of the kind of cation present in the solution, then it follows that the emf of an electrode reversible to the chloride ion is independent of the kind of chloride electrolyte in which it is immersed. Thus, it further follows that the emf of a cell composed of two electrodes reversible to chloride ions and the junction between two different chloride solutions of identical concentrations is just the emf of the junction. Many measurements by different workers have been made on cells containing the HCl (0.1 N) | KCl (0.1 N) junction and values distributed between 26.8 and 28.3 mv have been obtained.[2] Thus experiment, even granting the above assumption, does not furnish a conclusive test of the theory. In many cases involving other chlorides, the discrepancy between the predicted and the "observed" values is rather large.[3]

Since the graphical method is, at present, so limited by the lack of complete and precise data on the concentration variation of the transference numbers and the activity coefficients and since the analytical methods as yet cannot take the concentration variation into account even in the limiting-law region, theoretical calculations of the emf of hetero-solute junctions are of dubious accuracy--as, indeed, are the so-called experimental determinations which, at best, even in the limiting-law region, lack reproducibility.

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[1] Ibid., p. 243.

[2] Ibid., p. 230.

[3] Ibid., p. 236.

The Salt Bridge

Since in many kinds of electrochemical measurements (such as those of pH) liquid junctions are an unavoidable evil; since in most cases of practical importance the calculation of E_j is impossible (because of unknown solution composition) or at best is of doubtful validity; and since no reliable empirical method of obtaining E_j is generally available, for a long time methods of abolishing or at least minimizing E_j have been sought. The most common expedient is to interpose a concentrated solution of a binary salt (whose ions have nearly the same mobility) between the two solutions which would otherwise form a single junction. This "salt bridge" is usually composed of saturated potassium chloride solution but other electrolytes are occasionally used instead. In essence the salt bridge is a device which puts two liquid junctions of supposedly small and opposed emf in the place of the single junction of larger emf. The rationale behind this artifice will now be given.

Consider the system of two junctions formed by the three solutions $S_1(C_1) \Big| S\ (C) \Big| S_2(C)$ in which S is the salt-bridge solution of concentration C. For the $S_1(C_1) \Big| S\ (C)$ junction the Henderson equation becomes for uni-univalent electrolytes

$$E_j^{(1)} = \frac{RT}{\mathfrak{F}} \frac{C\,(U_+ - U_-) - C_1(U_+^{(1)} - U_-^{(1)})}{C\,(U_+ + U_-) - C_1(U_+^{(1)} + U_-^{(1)})} \ln \frac{C\,(U_+ + U_-)}{C_1(U_+^{(1)} + U_-^{(1)})} \, . \qquad (11)$$

An analogous expression obtains for $E_j^{(2)}$ but with the opposite sign. If it is arranged that $C \gg C_1$ and C_2 , then $E_j^B \equiv E_j^{(1)} + E_j^{(2)}$ becomes

$$E_j^B = \frac{RT}{\mathfrak{F}} \frac{U_+ - U_-}{U_+ + U_-} \ln \frac{C_2(U_+^{(2)} + U_-^{(2)})}{C_1(U_+^{(1)} + U_-^{(1)})} \, .$$

Now the logarithmic factor gives very roughly the expected emf of the $S_1(C_1) \mid S_2(C_2)$ junction. Thus, the salt-bridge diminishes the unaltered emf by roughly the factor $\frac{U_+ - U_-}{U_+ + U_-}$ which is small if the salt-bridge electrolyte has ions of nearly equal mobility. In water at 25°C at a concentration of 0.20 N, the cation transference number of KCl is 0.489.

Thus $$\frac{U_+ - U_-}{U_+ + U_-} = (2t_+ - 1) = -0.022$$

and if the theory were on firm ground we could confidently assert that the saturated potassium chloride salt bridge reduces the liquid junction emf to a few per cent of its unaltered value or, in most cases, to about one or two millivolts. An uncertainty of this magnitude can just be tolerated in many electrochemical measurements.

Unfortunately, the matter is scarcely this simple. Even taking for granted that the fundamental differential equation is correct, many assumptions (which have been previously stated) must be made before the above equation (11) emerges. In the case of saturated potassium chloride (4.2 N at 25°C) the assumption of constant mobility and an activity coefficient equal to unity throughout the concentration range to 4.2 N is utterly preposterous. Thus, the actual salt-bridge emf may be only a fraction of a millivolt or many millivolts--there is no way of knowing at present. The consensus seems to be that it is safe to assume the salt-bridge emf to be less than five (or, in rare cases, ten) millivolts. In summary then, the salt-bridge artifice is an expedient which probably reduces, but in no way eliminates, the uncertainty occasioned by the inclusion of a liquid junction in an electrochemical circuit. In the case of a concentration junction at low concentrations, theoretical calculation would seem preferable to the use of the salt bridge.

CHAPTER IV

THE VARIABLE CAPACITANCE METHOD OF MEASURING VOLTA POTENTIAL DIFFERENCE

Various techniques have been developed to measure the contact potential difference between two metals. Exhaustive lists of references on metal-metal contact potential experiments are available in the literature.[1,2] The techniques which have been most frequently employed are based on photoelectric, thermoinic, electron beam, gas ionization, and variable capacitance methods of measurement. The variable capacitance method (as was mentioned in Chapter I) was invented by Kohlrausch but refined by Kelvin, after whom it is usually named. This method of measuring metal-metal contact potential difference in vacuo, the first historically, fell into desuetude but has recently been revived in England. With the modern refinements employed, it is again believed[3] to be the method of choice for cases in which the metal sample is of sufficient size. However, by far most metal-metal contact potential differences have been determined from the photoelectrically or thermionically measured work functions. As has been mentioned previously, these measurements

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[1] H. B. Michaelson, J. Franklin Institute 249, 455 (1950).

[2] W. R. Harper, Proc. Roy. Soc. 205A, 83 (1951).

[3] J. C. Riviere, Proc. Phys. Soc. 70B, 676 (1957).

yield values usually in the range between one and five volts. The agreement between different workers is often poor and, at best, is within about eighty millivolts. However, the variation among measurements taken with the same apparatus employed in the identical manner is often only between twenty to fifty millivolts. This limit of reproducibility is thought to be caused by different amounts of surface impurities present even at the highest vacuum attainable.

Of the several techniques listed above, only those utilizing gas ionization and variable capacitance are adaptable to contact potential measurements between a metal and an aqueous solution since the unavoidable presence of water vapor precludes the possibility of accurately employing electron space currents. In the gas ionization technique, the gas between a narrow gap separating the two phases in contact is ionized (usually by polonium) and a potentiometric "IR drop" is adjusted so that no current flows in the circuit. At this state of balance the potentiometric potential difference is equal and opposite to the Volta potential difference between the phases.

In spite of the fact that the gas ionization method is perhaps somewhat simpler, the method utilized in the experimental work to be described later is the variable capacitance method. Of the two, the gas ionization method contains more potential ambiguities--for example, alpha particle bombardment could alter the surfaces. Furthermore, there is the practical consideration that a variable capacitance instrument can easily be adapted to the gas ionization technique whereas the converse is not necessarily true. An additional advantage is that in the later experimental work the solution surfaces were covered with a film of non-conducting liquid; in which case the gas ionization technique would probably be ineffective or at least ambiguous.

The Variable Capacitance Method

Since it has previously been shown that the insertion of a third electronic conductor between two others does not affect the Coulombic potentials of the original two, we shall for simplicity consider a system constituted of only two metals a and b which are fashioned into two opposing plates, the quadrants of a quadrant electrometer, and connecting wires as illustrated in Figure 1. a' and a'' are of the identical metal as a --the primes indicate that they can be at a different potential than a.

The theory of the experimental method will receive more detailed consideration in the next section. For now, suffice it to say that the potentiometric "IR drop" $\Delta V \equiv \varphi^a - \varphi^{a'}$ is adjusted in sense and magnitude until a "balance" is attained; that is, until a movement of plate b with respect to plate a produces no deflection of the quadrant electrometer. As will be made apparent later, this state of balance or null deflection implies that the opposed surfaces of a and b are at the same Volta potential.

Referring to Figure 1, we see that ψ^b may be written as

$$\psi^b \equiv \psi^{a''} + (\varphi^{a''} - \psi^{a''}) + (\varphi^b - \varphi^{a''}) + (\psi^b - \varphi^b)$$

or, in other notation,

$$\psi^b = \psi^{a''} + \chi_\varphi^a + \varphi^b - \varphi^a - \chi_\varphi^b. \qquad (1)$$

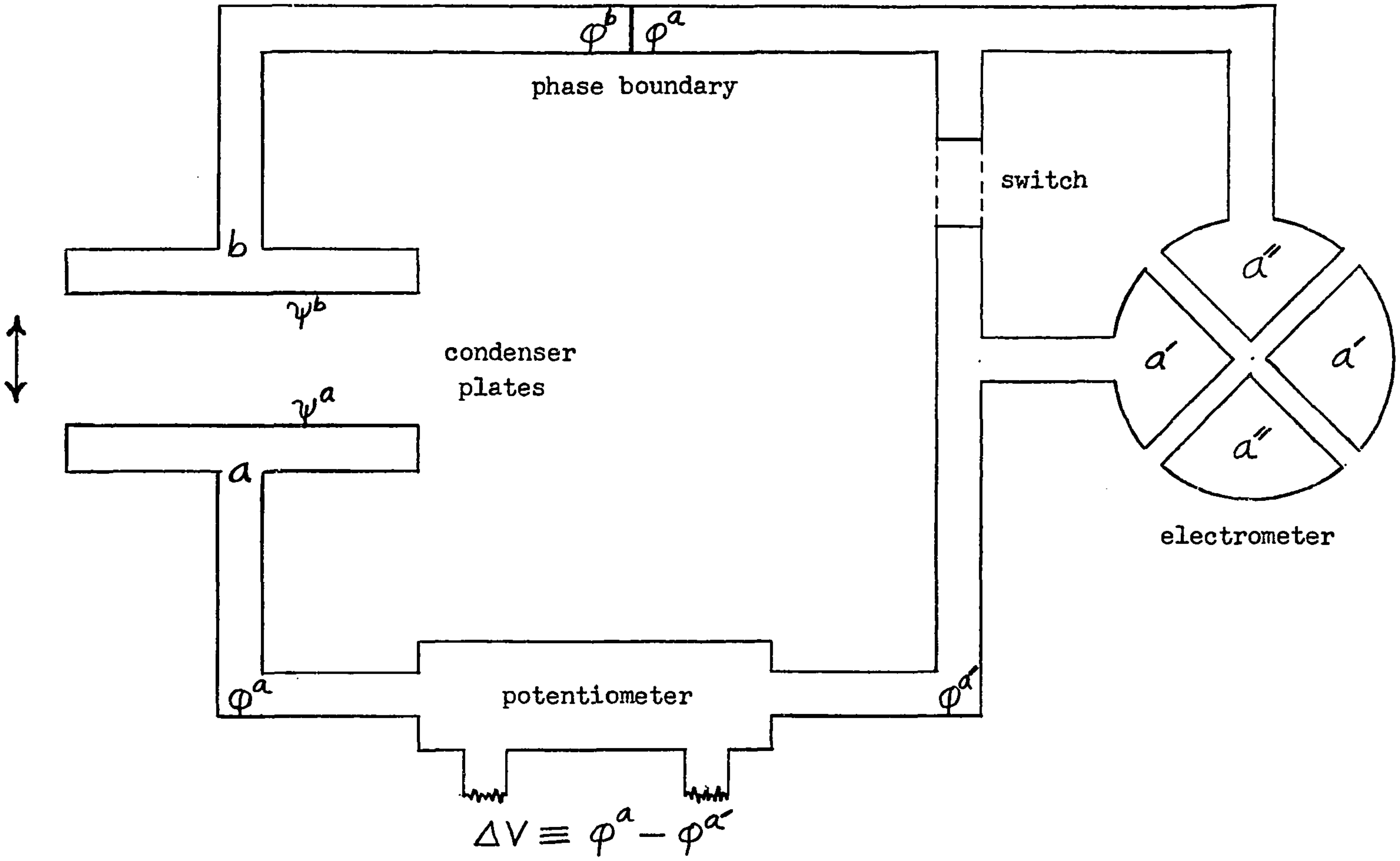

Fig. 1. The Variable Capacitance Instrument.

Similarly,

$$\psi^{a} = \psi^{a'} + \chi_{\varphi}^{a'} + \Delta V - \chi_{\varphi}^{a}.$$

Assuming* that $\chi_{\varphi}^{a'} = \chi_{\varphi}^{a}$ we obtain

$$\psi^{a} = \psi^{a'} + \Delta V. \qquad (2)$$

Subtraction of equation (1) from equation (2) gives:

$$\psi^{a} - \psi^{b} = \psi^{a'} - \psi^{a''} + \varphi^{a} - \varphi^{b} + \chi_{\varphi}^{b} - \chi_{\varphi}^{a} + \Delta V. \qquad (3)$$

Now in practice both pairs of quadrants are connected metallically by closing the switch (which makes $\psi^{a'} = \psi^{a''}$);* then the switch is opened and the plates are separated. If the switch operates correctly (a method of dealing with imperfect switches will be given in Chapter VI), then $\psi^{a'} = \psi^{a''}$ after the switch is opened also. At balance, as is shown by no deflection of the electrometer vane, $\psi^{a'} - \psi^{a''}$ still equals zero when the plates are separated. Thus, equation (3) becomes at balance

$$0 = \varphi^{a} - \varphi^{b} + \chi_{\varphi}^{b} - \chi_{\varphi}^{a} + \Delta V_0,$$

or, we have

$$-\Delta V_0 = \varphi^{a} - \varphi^{b} + \chi_{\varphi}^{b} - \chi_{\varphi}^{a}. \qquad (4)$$

Thus, ΔV_0 is the negative value of the contact potential difference between the metals a and b.

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*In practice this equality is probably not exactly true because of different surface impurities on even ostensibly identical pieces of metal. However, even if the equality is not at all true the derivation is still valid because the only effect of the inequality is to shift the "zero" of the electrometer.

In practice, of course, surface impurities such as oxides and adsorbed gases are almost inevitably present on the metal surfaces so that what is actually measured is the contact potential difference between the surface which happens to exist on b and the surface which happens to exist on a opposite b.

Here for conceptual simplicity we have considered a quadrant electrometer to be the potential-change detector. Indeed, this was also the instrument used in our earliest experimental investigations. In our later work we employed a vacuum-tube electrometer of special design. The treatment presented in this chapter is also valid for a vacuum-tube electrometer. This was verified in our work by showing that the measurements of contact potential using both instruments are identical within the experimental uncertainty.

Theoretical Sensitivity of the Variable Capacitance Method

Since the variable capacitance method is an electrostatic measurement, it is evident that the electrostatic shielding of the instrument must be extraordinarily good if high accuracy is to be attained. Details of the shielding construction will be given in Chapter VI.

For simplicity, as before, the system proper will be idealized to the case of only two metals with the shielding consisting of a third metal. It is easy to show that the derivation gives the same result for a system and shielding consisting of any number of different metals. Thus, the system to be considered here is that of Figure 1 surrounded by electrostatic shielding composed of metal s. The equivalent circuit is represented in Figure 2 in which $\hat{C}$ is the capacitance of the two opposed plates of metals a and b. C_s is the total capacitance between the

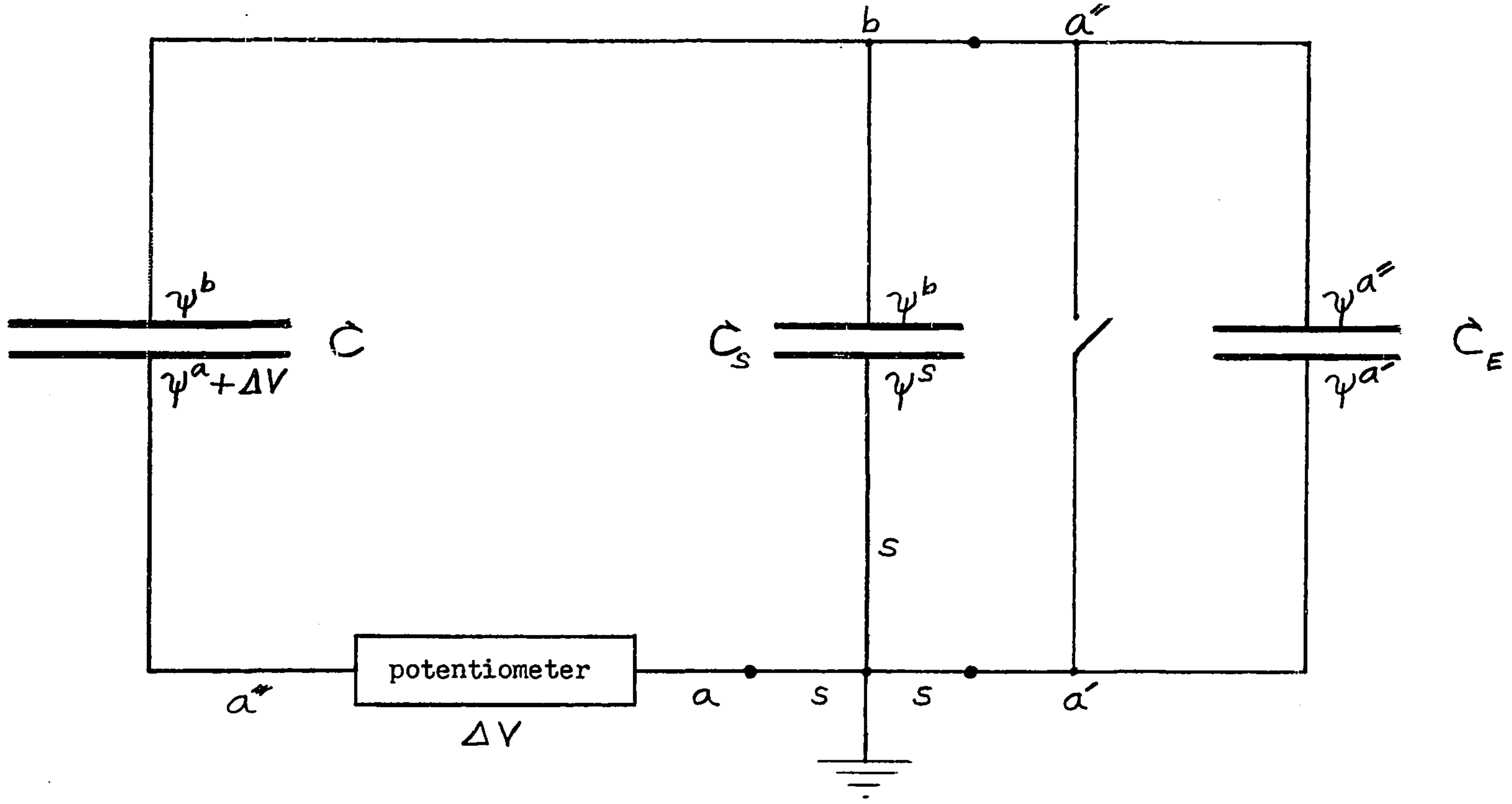

Fig. 2. The Equivalent Circuit of the Variable Capacitance Instrument

insulatable of "floating" part of the circuit and the electrostatic shielding, and C_E is the capacitance of the electrometer. As indicated in the figure, the Volta potential difference between the condenser plates is $\psi^b - \psi^a - \Delta V$ and that between the "floating" part of the circuit and the shielding is $\psi^b - \psi^s$.

We further introduce the notation that $C = C_0$ when the plates are at the distance of least separation and $C = C_0 - \Delta C$ when the plates are at the distance of maximum separation in the measuring process. Since motion is a requisite of the measurement, it must be true that C_S changes by at least a small amount. To allow for this we let C_s become $C_s + \delta C$ when the plates are at the distance of maximum separation.

Thus, with the plates at least separation and with the switch closed, the total electrostatic charge on the insulatable part of the circuit is

$$Q = C_0\left(\psi_0^b - \psi^a - \Delta V\right) + C_s\left(\psi_0^b - \psi^s\right). \tag{5}$$

We now assume that the switch behaves correctly and that the insulation is adequate so that the total charge remains the same after the switch is opened. Then, after the plates have been separated, we have

$$\begin{aligned} Q = {} & \left(C_0 - \Delta C\right)\left(\psi^b - \psi^a - \Delta V\right) \\ & + \left(C_s + \delta C\right)\left(\psi^b - \psi^s\right) + C_E\left(\psi^b - \psi_0^b\right). \end{aligned} \tag{6}$$

Elimination of Q between equations (5) and (6) and judicious algebraic manipulation enables us to write:

$$\psi^b - \psi_0^b = \frac{\left(\psi_0^b - \psi^a - \Delta V\right)\Delta C - \left(\psi_0^b - \psi^s\right)\delta C}{C_s + \delta C + C_E + C_0 - \Delta C} \tag{7}$$

where $\psi^b - \psi_0^b$ represents the voltage deflection read on the electrometer. Thus, at balance, ΔV_0 does not equal $\psi_0^b - \psi^a$, the contact potential difference between the metal plates, unless $(\psi_0^b - \psi^s)\delta \grave{C}$ is negligible. In Chapter VII design techniques will be described which make both $\delta \grave{C}$ and $\psi_0^b - \psi^s$ separately small so that their product is negligible. Assuming this to have been done, we have

$$\psi^b - \psi_0^b = \frac{\Delta \grave{C}}{\grave{C}_s + \grave{C}_E + \grave{C}_0 - \Delta \grave{C}} \left(\psi_0^b - \psi^a - \Delta V\right). \quad (8)$$

in which $\psi_0^b - \psi^a - \Delta V$ is the Volta potential difference between the plates when the switch is closed.

If the apparatus sensitivity $\mathcal{S}$ is defined by

$$\mathcal{S} \equiv \frac{\text{voltage deflection of electrometer}}{\text{voltage between plates}},$$

then
$$\mathcal{S} = \frac{\Delta \grave{C}}{\grave{C}_s + \grave{C}_E + \grave{C}_0 - \Delta \grave{C}}. \quad (9)$$

It is interesting to note that when $(\psi_0^b - \psi^s)\delta \grave{C}$ is negligible, the sensitivity does not depend on the existence of the phenomenon of contact potential. Equation (9) is of great value in determining the size and configuration which an apparatus must have in order to furnish a given sensitivity.

CHAPTER V

A METHOD FOR DETERMINING LIQUID-JUNCTION POTENTIAL DIFFERENCES

A Method for Measuring Liquid-Liquid Contact Potential Differences

The variable capacitance method of measuring the contact potential difference between two metallic conductors described in Chapter IV is also valid if the lower metal plate is replaced by a conducting liquid. In general this measurement will be of the metal-solution Volta potential difference rather than of the metal-solution contact potential difference because of the usual necessity of putting other electrodes in the solution. In this chapter we shall explore the possibility of measuring solution-solution contact potential differences by an elaboration of the variable capacitance method.

The measurement of solution-solution contact potential differences is complicated by the fact that we live in a gravity field. In a non-zero gravity field two liquid phases cannot face each other without the interposition of at least one wall of the containing vessels. For this reason and also because no all-liquid electrometer has yet been devised, it is necessary to use an intermediate metallic phase in the measurement. In a non-spinning artificial satellite it should be possible to measure liquid-liquid contact potential differences directly between two spheres of the liquids.

For more mundane laboratories the system schematized in Figure 3 is suggested. A single metal disk M serves as the Volta potential probe for solution α and for solution β. When M is over α the liquid switch S_L--a glass tube filled with solution β --is in the position drawn in order that the "circuit" be completed. When M is positioned over β, S_L is put into the position indicated by dotted lines in order to complete the β "circuit." E_o is essentially a reference electrode; its function is to connect solution β to the potentiometer. E_j represents the emf of the junction between solutions α and β. This junction may be either static or flowing but is represented here as a static junction in a matrix of glass wool. E_1 and E_2 are interchangeable electrodes which provide electrical contact while allowing the levels of α and β to be varied independently without disturbing the liquid junction.

Since the theory of each Volta potential measurement is the same as that developed in Chapter IV, we shall here show only that the difference of the two Volta potential measurements indeed gives the contact potential difference between the two liquids.

Measurement I: M over α

Using the notation of the previous chapters, we can write at balance (null electrometer deflection) $\psi^{\alpha} - \psi^{M} = 0$ in which

$$\psi^{\alpha} = \varphi^{\text{ground}} + \Delta V'_{\alpha} + E_o + E_j - E_2 + E_1 - \chi_{\varphi}^{\alpha}.$$

Whence,

$$\Delta V'_{\alpha} = \psi^{M} - \varphi^{\text{ground}} - E_o - E_j - E_1 + E_2 + \chi_{\varphi}^{\alpha}.$$

Now unless E_1 and E_2 are exactly identical they may introduce a net emf

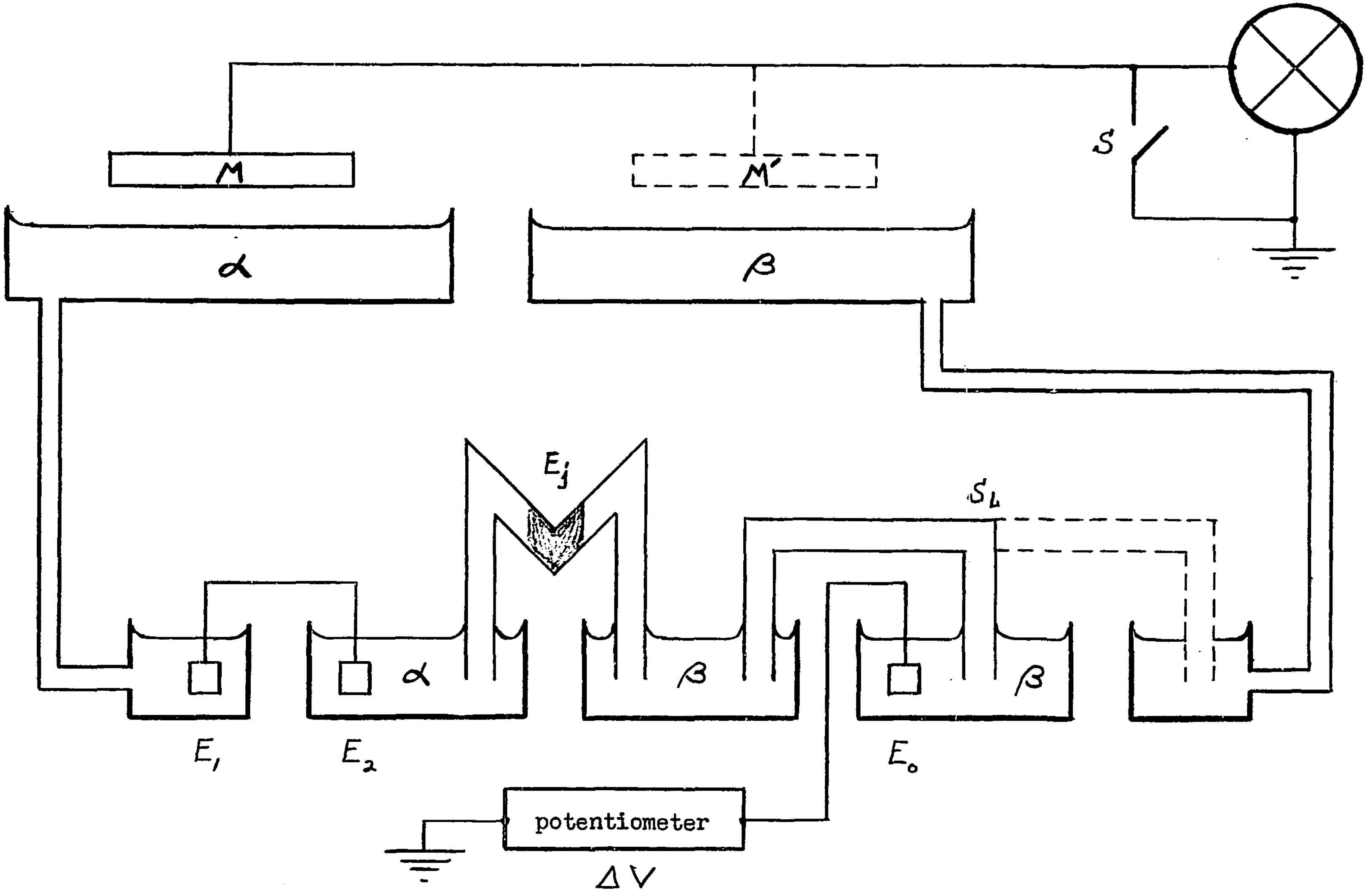

Fig. 3. The Principle of the Liquid-liquid Contact Potential Measurement

into the α circuit. In order to preclude this possibility, E_1 and E_2 are interchanged and a new balance is taken. Then

$$\Delta V_\alpha'' = \psi^{M} - \varphi^{\text{ground}} - E_o - E_j + E_1 - E_2 + \chi_\varphi^{\alpha}.$$

Thus, $$\Delta V_\alpha \equiv \frac{\Delta V_\alpha' + \Delta V_\alpha''}{2} = \psi^{M} - \varphi^{\text{ground}} - E_o - E_j + \chi_\varphi^{\alpha}.$$

Measurement II: M over β

Making the basic assumption (which can easily be checked experimentally) that changing the position of the metal Volta potential probe does not change its Volta potential, we can write for this case also

$$\psi^{\beta} - \psi^{M} = 0$$

in which $$\psi^{\beta} = \varphi^{\text{ground}} + \Delta V_\beta + E_o - \chi_\varphi^{\beta}.$$

Whence, $$\Delta V_\beta = \psi^{M} - \varphi^{\text{ground}} - E_o + \chi_\varphi^{\beta}.$$

The difference of the two potentiometric balancing potentials yields

$$\Delta V_\beta - \Delta V_\alpha = E_j - \chi_\varphi^{\alpha} + \chi_\varphi^{\beta} \qquad (1)$$

or, alternatively expressed,

$$\Delta V_\beta - \Delta V_\alpha = \varphi^{\alpha} - \varphi^{\beta} + \chi_\varphi^{\beta} - \chi_\varphi^{\alpha}.$$

Thus $\Delta V_\beta - \Delta V_\alpha$ measures the solution-solution contact potential difference.

Determination of the Liquid-junction Emf

We have seen that the difference of the two metal-solution Volta potential measurements gives the solution-solution contact potential difference. It is apparent from equation (1) that the liquid junction emf E_j would be determined if $\chi_\varphi^\alpha - \chi_\varphi^\beta = 0$, that is, if the two solutions had equal surface potentials. In the case of two different solvents this is definitely not true; in the case of dilute aqueous solutions it is probably true within limits as will be elaborated.

Several attempts, of which those of Hush[1] and Strehlow[2] are the most recent, have been made at calculating χ_φ for pure water. The most recent values given range from about - 0.3 to - 0.5 v (that is, the positive ends of the water dipoles point toward the gas phase). However, some uncertainty even remains concerning the sign of χ_φ for pure water. It is evident that such calculations, while of interest in themselves, are at present useless as an aid in determining E_j because of their quasi-speculative nature. Furthermore, whatever the value of χ_φ for pure water, it is only the variation of χ_φ with the concentration and kind of electrolyte which is of immediate interest here.

Fortunately, some experimental work of a different nature from contact potential measurements furnishes some evidence for the variation of χ_φ among different aqueous solutions. Görlich[3] confirmed earlier observations that water exhibits a true photoelectric effect and carried on extensive experiments under carefully controlled conditions. Electron scattering by water vapor was minimized by using reduced pressure and placing the collecting electrode very close to the solution surface. Several effects such as the influence of gas pressure and frequency on the

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[1] Hush, Aust. J. Sci. Res. <u>A1</u>, 482 (1948).

[2] H. Strehlow, Z. Elektrochemie <u>56</u>, 119 (1952).

[3] P. Görlich, Ann. d. physik <u>13</u>, 831 (1932).

photoelectric current per unit incident energy were studied. However, the data of importance here pertain to the effect of concentration and kind of solute on the threshold wave-length: it was found that the threshold wave-length was the same (2035 ±5 Å) as for pure water up to concentrations of 0.5 N. Altogether five different salts of different valence types were studied.

Thus, since the work function depends on the surface potential as well as the chemical potential (see Chapter II), it seems probable that χ_φ for aqueous solutions is a constant independent of concentration and kind of electrolyte up to perhaps 0.5 N. If this is so, equation (1) could be written as $\Delta V_\beta - \Delta V_\alpha = E_j$ and the liquid junction emf could be determined ipso facto by contact potential measurement and would thereby become the first phase-boundary emf to be at all determinable.

However, there is no need to rely blindly on this interpretation of the photoelectric measurements alone. To some degree a check is possible by ascertaining whether or not the contact potential differences agree with the calculated values of the liquid junction emf. As is made clear in Chapter III, the theory of E_j for the homosolute junction formed between very dilute ($<$0.01 N) solutions seems to be on firm ground. In the case of much-studied electrolytes such as HCl for which the relevant constants are known to relatively high precision, it might be surmised that the calculated values of E_j for very dilute solutions are accurate to within a few per cent. Thus, the measurement of the solution-solution contact potential differences between very dilute solutions of certain electrolytes can serve as a check on whether or not χ_φ is independent of concentration at low concentrations. At higher concentrations (up to

0.1 N) the theory is probably fairly reliable as long as the range of concentration between the solutions forming the homosolute junction is small.

Thus, once agreement has been found between the measured contact potential difference and the calculated liquid junction emf for different solutes forming homosolute junctions, one can with some confidence proceed to measure the essentially unknown emf of the heterosolute junction and the salt bridge. Almost none of the very important junctions in electrochemistry can be calculated with any confidence. This is especially true in pH measurements where the establishment of a rational scale of pH awaits the determination of the relevant liquid junction emf's. Various methods of forming the junction (including semi-permeable membranes) could be utilized and studied for their effects. Even the emf between solutions of unknown composition could be determined if the total concentration is known to not be too high.

Determination of Single-ion Activity

In practical chemistry and biology it is the liquid junction emf itself which is of direct importance while the determination of the activities of the individual ionic species is of derived importance. In theoretical chemistry the converse is true since knowledge of the elusive single ion activities would facilitate the calculation of many other properties of solutions and would serve as a check on several theories.

In accordance with the development given in Chapter III, the following equation for the emf E of an electrochemical cell with electrodes reversible to the anion can be written:

$$E = E_j + E_1 - E_2 = E_j + \frac{RT}{\mathfrak{F}} \ln \frac{a_-^{\alpha}}{a_-^{\beta}} \qquad (2)$$

in which E_1 and E_2 are the emf's of identical electrodes dipping into solutions α and β respectively. Thus, if E and E_j are measured, the ratio of the activity coefficients of the anion in solutions α and β can be calculated. Moreover extrapolation of β to extreme dilution gives the activity coefficient of the anion in α, and conversely.

However, a more direct way of determining the single-ion activities is available: if α and β in the contact potential apparatus are connected by E_1 dipping into α and E_2 dipping into β, then the measured contact potential difference gives

$$E_1 - E_2 = \frac{RT}{\mathcal{F}} \ln \frac{a_-^{\alpha}}{a_-^{\beta}}$$

directly. This technique should be the more reliable since the electrode emf's are more constant in time than is the liquid junction emf.

A simple check on the precision of the measurements (but, unfortunately, not on the assumed equality of the surface potentials) can be made by measuring $E_1 - E_2$, E_j, and E separately and comparing E with $E_j + E_1 - E_2$.

Regrettably, however, little inaccuracy in the determination of $E_1 - E_2$ can be tolerated if values of the activity coefficient precise enough to be of importance are to be obtained. For example, since

$$\frac{a_-^{\alpha}}{a_-^{\beta}} = e^{\mathcal{F}/RT\,(E_1 - E_2)}$$

or, $$f_-^{\alpha} = \frac{f_-^{\beta} C^{\beta}}{C^{\alpha}} e^{\mathcal{F}/RT\,(E_1 - E_2)},$$ we obtain

$$\frac{df_-^{\alpha}}{f_-^{\alpha}} = \frac{\mathcal{F}}{RT}\, d\,(E_1 - E_2) = 39.0\, d\,(E_1 - E_2) \qquad \text{at } 25^{\circ}\text{C}.$$

Thus, an inaccuracy of one millivolt in the determination of $E_1 - E_2$ would produce an inaccuracy of four per cent in the value of the activity coefficient. A check on the validity of the extended Debye-Hückel theory would require an accuracy of at least two per cent.

CHAPTER VI

THE EXPLORATORY EXPERIMENTAL WORK

The Exploratory Apparatus

The original purpose of our investigation was to make an attempt at determining phase-boundary potential differences. Specifically, our main interest lay in a measurement of the metal-solution emf--the classical problem of electrochemistry. Our tentative intent was to effect the determination by means of contact potential measurements. Many paper-and-pencil stratagems were devised--quadrant electrometers with liquid-film vanes, quadrant electrometers with liquid quadrants, and variable-capacitance electrometers with both metal and liquid encased in identical plastic films--but all shared the same shortcoming of introducing as many unknown phase-boundary potential differences as they abolished. One superficially promising artifice involved abolishing the water interface and its concomitant dipole orientation by using a gradual gradient of various organic solvents from oil on top to water on the bottom and performing the contact potential measurement with a "clean" Volta potential probe above the oil in an inert gas at reduced pressure. However, the coup de grace was administered to our naive hopes by the eventual realization that a Coulombic potential difference would even exist between perfectly clean metal and vacuum. It was then sadly admitted that, because of differing surface potentials, contact potential measurements offer no possibility of determining phase-boundary potential differences between unlike phases. We had been misled by the older literature which assumed that a measurement of the contact potential difference between two perfectly clean metals is per se a determination of their phase-boundary potential difference.

We then directed our attention toward the possibility of using the contact potential technique to determine the junction emf between dilute aqueous solutions which could be expected to have nearly identical surface potentials. The photoelectric work of Görlich mentioned previously strengthened the contention of equal surface potentials. Measuring the contact potential difference between two solutions seemed to promise more experimental simplicity than the classical measurement between two metals, since the excruciatingly meticulous vacuum technique necessary to obtain and maintain clean metal surfaces would be neither necessary nor possible. However, as was later amply validated in the laboratory, two other considerations nullify this advantage: the need for at least an order-of-magnitude greater sensitivity than in the metal-metal case with the attendant need for special electrostatic shielding and the necessity of obtaining solution surfaces totally free of organic dipoles. These requirements were destined to make the final apparatus much larger and more elaborate than was originally forseen and to necessitate a corresponding refinement of technique.

In order to gain experience with contact potential measurements in general and to carry out some preliminary measurements designed to show what equipment and techniques would be necessary for the ultimate measurements, we early constructed a simple, small instrument which we shall here designate as the "exploratory apparatus." This apparatus consisted externally of a one-foot cube constructed of galvanized sheet iron on five sides. To the open side a brass flange was soldered and was provided with bolts so that the hood could be tightened down against a gasket on an aluminum base-plate in order to furnish an air-tight seal. Two Lucite windows were provided and a large rectangular projection of galvanized sheet iron was fashioned into one side to furnish a niche for storing the plastic sheet as described in the Appendix. This sheet iron hood and the aluminum base plate formed an essentially air-tight Faraday cage.

In the early experiments the contact potential difference was measured between two accurately plane, horizontally parallel, metal discs of six inch diameter. At first, a brass and aluminum pair of plates were used; these were later replaced by a brass pair plated heavily with nickel and gold. The upper plate was rigidly supported by a polystyrene rod attached to a supporting framework and its angle of tilt could be accurately adjusted. The lower plate was attached by means of a polystyrene rod to a five-eighth inch diameter vertical shaft passing through the one-half inch aluminum base plate and controlled in vertical translation by a finger-manipulated split-clamp and adjustable stop-clamp. Near one corner a similar vertical shaft was provided to furnish a support for a rotatable plastic sheet (see Appendix).

The lower plate was connected to a potentiometer while the fixed, upper plate was connected through a grounding switch to an electrometer. The "floating" or upper plate-switch-electrometer part of the circuit was insulated by polystyrene of one-inch minimum surface path length and was thoroughly shielded electrostatically by sheet metal. (Screen wire--probably because of static charge carried by falling dust--did not prove totally effective.) Since ordinary solid-dielectric coaxial cable had too much capacitance, the connections were made with air-dielectric, aluminum flexible tubing of two-inch internal diameter. The schematic diagram of this apparatus is that shown in Figure 1 of Chapter IV.

Considerable difficulty was experienced in devising a suitable grounding switch. (No discussion of this problem was found in the contact-potential literature.) Ideally, when the switch is opened (system ungrounded), the system should stay at ground potential except for very slow leakage drift. In practice, with four different types of switch contacts this condition was never realized. Whenever contact with ground was broken, large deflections, random in magnitude and sense, occurred. These deflections naturally make the contact potential measurement unreliable, since a requisite of the measurement is that the potential of the "floating" part of the circuit at the moment the plates are separated be the same as when it is grounded. These potential changes at the instant contact is broken are probably due to last-millisecond transfer of charge as the two metal oxide films separate. A large part of this charge transfer is due to sixty-cycle stray fields from alternating currents which induce alternating emf's in the shielding and ground connection. (A discussion of this effect will be given in the chapter devoted to the final apparatus.) Since, even when all alternating currents in the room were turned off, a smaller but still appreciable and mostly unidirectional effect remained, a small part of the effect is probably due to intrinsic properties of the separating oxide films.

The problem was finally solved by accepting these potential fluctuations of the switch as inevitable (they were found to also occur between tungsten contacts in a vacuum) and designing a variable capacitor (charged by contact potential difference) which afforded control over the potential of the "floating" system after the switch was opened. The variable capacitor and switch were combined in a single unit by constructing a large rocker-arm double-dip mercury switch in which the two mercury wells were grounded and the metal rocker-arm was connected to the "floating" part of the circuit. A second rocker-arm switch--included for another purpose--was positioned beside the first. Well-cleaned polystyrene of one-inch minimum surface path provided the insulation and a 8x8x10 inch cage of sheet aluminum provided electrostatic shielding. The shielding was completely maintained in spite of rocker-arm motion by having the handle move an aluminum strip along with the rocker-arm. Contact with the mercury was made by small amalgamated brass rods on either end of the rocker-arm. The mercury wells were made of plastic after it was discovered that wells made of brass with three-eighth inch thick containing walls allowed the mercury to diffuse through at the rate of two drops an hour! The internal contact potential fields were adjusted by lining the inside of the cage with aluminum foil and, by trial and error, putting pieces of aluminum foil around the rocker arms. When the fields were thus adjusted, movement of the rocker-arm between the two grounded positions allowed the potential of the "floating" part of the circuit to be adjusted (either positively or negatively) to bring the electrometer back to its zero (grounded) position and thus compensate for the deflection caused by breaking ground contact. The second rocker-arm may be used as a "vernier" adjustment for the internal contact potential fields. This whole procedure, while difficult to describe in detail, can be learned easily with practice.

Since, when the work was started, no commercial vacuum-tube electrometer possessed the requisite high input impedance, low grid current, and high sensitivity necessary for precise contact potential measurement, the early measurements were made with a standard quadrant electrometer. This instrument furnished a sensitivity (in terms of extreme variation) of about ±8 millivolts and was used for about seven months. Its chief disadvantage lay in its relatively long period so that a series of null determinations required about forty-five minutes. Moreover, low zero-drift was only attained after the suspension was aged *in situ* for about a month; thus, changing the sensitivity by changing suspensions was impractical.

Meanwhile, a line of high impedance, high sensitivity vacuum-tube electrometers (Keithley Instruments, Inc., Cleveland, Ohio) had become available and the model 200B was purchased. This electrometer has a battery-powered, two-stage balanced-bridge amplifier with a cathode-follower output. The input tubes are a matched pair of Raytheon #5886. The full-scale voltage range is variable from eight millivolts to twenty volts. Because of practically complete negative feedback, the voltage drift after two hours warm-up is less than one millivolt an hour. The input impedance is greater than 10^{14} ohms and the grid current varies from about 4×10^{-15} ampere to about 3×10^{-14} ampere depending on the actual matched pair of input tubes used and on their age. Accuracy on all scales is within two per cent and is essentially independent of age. For our work a very important feature of this instrument is that the needle can be electrically centered on the scale, thus enabling the instrument to be used like a galvanometer. While the life of the batteries is rated at four hundred hours, it not infrequently happens that one of the miniature thirty-volt batteries develops emf fluctuations after a hundred hours or less of operation. Experience has shown that it is advisable to replace the D-cell filament supply after two hundred hours and to keep a complete complement of replacement tubes on hand--the #5886 tubes sometimes go bad in less than a thousand hours.

Besides the advantage of higher sensitivity, the chief advantage of the vacuum-tube electrometer over the quadrant electrometer is its much faster response time. With the vacuum-tube instrument the exact course of the potential change as the plates are separated can be observed and extraneous fields due to shielding contact potentials or to static charge can thereby be detected. And, most important of all, the time required for a series of null determinations is reduced from about forty-five minutes to about five minutes. A disadvantage of the vacuum-tube electrometer is that its grid current charges the "floating" part of the circuit after ungrounding. In the case of the exploratory apparatus of about 110 $\mu\mu f$ total capacitance, a grid current of about 2×10^{-14} ampere caused a voltage drift of 12 mv/min toward the positive side of the scale. In practice the rocker-arm switch was moved to put the needle to the negative side of zero and the plates were separated at the instant the needle crossed zero under the impetus of the grid current. But, of course, the steady needle motion introduced some uncertainty into the measurement, so that, while the intrinsic (no grid current) sensitivity of the apparatus was calculated to be two millivolts, the effective sensitivity was only about four millivolts. In the case of the final apparatus to be discussed later, the total capacitance was so much higher that the grid current had inappreciable effect on the sensitivity.

The Exploratory Experiments

Experiments with plates made of brass and aluminum (including those with plastic described in the Appendix) were made over a period of five months using the quadrant electrometer. Besides the plastic-effect data, most of the other data have to do with the functioning of the apparatus components such as the switch, the effectiveness of the shielding and insulation, the effect of relative humidity on the measurement, and the long-time stability of the plate surfaces. Since these data have no appreciable significance beyond showing that the apparatus was functioning as it should, that relative humidity had only a slight effect (around fifteen to twenty millivolts) on the metal-metal contact potential difference, and that the contact potential difference decreases at an average value of about three millivolts a day with day-to-day fluctuations of five to fifteen millivolts, the data will not be reported in detail here. As might be expected, it was also found that care must be taken not to charge the insulators since such static charges cause strong extraneous fields which disturb the measurement for several days.

For the next set of measurements the brass and aluminum plates were replaced by nickel and gold plated plates of six inch diameter. The initial C.P.D. was 368 ± 3 mv (gold negative) and after two weeks stabilized at 384 mv. Daily variations were then within the three millivolt uncertainty with some indication of being only about one millivolt. Interchange of the plates (after the static charge on the supporting insulators had dissipated) caused no measurable difference in the C.P.D. other than the obvious change of sign of the balancing potential.

Spurred on by our previous discovery of contact charging between a metal and a plastic and the strong effect of the "storage" field strength (that field strength, of overnight duration, between the plates), we decided to investigate the behavior of the gold and nickel plates under the same experimental conditions as described in the Appendix but without the presence of plastic. To our surprise we indeed found an effect but one which is independent of the "storage" field strength. We found that alteration of the "storage" separation of the plates produced a small but unquestionable effect. With the plastic we had found an effect of the order of a few volts depending on the magnitude and sense of the field but independent of whether the field was caused by the intrinsic metal-metal C.P.D. acting across the gap or whether the field was applied potentiometrically; here we found an effect of around twenty millivolts dependent only on the "storage" gap between the plates.

The discovery and attempted elucidation of this effect took six months during which time the equilibrium C.P.D. at the distance of least separation (about two millimeters) drifted from 384 mv to 343 mv. During this time the following facts concerning this effect were discovered:

a) Changing the "storage" gap from two millimeters to fifty millimeters <u>reduces</u> the C.P.D. by an amount varying from fifteen to twenty-five millivolts with the most frequently occuring change being a little less than twenty millivolts. The new equilibrium C.P.D. is usually established in about two days.

b) Changing the "storage" gap from fifty millimeters to two millimeters <u>raises</u> the C.P.D. by an amount varying from twelve to twenty millivolts with the most frequently occuring change being about seventeen millivolts. The new equilibrium C.P.D. is usually established in about three days.

c) The effect of all gap separations from about ten to fifty millimeters are equivalent while those from two to ten millimeters produce effects roughly inversely proportional to the gap separation.

d) Overnight "storage" field strengths from about -25 volts/cm to +25 volts/cm produce no measurable change in the C.P.D.

e) Relative humidity changes in the normal range do not seem to have an appreciable influence on the above effects although 100 per cent relative humidity reduces the magnitude of the effect to about four millivolts or less. Saturation humidity reduces the C.P.D. between gold and nickel plates by about forty millivolts. All humidity effects are approximately reversible.

f) The effect is not due to different amounts of light incident on the oxide films depending on the separation of the plates. The effect was shown to occur the same in total darkness (obtained by covering the Lucite windows of the hood) as in daylight.

g) The effect is not caused by the fact that at different gap separations the metal-plastic boundaries of the insulators are subjected to slightly different fields of contact potential origin and thus could be expected to acquire different charges. The effect persisted unchanged when all plastic was carefully shielded electrostatically from the metal plates.

h) The effect is not altered when the plates are interchanged.

i) When two gold plates were used--C.P.D. about 150 mv--the effect remained but was slightly diminished.

j) The effect is independent of the kind of electrometer used in the measurement. When the vacuum-tube electrometer was put into service the same balancing potentials were obtained and the same effect at the "storage" gap separation was noticed.

k) The effect probably remains when the hood is removed. However, the data in this situation are not very reproducible due to stray electrostatic fields.

No satisfactory hypothesis capable of bringing some degree of order out of the chaos of these observations has been found. Again here, as in the case of contact charging at the metal-plastic boundary, the effect should be investigated in a vacuum.

When measurements at essentially 100 per cent relative humidity were attempted it was found that the electrometer needle upon ungrounding moved across the scale within one or two seconds thus rendering measurement impossible. Since this voltage drift only occurred very close to saturation humidity, it was assumed that surface conductance along the polystyrene insulators due to a film of adsorbed water was responsible. A thick coating of silicone vacuum grease was applied to the insulators but this had no appreciable effect on the voltage drift. When the polystyrene insulation was replaced by polyethylene, the drift was appreciably but not sufficiently reduced. Thereupon the insulators were fashioned from Teflon (Du Pont tetrafluoroethylene polymer) and the residual (grid-current) voltage drift became totally independent of the relative humidity in the chamber. In later work the Teflon exhibited no measurable conductivity even when continuously subjected for weeks to an atmosphere saturated with vapor from aqueous HCl solutions. However, in laboratory air and up to roughly saturation conditions, polystyrene is always an excellent insulator. In every case, however, surface conductance is inappreciable only if the insulators are carefully cleaned and kept free of surface contaminants such as finger grease.

Concurrently with the exploratory work just described a new instrument was designed and built. This instrument is a quadrant electrometer in which the diagonally opposed quadrant pairs are the solutions between which the contact potential difference is to be measured. The instrument will only be described briefly here, since, although the principle of the measurement is sound, the techniques of its use turned out to be so difficult as to render it of doubtful value.

The quadrant vessels, square boxes $2\frac{1}{2}$x$2\frac{1}{2}$ inches with one-inch depth, were constructed of polystyrene sheet and were individually supported on polystyrene posts. In use they were filled brimful. A four-inch long, sixty-degree central angle, butterfly-shaped deflecting vane was constructed from flat aluminum foil. A tiny galvanometer mirror was affixed to the vertical stem of the vane and deflected a spot of light onto a distant scale. The deflecting vane was suspended from an insulated mechanical system possessing vertical, horizontal, and rotational degrees of freedom which was attached to a rigid framework a foot high. A gold suspension of 0.001 inch diameter (before it was rolled into a ribbon) and five-inch length with an air gap of two millimeters between the vane and the quadrant solutions furnished a sensitivity of about one-third of a millivolt at a scale distance of 130 centimeters when a potential of 68 volts was applied to the vane. The period was slightly more than a minute.

Air-tight enclosure and electrostatic shielding were provided by a hood constructed of galvanized sheet iron with a flange bearing against a sponge-neoprene gasket. Several mechanical adjustments including leveling screws were provided. The junction between the solutions was made in a separate chamber on the same base plate containing four glass vessels which allowed the level of each solution to be adjusted separately, provided a means of forming the junction, and provided connections via interchangeable silver chloride electrodes to the potentiometer. The adjustable-height junction chamber vessels were connected to the respective quadrants by means of Tygon (polyvinyl chloride) tubing.

Many experiments were carried out in order to ascertain the effect of vane and suspension shape and size, vane-solution air-gap distance, quadrant-quadrant air-gap distance, and vane potential on the sensitivity and linearity of response of the instrument. In general it was found that the proper adjustment of these parameters is important but not critical to the performance of the instrument. However, before even these tests could be carried out it was necessary to minimize the intra-enclosure convection currents by surrounding the quadrants and the vane by a gold-plated, heavy steel, capped cylinder of eight inch diameter and three inch height which effectively limited vertical convection. The effect of extraneous contact potentials was minimized by the uniformity of the gold-plate and by carefully leveling and centering the cylinder. This cylinder to some extent thus compensates for the fact that a liquid-quadrant electrometer lacks the intrinsic convection and electrostatic shielding possessed by the ordinary quadrant electrometer.

Unhappily however, while the vertical position of the hollow quadrants in the ordinary electrometer is not of critical importance, the relative vertical position of non-hollow quadrants is of extreme importance. The effect is caused by a combination of the contact potential difference between the vane and the quadrants and the capacitance between the vane and the quadrants. For the ideal case in which all four quadrants would lie in a level plane, it is easy to see that the standard theory of the quadrant electrometer is valid with the magnitude of the deflection reduced by a factor of one-half. In the actual instrument a change in relative height of the liquid-quadrant pairs of only about three thousand Angstrom units produces a detectable deflection of the vane. Thus--and to our considerable chagrin--we have built an extremely sensitive relative-height detector. We have worked out a theory for this instrument which includes the effects of the several contact potential differences and the torque caused by a relative height difference. Unfortunately, this theory is much more complicated than that of the ordinary quadrant electrometer and this complication is reflected in the involved prescription for the use of the instrument. Briefly, what one finds is that the instrument can indeed be used to measure liquid-liquid contact potential differences if both the vane-liquid contact potential difference and the quadrant-pair height difference are reduced to a minimum. From the theory means were found for balancing out the vane-solution contact potential difference and of electrically determining when the solution pairs are equal in height to within about three thousand Angstrom units. This procedure relies on much switch reversing, trial and error in adjusting potentiometric potentials, and finally plotting a graph of the differences of the differences (under various switch reversals) of the deflection readings against very small changes (applied by means of finely pitched screws) of relative solution-quadrant height. When all this has been done--which takes over forty-five minutes under optimum conditions--and if everything stays constant, then the instrument can be used to measure the solution-solution contact potential difference.

The main weakness of the system lies in the zero drift of the suspension. Even with suspensions which have aged in situ for several months, the zero drift in an hour is equivalent to five to twenty millivolts. This drift appears to be random in sense and magnitude, is not correlated with changes of room temperature, and after ageing was roughly the same for three suspensions. Perhaps very careful annealing in situ would reduce the drift to a manageable amount but this was not attempted. However, even if the drift were nil, a problem remains in that for most cases of interest the contact potential difference between the solutions caused by changing surface conditions varies considerably in an hour and thus would vitiate the complicated procedure outlined above.

In summary then, the liquid-quadrant electrometer for measuring contact potential differences between liquids is a valid instrument in principle and can be made highly sensitive; however, even at best, it is in practice limited to cases in which the contact potential difference does not change appreciably in an hour. Moreover, it would seem almost impossibly difficult to obtain clean solution surfaces in it (in order to measure the liquid-junction emf) by the sweeping technique used with the final apparatus. A possible way out might lie in using insoluble films of non-polar organic liquids in the manner described in the last chapter. However, because of its limitations and difficulties, work with this instrument was reluctantly discontinued and our attention was given to building an elaborate variable capacitance instrument to take its place.

The next set of experiments to be considered here involves the final work with the exploratory variable capacitance apparatus concerned with the behavior of the system when metal-solution Volta potential differences were measured. For this work the upper six-inch gold plate was replaced by a four-and-a-half inch gold plate and the lower nickel plate was replaced by a six-inch diameter, one-inch deep Lucite box which served as the solution vessel. Connection was made by means of Tygon tubing to a small Pyrex solution vessel housed in an ancillary chamber in which a silver chloride electrode was immersed in order to furnish connection to the potentiometer. In order to prevent electrode emf changes due to alternating solution level changes, the silver wire stem of the silver chloride electrode was thoroughly coated with acrylic spray before deposition of the silver chloride. Thus, the solution only came into contact with silver chloride and plastic and the solution surface only touched plastic.

In this system the solution vessel was moved up and down to vary the capacitance and the gold plate, connected to the special switch and electrometer, remained fixed. The smaller gold plate reduced the sensitivity somewhat so that with an air gap of about 2 mm, the (extreme variation) sensitivity was ± 5 mv. The vacuum-tube electrometer was used in this work. No definite variation in the measured Volta potential difference could ever be traced to the fact that some bulk motion of the solution occurred during the measurements. (However, in order to be safe, the final apparatus was designed to avoid this possibility.)

The metal-solution Volta potential experiments which were conducted with this apparatus occupied a period of about two-and-a-half months. Measurements were taken with 0.001 N and 0.01 N HCl solutions made with doubly distilled water. The experimental results can be summarized as follows:

a) No effect caused by changing the overnight "storage" air gap distance between plate and solution could be found which was greater than the ± 5 mv uncertainty.

b) No effect caused by changing the "storage" field strength could be found.

c) The gold-solution Volta potential difference (which included the silver-chloride electrode emf, the silver-gold Galvani potential difference, and the gold-solution contact potential difference) could not be reproduced (between different fillings from the same bottle of solution) either initially or terminally. The initial Volta potential differences varied over a range of roughly eighty millivolts despite many precautions taken to insure cleanliness and duplication of procedure. The terminal or steady-state Volta potential differences (attained after about two-week intervals) varied over a range of roughly a hundred millivolts.

d) When the Lucite vessel was filled more than brimful, allowed to stand for more than a week in order to come to an approximately steady Volta potential, and then swept consecutively by two carefully-cleaned, Lucite-coated brass strips (in order to remove the surface film); the Volta potential difference increased by roughly four hundred millivolts. However the variation among ostensibly identical runs spread over a range of roughly seventy millivolts which was also roughly the spread among the different post-sweeping measurements. After a week or less the Volta potential difference would again be in the neighborhood of what it had been before the sweeping and would remain more or less constant.

e) With a large air gap between the plate and the solution, removal of the galvanized iron hood for half an hour (after which it was replaced) resulted in a change in the Volta potential difference of about fifteen to fifty millivolts depending on the age and treatment of the gold surface. After about twelve hours adsorption equilibrium was again re-established as indicated by the fact that the Volta potential difference was constant and equal to the value before the hood was removed to within about ten millivolts. This lack of precise adsorption reversibility precluded the possibility of using this instrument to measure solution-solution contact potential differences, since the hood would have had to have been removed for the cleaning and refilling not to mention sweeping the solution surfaces.

The salient points of these exploratory data are: (1) the lack of sufficient reproducibility exhibited by either the initial (after filling) or the steady-state (after more than a week) solution Volta potential demonstrates that some means of cleaning the surfaces must be provided, (2) the lack of sufficient reproducibility shown by the sweeping process employed shows that a better and more carefully controlled sweeping method is needed, and (3) the lack of sufficient water-vapor-on-gold adsorption reversibility indicated that an apparatus must be so designed that the saturation atmosphere is not disturbed when the sweeping process is carried out and the two solutions between which the contact potential difference is desired must be enclosed in a single chamber. Moreover, for sufficiently accurate determinations of liquid junction emf's, the sensitivity must be increased at least ten-fold.

CHAPTER VII

THE FINAL APPARATUS

Over-all Design Considerations

While the exploratory apparatus with Teflon insulation performs quite well as a metal-solution Volta potential electrometer, its limitations preclude its being used to measure solution-solution contact potential differences with the necessary accuracy. Foremost among these limitations is sensitivity which must be increased in the final apparatus so that one-third of a millivolt can be detected without difficulty.

The actual sensitivity of a variable capacitance instrument depends on the intrinsic sensitivity (that with no voltage drift after ungrounding) and upon the Volta potential drift of the "floating" part of the circuit. With good insulation the voltage drift is due entirely to the fact that the grid current of the electrometer input tube charges the capacitance of the floating system. Since little control can be exercised over the grid current, the voltage drift can be minimized only by making the total capacitance of the floating system as large as is consistent with other demands.

In the previous chapter, we referred to the apparatus sensitivity in terms of the least potential difference which can be reproducibly detected. We now pull a semantic switch and return to the definition of sensitivity used in Chapter IV. By the intrinsic sensitivity we shall mean the voltage deflection of the electrometer per unit of metal-solution Volta potential difference. Then, by equation (9) of Chapter IV, the intrinsic sensitivity is given as

$$S = \frac{\Delta C}{C_s + C_E + C_o - \Delta C} \; .$$

In this equation $C_s + C_E$ is the total capacitance of every part of the "floating" system except that between the Volta potential probe and the solution, C_o is the capacitance between the Volta potential probe and the solution at the distance of least separation, and ΔC is the change of capacitance between the Volta potential probe and the solution as they are separated to the distance of maximum separation during the measurement process. Thus $C_s + C_E + C_o - \Delta C$ represents the total capacitance of the "floating" system when the metal disk and the solution are at the distance of maximum separation.

Under the simplifying assumption that the capacitance between the Volta potential probe disk and the solution is that of a parallel plate condenser with no edge effects, the following useful relation can be easily obtained:

$$S = \frac{d/d_o - 1}{1 + \frac{d}{d_o} \cdot \frac{C_s + C_E}{C_o}} = \frac{d/d_o - 1}{1 + \frac{4\pi d}{A}(C_s + C_E)}$$

in which A is the area of the Volta potential probe disk, d_o is the gap distance at least separation, and d is the gap distance of maximum separation during the measurement process. As might be anticipated, when d becomes very large, the intrinsic sensitivity approaches $C_o/C_s + C_E$.

We now proceed to utilize the equation for S as a means of determining A for an instrument which, with the Keithley Model 200B electrometer described in the preceding chapter, will detect at least one-fourth of a millivolt. For this electrometer C_E is about $6 \mu\mu f$ and is negligible for our purposes. Experience has shown that a metal-solution air gap distance of about 2 mm is the practical minimum. Somewhat arbitrarily, we take the distance of maximum separation to be 15 mm since at too great a separation extraneous fields are admitted under the shielding around the Volta potential probe and, moreover, the sensitivity does not depend very much on the value of d chosen if this value is beyond about 10 mm. Also somewhat arbitrarily, we choose the desired intrinsic sensitivity to be unity, since on the lowest electrometer scale deflections of 0.1 mv can be easily read. On the basis of experience with the exploratory apparatus, we choose 100 statfarads as the total shielding capacitance. From the preceding equation we can obtain

$$A = \frac{4\pi d\, C_s}{\dfrac{d/d_0 - 1}{S} - 1}$$

which, when the above values are inserted, gives an area equivalent to that of a circular disk of approximately 8.5 inches diameter.

Since the required area is directly proportional to the shielding capacitance, it might be argued that reducing the latter would reduce the size requirements of the apparatus significantly. This supposition, however, ignores two practical considerations which are very important. First, reduction of the total shielding capacitance to less than about 60 statfarads is impractical, since the adjustable-capacitance switch requires about 30 statfarads and for reasons which will become clear later the remaining shield capacitance cannot be reduced below about 30 or 40 statfarads. A second and even more important consideration results from the fact that the grid-current-caused voltage drift after ungrounding is inversely proportional to the total capacitance of the "floating" system. Thus, even though a smaller instrument might possess an intrinsic sensitivity of unity, its actual sensitivity would be much less because the larger voltage drift would prevent the establishment of accurate null determinations.

As a numerical illustration, we shall here take the values from the actual final apparatus: diameter of probe disk is 9.5 inches, $C_S + C_E$ is about $105 \mu\mu f$, d_o is 2 mm, and d is 15 mm. For one matched pair of electrometer tubes, the grid current was 2×10^{-14} ampere. The intrinsic sensitivity is calculated to be about 1.3. C_o is about $210 \mu\mu f$. Thus the voltage drift after ungrounding with the probe at the least distance is

$$\frac{dV}{dt} = \frac{2 \times 10^{-14} \text{ amp}}{315 \mu\mu f} = 0.06 \frac{\text{mv}}{\text{sec}} .$$

Since separation of the plates and perception of the deflection of the electrometer needle requires about two seconds (with the final apparatus) and about one extra second is needed for variations in response time, it is clear that the uncertainty in a null determination due to the voltage drift is about 0.2 mv. With very small voltage drift (as was later obtained using a particular matched pair of tubes) the sensitivity was such that measurements could be made within 0.1 mv. It is thus clear that the total capacitance of the instrument is important in determining the accuracy of measurement and that (with the usual matched pairs of these electrometer tubes) a smaller instrument can not--as was shown by the exploratory apparatus itself--provide the requisite accuracy.

The over-all schematic diagram of the final apparatus appears in Figure 3 of Chapter V. The troughs holding the two solutions are mounted side-by-side and the 9.5 inch diameter Volta potential probe turns from one to the other. The chosen diameter of the metal probe determines within broad latitudes the size of the solution troughs. Since electrostatic shielding is the more complete the larger the solution surface, a diameter of 13.5 inches was chosen for each of the solutions, thus providing two inches between the edge of the probe disk and the edge of the solution. A concomitant advantage of large solution troughs arises from the fact that the large volume-to-wall-surface ratio renders possible wall impurities less important. The Volta potential probe (1), two solution troughs (2), and the electrostatic shielding to be described later are enclosed in the main chamber, as shown in Figure 4. For the photograph, a side panel of the shielding has been removed for clarity and the two (inner) hoods for the junction chamber (3) and the main chamber (4) have been raised. The lower part (5) of the outer, thermostatic hood runs horizontally across the photograph and the upper part (6) in its raised position can just be seen in the upper left corner of the photograph. The wall-mounted platform with thermostatic hood (7) for holding two five-gallon carboys of the solutions forming the flowing junction can be seen at the upper right of the photograph. It is mounted slightly behind the apparatus proper. The junction chamber (8) containing the five vessels shown in Figure 3 and the attendant mechanisms can be seen at the right of the main chamber. The variable-capacitance switch (9) described in Chapter VI can be seen beneath the apparatus mounted on a very massive iron stand

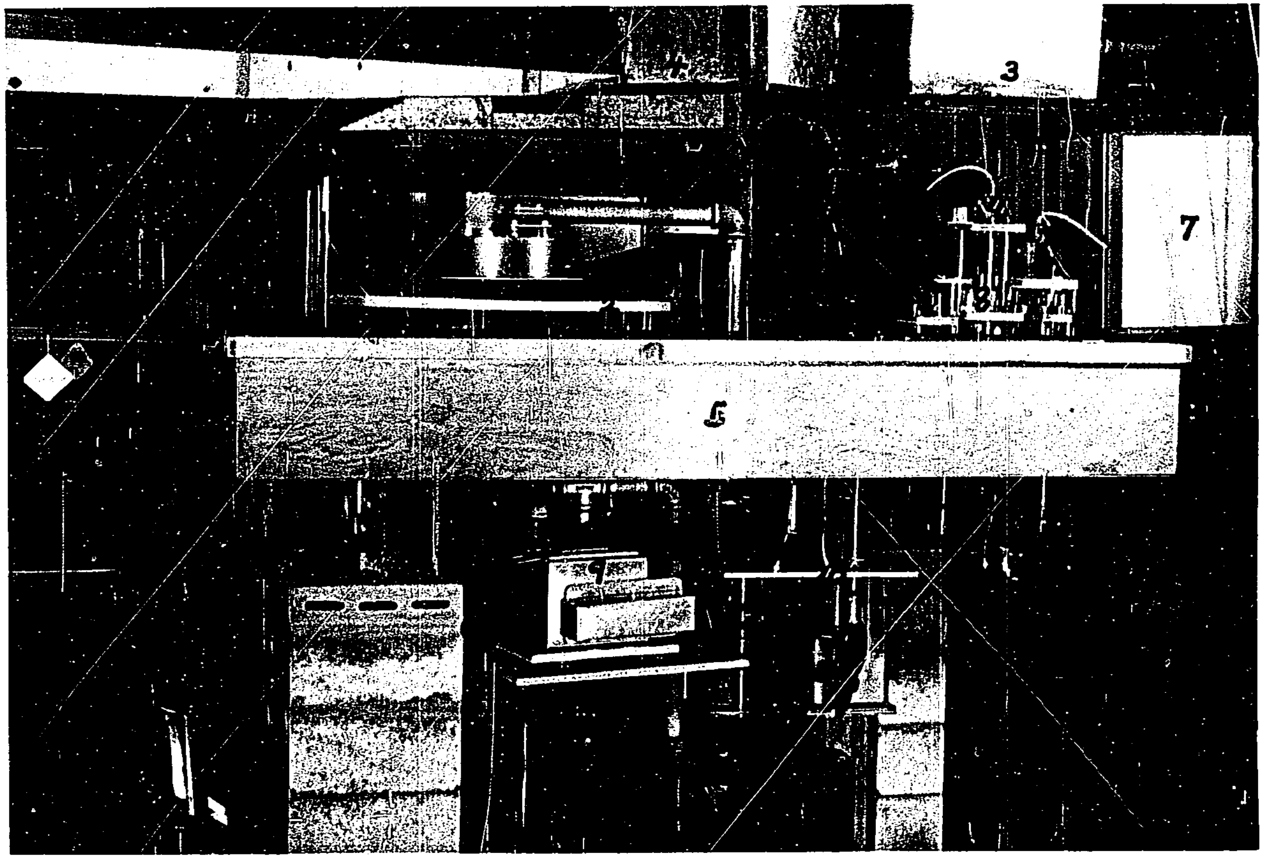

Fig. 4. An Over-all View of the Final Apparatus

which also supports the elctrometer which is hidden from view here. The three other photographs to be referred to later show the components in more detail. As is indicated by the presence of the swivel chair in the lower left corner of Figure 4, the experimenter sits underneath the apparatus and a bit to the left of center in order to make the observations.

The structural foundation of the apparatus is provided by a welded trapezoid of 2x2$\frac{1}{2}$ inch angle iron lying on three piers of concrete blocks at a height of 44 inches above the floor. The centers of the piers are located at the corners of an isoceles triangle of 48 inch base and 66 inch sides. The center-line dimensions of the angle-iron trapezoid are (parallel sides) 48 inches and 12 inches, (non-parallel sides) 62 inches. In Figure 4 the larger base of this isosceles trapezoid is to the left. Four 1$\frac{1}{4}$ inch diameter, 19 inch long steel uprights, threaded for the upper ten inches, serve to attach a horizontal 1x3 inch aluminum angle framework of 36x52 inches extreme dimensions to the angle iron framework. This aluminum framework consists of a $\frac{1}{2}$x12x23 inch aluminum plate as well as six aluminum angle members. This entire structural framework is designed to provide great rigidity so that the solutions in the troughs would not be agitated during a measurement. Two $\frac{1}{2}$x10x48 inch aluminum plates (10) are mounted side-by-side directly across the angle-iron trapezoid to furnish support for much of the mechanism to be described later and, secondarily, to provide shelf space for several of the potentiometer components.

The floor of the main chamber hood is positioned 4 inches below the aluminum framework and is secured by means of large bolts and washers turning on the threads of the four 1$\frac{1}{4}$ inch diameter support posts. The bottom (fixed) part of the main chamber hood is constructed from 3/4 inch thick plastic-coated plywood and consists of a 48x78 inch sheet (with one corner truncated) with $7\frac{1}{2}$ inch vertical walls capped with a plywood flange to provide gasket area. The plywood sheet also supports the junction chamber and considerable ancillary apparatus. The horizontal dimensions of the main chamber proper are nominally 48x56 inches. The gaskets of the main chamber and the junction chamber are elaborately constructed arches of 3/16 inch thick sponge Neoprene stuffed with cotton. A portion of these gaskets is shown in Figure 4 and Figure 5. The removable part of the main chamber hood is constructed of galvanized iron sheet which is supported externally by a welded angle-iron framework which also serves as a gasket flange on the bottom. A 1/16 inch extension of the sheet metal bites into the sponge Neoprene gasket. The hood can be easily raised and lowered by means of a ceiling-mounted block and tackle. With the top, galvanized part lowered the nominal dimensions of the main chanber are $48\text{x}56\text{x}27\frac{1}{2}$ inches. (Actually, the main chamber is in its horizontal dimensions an irregular pentagon with the "side" toward the junction chamber being really two sides meeting symmetrically at an angle of 113 degrees. Because of the presence of water vapor and usually HCl also during the operation of the instrument, the apparatus of and in the main chamber is constructed, wherever practicable, of difficultly corrodible metals. The zinc lining of the galvanized hood and all wood are thoroughly coated with clear acrylic plastic. All shaft or tubing openings are sealed with Neoprene, Teflon, or felt so that the main chamber is air-tight.

The junction chamber hood is a rectangular parallelepiped of 12x20 inches horizontal dimensions and 27 inches vertical dimension. Like the main chamber, its lower (fixed) part is constructed of 3/4 inch thick plastic-coated plywood with walls $7\frac{1}{2}$ inches high. The internal supports and mechanism of the junction chamber are mounted directly on an aluminum base plate which is fixed to the large plywood sheet which also supports the main chamber. The upper portion of the junction chamber hood is constructed of galvanized sheet iron and is attached to the ceiling by a pulley mechanism. Again here, the zinc coating and wood are plastic coated and easily corrodible metals have been avoided.

The bottom of the outer hood is supported by large nuts and washers turning on the threads of the four $1\frac{1}{4}$ inch diameter support posts at a distance of 9 inches below the aluminum framework. It is constructed of $\frac{1}{4}$ inch thick plywood and supported by wooden frameworks which also serve at the proper places as gasket flanges. The bottom (fixed) part is 14 inches high and the top part--which is supported, rolled out of the way, raised or lowered, and positioned by a fairly elaborate mechanical system fixed on the ceiling--is 24 inches high. The horizontal dimensions of the outer hood are 60x90 inches with one corner truncated. A minimum of five inches of air space is thus included between the inner and outer hoods on all six sides in order to facilitate the establishment of thermal equilibrium by means of convection currents as well as to provide room for hands and arms during adjustments. The outer hood is air-current tight and all shaft openings are sealed with felt or Neoprene. The chief function of the outer hood is to act as an air thermostat. Provision is made for controlling the temperature (particularly at 25°C) of the main chamber and especially the junction chamber by means of nine distributed fifteen-watt incandescent lamps connected through a sensitive bimetallic thermoregulator. Temperature sensing is by means of nickel-copper thermocouples in the inner chambers and in the solutions themselves. During the summer control of the temperature at 25°C would require room air conditioning.

The Solution System

Figure 5 is a photograph of the two solution troughs, the sweeping apparatus, the Volta potential probe assembly, and the electrostatic shielding. The nearer side panel of the shielding has been removed for this picture. The two solution troughs, each machined from a 1x15x20 inch sheet of low density polyethylene, are constructed as identically as possible. Their function is to contain the solutions and guide the sweeping assemblies as they are pulled across. The sweeping assemblies are constructed entirely of plastic with the sweepers (two to each assembly) being edgewise-oriented Teflon strips accurately machined and mounted so that the two bottom edges of the sweepers lie in a plane. In the photograph the nearer sweeping assembly is shown in the pre-sweeping position while the farther sweeping assembly is in the post-sweeping position on two polyethylene runners. The sweeping assemblies are attached by nylon cord to four $\frac{1}{2}$ inch diameter, 42 inch diameter, 42 inch long polystyrene rods--one rod on each side of each trough--which pass through the electrostatic shielding tanks, the lower inner hood, and the lower outer hood. Thus, the sweeping can be performed inside an air-tight, thermostatic enclosure. A portion of these rods can be seen at the extreme left center of Figure 4. Their bushings are made of Teflon so that the usual stick-slip of sliding friction, which would be deleterious to the sweeping process, is avoided.

The solution vessel of each trough is a conical concavity in the shape of a very shallow funnel of 13.5 inches diameter and 5/8 inch central depth machined into the 1 inch thick polyethylene sheet. Since polyethylene is essentially non-wettable by water, the solution is "heaped" about two millimeters above the trough surface. A rectangular indentation

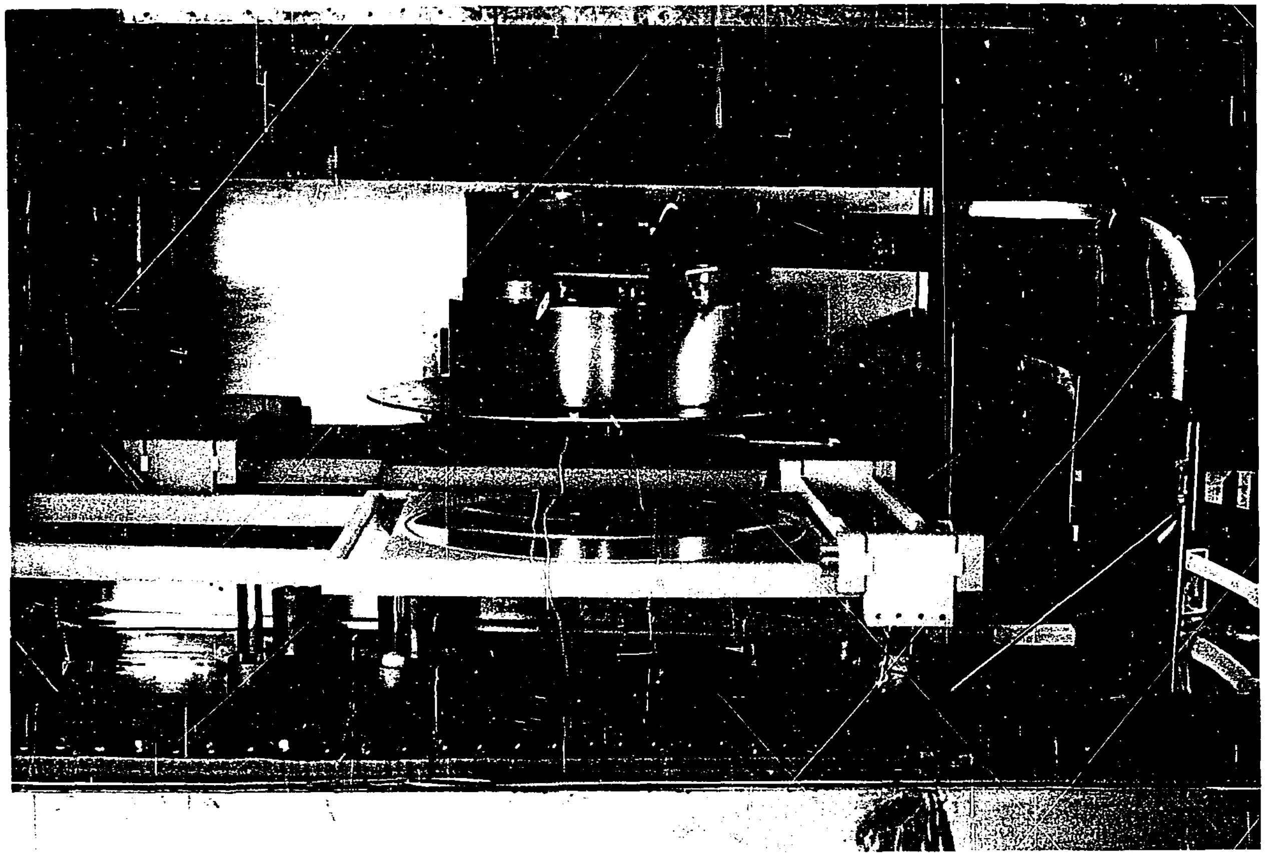

Fig. 5. The Solution Troughs and the Probe Assembly

is milled into one end of each trough to catch any excess solution which may be carried along with the sweepers. A 5/8 inch I.D. polyethylene tube is heat welded to the center of each trough to provide connection to the junction chamber vessels. Eight polystyrene posts provided with leveling screws are attached to the aluminum angle frame-work and pass upward through cylindrical "boots" in the shielding tanks in order to furnish support for the troughs. Each trough is provided with machined recesses for the support posts so that it may easily be removed for cleaning and then quickly repositioned. Eight other plastic posts, likewise passing through cylindrical "boots," provide support for the four polyethylene runners. The centers of the two solution troughs are 21 inches apart so that their nearer edges are 6 inches apart and their outer edges are approximately 6 inches from the closest plywood wall of the inner hood.

A close-up photograph of the junction chamber apparatus is shown in Figure 6. The arrangement is similar to that of the schematic diagram of Figure 3. The six solution vessels are Pyrex cylinders of 63 or 70 mm diameter and about 6 inches height. The solution vessel at the extreme left is mounted on an adjustable-height table and is connected to the nearer trough in Figure 5. The vessel to the right holds one interchangeable electrode and one tube from the junction cell. The junction cell is the oddly shaped piece of glassware with two neoprene stoppers in the upper central part of the photograph mounted high on its own table--its odd shape derives from the requirements that intersolution mixing be minimized, that a plug of Pyrex glass wool can be inserted and removed easily, and that the motion of the junction due to siphoning movement caused by slight initial inequality in the heights of the two solutions be minimized. The next vessel to the right holds one tube of the junction cell and one tube

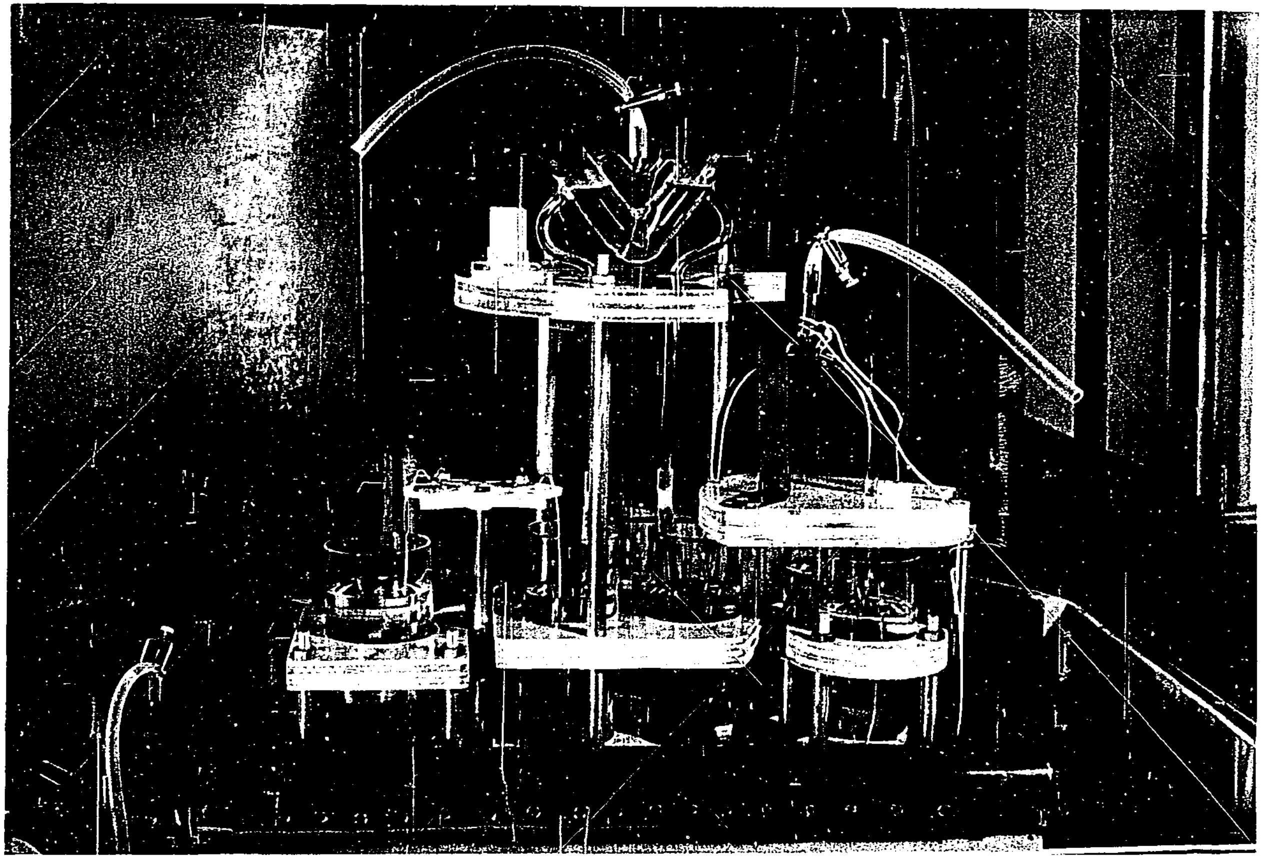

Fig. 6. The Junction Chamber Apparatus

of the liquid switch when the latter is in one of its two positions. The vessel at the extreme right holds the silver-chloride reference electrode E_0 and one tube of the liquid switch. When the liquid switch is in the other position than the one shown, one of its tubes dips into the vessel behind (and almost hidden by) the vessel at the extreme right. This vessel is mounted on an adjustable-height table and is connected to the more distant trough in Figure 5. A sixth vessel, not included in the diagram of Figure 3, is provided so that a salt bridge can easily be set-up by using another junction cell beside the one shown and turning the latter to a different orientation: this vessel appears behind the nearer two on the central table. The liquid switch, mounted on its own rotatable platform appears above the vessels at the right. It consists simply of an inverted yoke-shaped Pyrex tube drawn down to capillary ends and mounted so that one of its tubes is on the axis of rotation. The vertical spacing and rotational restraints are provided by a mechanical system so that moving the switch from one vessel to another can be done blindly from beneath the outer hood without removing the junction chamber hood. Indeed, all of the variable-solution-height and interchangeable-electrode controls can also be operated from beneath the outer hood.

The two vessels on adjustable-height tables are connected to their respective solution troughs by Tygon tubing, glass connecting tubes, and finally 3/4 inch I.D. Tygon tubing which connects directly to the polyethylene tubing heat welded to the troughs. Along the way provision is made for mounting two 4 ounce volume rubber squeeze bulbs which allow the solution level in the troughs to be varied quickly in order that a measurement of the Volta potential difference can be made while the metal probe is stationary. This serves as a check on the other, more convenient method of measurement. The squeezing of each of the bulbs is done between two metal plates, the lower of which is moved by a long vertical shaft extending down through both hoods and the ½ inch aluminum plate attached to the angle iron framework of the apparatus proper. Each of these shafts is moved up and down by a cam (11 in Figure 4) which is attached to a long horizontal rod terminating at the operator's position beneath the apparatus. Thus, the bulbs can be squeezed while the electromoter needle is being observed.

The Volta Potential Probe and the Electrostatic Shielding

Equation (7) of Chapter IV demonstrates that a variable-capacitance null determination does not measure the Volta potential difference unless $(\psi_0^b - \psi^s)\,\delta\hat{C}$ is negligibly small in comparison with $(\psi_0^b - \psi^a)\Delta\hat{C}$. Thus we must seek to make both the contact potential difference between any part of the "floating" system capable of movement and its shielding negligibly small and the change of capacitance between it and its shielding (due to the motion) also negligibly small. Since motion is a requisite of the measurement, $\delta\hat{C}$ cannot be completely eliminated but it can be markedly reduced by arranging that the shielding of the Volta potential probe move rigidly with it. $\delta\hat{C}$ can be further reduced by making the capacitance between any necessary stationary shielding and the probe disk very small. The only practical way to minimize $(\psi_0^b - \psi^S)$ is to give the Volta potential probe and all of its shielding identical conducting surfaces. By the same token, any movable part of the "floating" system and its shielding must have identical surfaces.

For purposes of illustration, let us consider the following typical numerical example:

$$\psi_0^b - \psi^s = 900\text{ mv}, \qquad \delta\hat{C} = 5\mu\mu f,$$

$$\hat{C}_s + \delta\hat{C} + \hat{C}_E + \hat{C}_0 - \Delta\hat{C} = 150\ \mu\mu f$$

whence $$\frac{(\psi_0^b - \psi^s)\,\delta\hat{C}}{\hat{C}_s + \delta\hat{C} + \hat{C}_E + \hat{C}_0 - \Delta\hat{C}} = 30\text{ mv}.$$

Thus, in order to have an error of no more than 0.3 mv in the measurement we must insure that $\psi_0^b - \psi^s \leq 90\text{mv}$ and $\delta\hat{C} \leq 0.5\mu\mu f$. Since, as was found in the exploratory experimental work, even ostensibly identical metal surfaces may in air have a contact potential difference of as much as 100 mv, it is mandatory to make $\delta\hat{C}$ as small as practicable. In the actual apparatus every part of the "floating" portion of the circuit which moves during a measurement (except, of course, the variable-capacitance switch which depends on contact potentials for its effect) is shielded by metal having a surface "identical" to that of the moving part. Moreover, $\delta\hat{C}$ for each moving part is probably less than 0.3 $\mu\mu f$. Besides the problem of the metal-metal contact potential differences, the problem of metal-insulator contact charging (see Appendix) must be dealt with. Since the effective contact potential difference between a metal and an insulator at their surface of contact may be of the order of one volt, it is apparent that this too could cause extraneous fields which would induce potentials on any moving part of the floating system. In the apparatus all metal-plastic boundaries in the vicinity of moving parts have been shielded from those parts. For example, the cylindrical metal "boots" in the bottom of the large shielding tanks have the function of shielding the metal-plastic contact at the bottom of each support post from the Volta potential probe. This is also one of the reasons why the sweeping assemblies incorporate no metal. Throughout the main chamber, no unshielded metal-plastic contact exists.

Since in operation the main chamber is to contain water vapor and--what is worse--usually HCl vapor too, the ideal coating for the Volta potential probe would probably be platinum or gold. (In the exploratory work it had been observed that gold was somewhat more stable in time than nickel.) Unhappily however, the coating on the large and elaborate shielding must be the same as that on the probe. An estimate on the job of gold plating the necessary shielding amounted to so large a sum of money that it was decided to use nickel plate instead. All of the shielding was then nickel plated on all sides. The Volta potential probe was nickel plated especially heavily.

The shielding to which the Volta potential probe is rigidly attached as it moves up and down and rotates from one solution trough to the other is shown centered above the more distant trough in Figure 5. The 9.5 inch diameter probe disk is accurately machined plane with smoothly rounded edges and is mounted concentrically flush with the bottom of a 13 inch diameter steel cylinder of 4.5 inch height. A 20 inch diameter steel flange is soldered to the bottom of the shield cylinder and serves as a 3.5 inch barrier for possible extraneous fields. The probe disk is rigidly attached to the top of the shielded cylinder by means of a $1\frac{1}{2}$ inch diameter Teflon rod of 4 inch length. The 4 inch length serves the dual purpose of minimizing the probe-to-shielding capacitance and providing a long surface insulation path against the possibility of adsorption of aqueous HCl vapor in the possibly supersaturated region above the solution surrounded by the shield cylinder when the probe is kept very close to the solution. The shield cylinder and flange are attached to the horizontal steel tubing by means of a sliding-adjustment clamp and four leveling screws. The image of the probe disk mounted in its shield cylinder is shown in Figure 5 reflected in the solution in the nearer trough. A gap of about two inches exists between the rim of the probe disk and its shield cylinder. A #30 B. & S. nickel wire runs from the probe disk through a 5 inch diameter disk of $\frac{1}{4}$ inch thick Teflon mounted in the bottom of a 5 inch diameter cylinder which is brazed end-on to the steel tubing and which has a removable lid so that a hand can be inserted to make adjustments and the final wiring connections. The #30 B. & S. nickel wire then passes through a Teflon disk insulator in the end of the steel tubing and thence, under tension, runs concentrically through the tubing. The first Teflon insulator was made large so that a minimum insulation path of more than two inches could be attained everyplace where the insulation was exposed to an aqueous HCl atmosphere. The five inch cylinder and the steel tubing were made gas-tight with Teflon sealant so that no water vapor can gain admission to the smaller insulators inside. The horizontal length of the steel tubing terminates in an elbow which joins it to a 42 inch length of vertical steel tubing. The dimensions of the probe shielding assembly are such that the center of the probe disk swings in a circular arc of precisely 24 inch radius. The tubing used is cold-drawn, seamless mechanical tubing of 2 3/8 inch O.D. and 3/16 inch wall thickness. This size tubing was chosen to satisfy the demands of low capacitance per unit length (about 3 $\mu\mu f/ft$ with #30 wire), high mechanical rigidity, and an insulation path of at least one inch. For these requirements this size tubing seems to be close to the optimum, since larger tubing would not perform significantly better. At every corner the wire passes through a precisely oriented, tiny hole in a 5/8 inch diameter Teflon rod which, together with the wire tension, assures coaxiality. The tubing is nickel plated on the inside as well as on the outside since, in spite of the tension some oscillation of the long wire could occur during the measurement.

To complete the discussion of the main-chamber shielding, the large shielding tanks will now be discussed. These tanks may be seen in Figures 4 and 5. In both photographs the side panel of the nearest tank has been removed for clarity. The side panel of each tank slips on and off easily to allow wide access to the solution troughs and sweeping assemblies. The two tanks sit side-by-side and are identical except that one is the mirror image of the other. Each is of nickel plated sheet iron, has the nominal dimensions of 18x20x40 inches, and sits directly on the aluminum angle framework. Thus, when the solution troughs and runners have been removed, the tanks can be lifted up and out over the polystyrene support posts for cleaning. The cylindrical "boots" previously referred to not only have the function of shielding but also enable the tanks to hold an inch or so of solution should this prove necessary by accident or design. The side panels have windows made from nickel plated wire screen which center symmetrically with the solution surfaces and are in line with the Lucite windows of $4\frac{1}{2}$x$10\frac{1}{2}$ inches on both sides of the inner and outer hoods. The Lucite windows are thick and mounted between heavy, plane flange rims so that almost no optical distortion occurs. This planarity allows accurate measurements of the disk-solution air gap distance to be made even when both hoods are closed. A fluorescent lamp is mounted on one side of the apparatus and aligned with the top of the solutions so that a telescopic vernier cathetometer mounted across the room sees the air gap sharply outlined against a broad, diffuse light source. The air gaps are crudely adjusted by adding or subtracting solutions and are finely adjusted by turning the large screws on shafts beneath the lower hood which raise or lower the appropriate junction chamber vessels. The minimum distance between the Volta potential probe disk and the shielding tanks is about seven inches and even then the probe is mostly shielded from the tanks themselves since any extraneous field would have to pass between the previously mentioned 20 inch flange and the solution. With these elaborate precautions incorporated in the electrostatic shielding, it is perhaps not surprising that evidence of imperfect shielding has only been found experimentally with this apparatus when the solution troughs themselves bear static charge.

To conclude the discussion of the apparatus of the main chamber it should be mentioned that no hydrocarbons were used as sealants or lubricants because of the remote possibility that by means of their slight volatility they could contaminate the solution surfaces. For this reason also, all wood was thoroughly coated with plastic. The hazard of greatest moment, however, is constituted by the fatty acids (especially those from human skin) which could conceivably volatilize from the surfaces of the main chamber to form a monomolecular layer on the solution surfaces. Because of their relatively great dipole moment (in common with most non-hydrocarbon organic compounds) fatty acid molecules readily spread to form monomolecular layers which may change the solution Volta potential by four hundred millivolts or so. All components of the main chamber were thoroughly cleaned before their final assembly and care was taken that they were not contaminated with skin grease during the assembly and the later operation of the instrument. However, it is obvious that keeping an apparatus of this size free from trace amounts of organic impurities is a practical impossibility.

The Mechanical System

We have seen that the probe disk is rigidly attached to a large shielding assembly which in turn is attached to a 24 inch horizontal section of 2 3/8 inch O.D., 3/16 inch wall seamless steel tubing which connects by means of an elbow and pipe threads to a 42 inch vertical length of the same tubing. This vertical tubing passes through a graphite-lubricated brass bushing mounted on the aluminum plate of the upper structural assembly, through double-felt-lined holes in the two hoods, and finally through a brass bushing mounted on one of the aluminum plates rigidly attached to the angle-iron trapezoidal framework. A portion of this vertical tubing can be seen in Figure 7 just to the left of the electrometer dial which appears as the rectangular white area toward the upper right of the photograph. Firmly attached to the tubing by means of large Allen bolts in an adjustable split-clamp is a large $\frac{1}{2}$ inch thick brass "helm" which has the form of a semicircle with radial handles. This "helm," shown in a raised position in the photograph, is used to steer the Volta potential probe assembly when it has been raised sufficiently by a screw-type car jack to clear the 1 inch diameter guide post which slips precisely into two holes in the "helm" having a central angle of $51^\circ\ 46'$ between them. The jack can raise the "helm" six inches so that the probe assembly will just clear the shielding tanks and can be swung out beyond

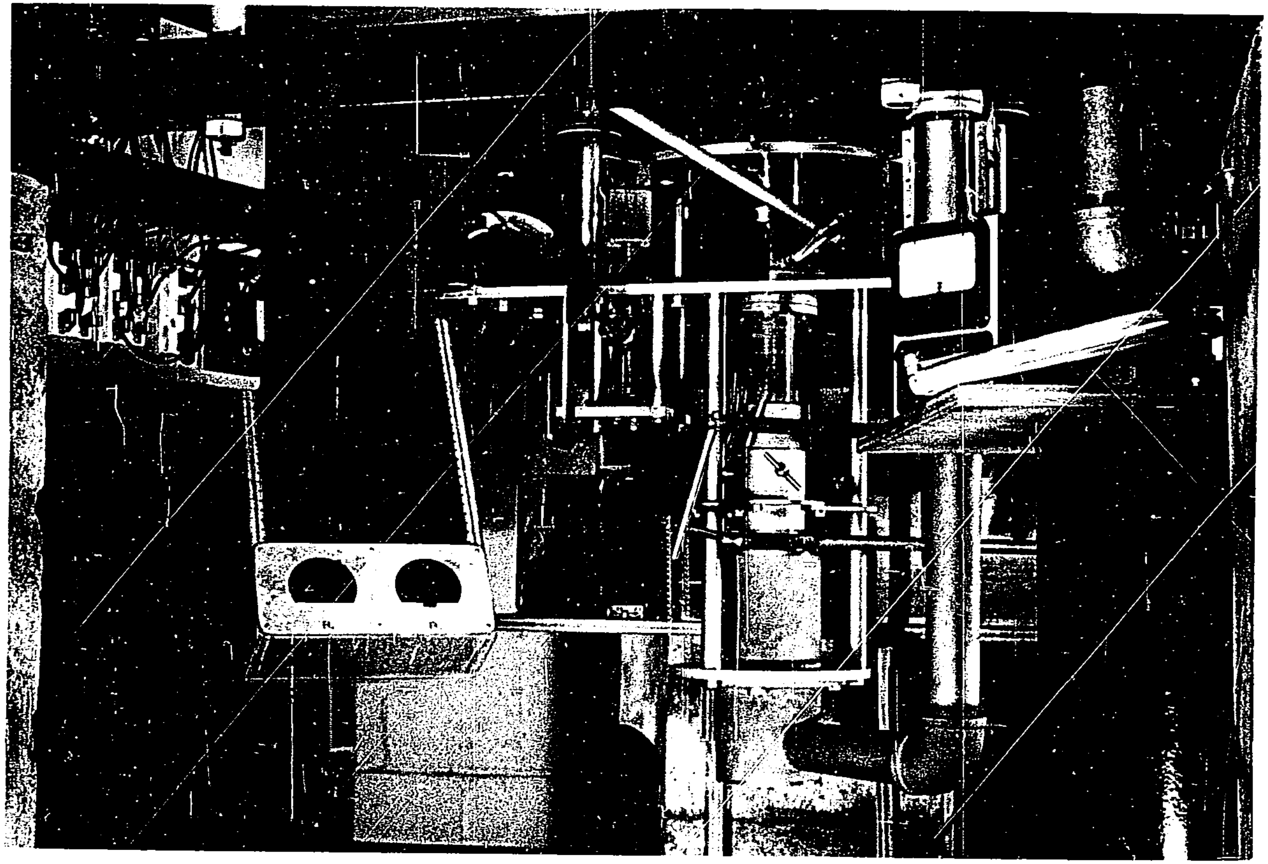

Fig. 7. The Underside Instrumentation

the outer hood of the apparatus for cleaning and adjustment. The jack also serves to raise the probe assembly so that the sweeping assembly can pass beneath it. A large-mechanical-advantage system is necessary, since almost two hundred pounds force is required to raise the whole assembly.

In the lowered position the guide rod is in one of the two precisely aligned holes in the "helm" and thus the Volta potential probe is centered over one of the two solution troughs. In this position the "helm" sits on a rigidly mounted cam surface to which is attached a 14 inch long arm-and-handle assembly which gives the necessary mechanical advantage. A portion of this lever arm may be seen running obliquely up out of the picture in Figure 7. This cam assembly, which is mounted on the bottom aluminum plate, allows the probe assembly to be quickly and smoothly raised to a maximum of one-half inch.

Because of the slightly microphonic behavior of its vacuum tubes, the electrometer must remain stationary during the measurement. Therefore, the problem of how to couple the moving (during a measurement) wire of the probe assembly to the stationary electrometer arises. Any twisting or pulling of the wire along an insulator must be avoided because this has already been shown in the exploratory apparatus to cause static charging. Dipping an amalgamated wire into a cup of mercury avoids static charging but causes a spurious voltage deflection due to the contact potential difference between the fresh mercury surface and the shielding and to the change in capacitance. The problem was effectively solved by mounting a six-inch long, thin coil spring of #30 nickel wire coaxially in a nickel-plated cylinder of 11 inch length and 5 inch diameter. Thus, when the spring is elongated $\frac{1}{2}$ inch during a measurement the change of capacitance amounts to only a few tenths of a micro-microfarad and, besides, the contact potential difference is also small. In order that the spring not be inelastically distended when the jack is raised, provision is made for disengaging the smaller cylinder connected to the upper portion of the spring and holding it fixed while the 42 inch vertical tubing connected to the probe assembly is moved. The wire passing coaxially down the 42 inch tubing terminates in a 1/8 inch diameter, 10 inch long length of amalgamated brass tubing which dips into a long slim cylindrical mercury well made from steel which is held by the uppermost of the three telescoping cylinders. This mercury well allows rotation and vertical translation of the probe assembly while contact is maintained and the spring remains undeformed. During a measurement the three large, finger-operated set screws on the upper cylinder are tightened and the three set screws on the middle cylinder are loosened so that the brass tube dipping in the mercury well does not move while the nickel spring elongates one-half inch. The internal mechanism within the cylinders is rigidly mounted with Teflon insulation of approximately one-half inch minimum path length. Before the upper part of the probe assembly was mounted, a test was conducted to ascertain whether or not the nickel spring and nickel cylinder arrangement produces an appreciable voltage deflection when the spring is elongated one-half inch. It was found that movement of the spring produced a negative deflection of about 0.2 mv which seemed to duplicate every time (and thus would be subtracted out anyway in a contact potential difference determination). On the other hand, when the spring was held stationary and the amalgamated brass tube was moved one-half inch upward in its well of mercury, a negative voltage deflection of about 19 mv was observed which failed to duplicate within about 2 mv. Thus, it seems that the spring-and-cylinder stratagem solves the problem of obtaining relative motion without an appreciable change in Volta potential of the "floating" system.

The probe-to-electrometer part of the circuit is completed by #30 wire in steel tubing of the same diameter as used in the other parts. The tubing emerges horizontally from the bottom of the spring-cylinder, goes vertically upward and then over to the electrometer and the variable-capacitance switch mounted on the massive iron stand. (A writing table obscures the electrometer controls in the photograph.) Again, as before, the wire is mounted coaxially under tension on Teflon insulators. It was found that this part of the coaxial system had to be braced very rigidly in spite of the inherent rigidity of the steel tubing otherwise vibrations of microscopic amplitude would cause appreciable potential oscillations. Although it is not readily apparent from the photograph, the diverse controls from the switch-board on the extreme left to the variable-capacitance switch on the extreme right are arranged in a semi-circle around the operator. The only control which cannot be reached from the operator's seat is the liquid switch handle which must be turned from beneath the junction chamber.

The Electrical System

The special vacuum-tube electrometer and variable-capacitance switch were described in some detail in Chapter VI and will not be further considered here. The two identical decade resistance boxes can be seen in Figure 7 mounted side-by-side in an obliquely inclined wooden rack. These General Radio Type 1432 (accuracy ± 0.05 per cent except the 0.1 ohm step decade) resistor decades with 1.0000 ma of current through them enable the balancing "IR drop" to be adjusted from zero to over five volts in steps of 0.1 mv. A standard cell, a Wolff standard resistance box, and a Rubicon light-spot galvanometer of 3×10^{-9} amp/mm sensitivity comprise the other major components of the potentiometer. The working current is supplied by four large (#6) dry cells which, together with the standard cell, are enclosed in an air-current-tight wooden box which minimizes emf fluctuations caused by short-term room temperature fluctuations. Experience has shown that these large dry cells have a useful life of more than six months even if the working current is never interrupted. Under these conditions the working current remains so constant that it need not be standardized more than once a day. This potentiometer may, through the proper electrical connections, also be used to measure the emf of the concentration cell formed in the junction chamber as described in the last part of Chapter V with the electrometer used as an ultra-high-impedance galvanometer. The Rubicon galvanometer is also used to measure the emf of the several copper-nickel thermocouples distributed throughout the apparatus. By means of another decade resistance box which can be put in series with the galvanometer, the resistance can easily be adjusted so that 75 mm on the scale is equivalent to 25°C.

In the preceding chapter, it was mentioned that induced emf from alternating current affected the operation of the apparatus. Since, a priori, alternating currents would not likely be suspected to cause trouble in a perfectly shielded electrostatic instrument, a further discussion of this interesting effect will be given here. When the apparatus was first put into operation, it was noticed that the random (in sense and magnitude) electrometer deflections that occur when the "floating" part of the circuit is ungrounded were considerably larger than those experienced with the exploratory apparatus--indeed were so large on the average that the variable-capacitance switch could only bring the system back to zero only about one time in three. Furthermore, to avoid slamming the needle against a stop pin, it was necessary to use a less sensitive scale on the electrometer while the switch was opened and then switch to a more sensitive electrometer scale for the measurement. This procedure causes some uncertainty in the zeroing of the needle on the scale.

An investigation revealed that the effect was reduced by an order-of-magnitude when all sixty-cycle per second alternating voltages in the room were turned off. The residual deflections were then still somewhat random in magnitude but were almost always in one sense. It was subsequently found that the residual deflections were essentially the same when only the power to the apparatus was switched off at the wall outlet. The alternating current normally supplies the galvanometer lamp, the fluorescent lamp, and the incandescent lamps in the thermoregulatory circuit. When the current was interrupted at the lamps rather than at the wall panel, the deflections were about the same as when the current was flowing. Thus the effect is not due to alternating magnetic fields caused by the currents but is due to an electrical alternating potential from the power wires. Trying different ground connections and running the ground wire (to which the structural framework, all shielding, and the electrometer are connected) out from different sides of the apparatus produced no noticeable difference in the effect. Shielding some of the power wires coaxially only made the effect worse; presumably because this shielding had to be connected to the same ground as the apparatus. Eventually it was decided to eschew further attempts at shielding these potentials and merely to turn off all power to the apparatus at a wall switch during each measurement. For precision thermoregulation it would be necessary to supply the thermoregulatory lamps with filtered direct current but this was not required for our work. Thus, it also eventuates that our early choice of a battery-powered electrometer was fortuitously fortunate.

An interpretation of these phenomena can be given as follows: the alternating electrical fields from the power lines induce alternating potentials in the metal of the grounded chassis and shielding of the apparatus. When the probe-to-electrometer part of the circuit is ungrounded and thus "floating," it is not appreciably affected by the alternating potentials and therefore a tiny sixty-cycle potential fluctuation exists across the electrometer which is too small and of too high a frequency to be apparent as a needle oscillation. However, in the millisecond instant when, on the atomic scale, the mercury and the amalgamated brass rod of the variable-capacitance switch are just separating, an electrostatic charge is given to the almost-"floating" system across the separating contact. The magnitude and sign of this charge depends on the portion of the sixty-cycle period which happens to exist in the power wires during the instant the switch contact is broken. As might be anticipated, the average magnitude of these deflections also depends on the capacitance of the "floating" system--when the probe assembly is raised high above the solutions, the average magnitude of the deflections is increased several-fold. Since a much smaller and unidirectional effect persists after all alternating potentials in the vicinity of the apparatus have been turned off, it is reasonable to suppose that these unidirectional electrometer deflections are caused by charge transfers at the moment contact is broken having their origin in the intrinsic properties of the metal surfaces themselves.

CHAPTER VIII

EXPERIMENTAL TECHNIQUES AND RESULTS

Introductory Discussion

In a strict sense all that has been discussed in the previous chapters has been merely a prologue--although quite a necessary one--to the experimental work now to be reported. In the introductory chapter we labeled the unfolding drama of attempts at determining single phase-boundary potential differences a "comedy of errors"; that it may well be, but it is now certain that the experimental work reported here will by no means constitute the last act of that drama. Our hope is that these experiments will point toward a method by which the goal of precision determination of liquid-junction potential difference can eventually be attained.

Altogether, about 1400 Volta potential difference measurements were taken with the final apparatus. Most of these measurements were concerned with evaluating the performance of the apparatus and its several components under varying experimental conditions. This was necessary in order to be able to interpret the solution-solution contact potential difference measurements with some assurance.

The numerical values of the individual solution-probe Volta potential differences are meaningless and need not be recorded here, since an individual Volta potential difference is constituted of the silver-chloride electrode emf, the silver-nickel Galvani potential difference, the nickel probe surface potential difference, and the solution surface potential difference--none of which are individually determinable. However, as has been explained previously, the difference of two solution-probe Volta potential differences determines the solution-solution contact potential difference under the assumption that all four of the individual phase-boundary potential differences remain constant during a measurement. Moreover, as will become clear later, some idea as to the individual variations of the separate potentials under varying experimental conditions can be distilled from the vast number of Volta potential difference measurements which have been recorded. For now, it is sufficient to note that, under normal conditions, only the two surface potentials are subject to variation with time. It may be of interest that the Volta potential differences measured with the final apparatus under widely varying conditions lie in the range from -300 to +300 mv.

The precision of the individual Volta potential difference measurements normally varies from ±0.1 mv to ±0.4 mv (in terms of extreme variation) depending on

a) the grid current of the particular pair of matched electrometer input tubes being used,

b) the time rate of change of the surface potential differences, and

c) the distance across the probe-to-solution air gap.

Of these, (c) is of least importance: whether the gap distance is two or three millimeters is not critical. However, under conditions where static charge is present, the precision may be as poor as ±30 mv. The precision of most of the normal measurements reported in this chapter is close to ±0.2 mv and ±0.1 mv is not at all uncommon when time variation is slight.

Each individual Volta potential difference measurement is actually a series of null determinations made in quick succession. Naturally, finding that "IR drop" which will just balance out the Volta potential difference is a trial-and-error process involving many separate upward movements of the probe disk. However, with sufficient practice and experienced "intuition" the annulling "IR drop" can be found fairly quickly. After a balance has been attained, a series (usually five) of additional, check balances is quickly made to insure that a reading to within the sensitivity of the instrument is obtained and to ascertain the precision of the measurement. This procedure usually takes from one to eight minutes depending on time rate of change and on the foreknowledge as to the approximate reading expected. However, the time between measurements on the two solutions is somewhat longer because of the added mechanical manipulations necessary. This time usually varies from four to ten minutes and is normally about five or six minutes.

Organic Surface Films

From the work done with the exploratory apparatus, it was evident that one of the problems involved in determining liquid-junction emf's from contact potential measurements would be to control the amounts of organic impurities present at the solution-air interfaces; and indeed, the final apparatus was designed with this problem of organic impurity in mind. The knowledge of the change in surface potential brought about by the orientation of relatively insoluble dipolar molecules at the surface of aqueous solutions is by no means new.[1] Along with the very extensive work carried out during the last four decades on the properties of surface films (usually monomolecular layers), some surface potential measurements have been performed on an ancillary basis using a polonium-coated probe supported above the solution. The difference between the surface potential of "pure" solution (cleaned by a sweeping technique) and the same solution covered with a monomolecular layer of a non-volatile organic substance is called the "surface potential" of that substance. However, the limited reproducibility and difficult interpretation of these measurements has greatly restricted their significance. The present consensus is that the only utility of these measurements is to show the homogeneity or degree of "patchiness" of the surface film. The measured "surface potentials" of most relatively insoluble organic dipolar substances lie in the range from about 200 to 500 mv. The precision of these measurements is usually in the neighborhood of ±20 mv. Alternatively, from a knowledge of the number of organic molecules per unit area and of the dipole moment of each molecule, the "surface potential" of compressed (that is, vertically oriented) monomolecular films can be calculated.[2] For hydroxylic compounds such as fatty acids and alcohols having dipole moments of about 1.7 Debye units, the calculated "surface potentials" turn out to be in the neighborhood of 2500 mv. The huge discrepancy between the calculated and measured values is usually attributed to the

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[1] N. K. Adam, The Physics and Chemistry of Surfaces (Oxford Univ. Press, London, 1941), p. 33.

[2] W. O. Harkins, The Physical Chemistry of Surface Films (Reinhold Pub. Corp., New York, 1952), p. 129.

orientation of water dipoles under the film caused by the presence of the film and to the formation of a "gegenion" atmosphere in the solution beneath the film. However, especially in view of the poor reproducibility usually obtained, a portion of the discrepancy might arise because the solution surface is not perfectly free from organic impurities at the beginning.

For our work, the implication of these facts is clear: in order to achieve a reproducibility of about ±0.5 mv, the maximum permissible surface concentration of dipolar molecules is in the neighborhood of one-thousandth of the number of molecules necessary to form a monomolecular layer. Thus, since the monomolecular layer is the stable configuration of most surface films on solutions, in a sense the "background" potential is about ten times larger than the solution-solution potential to be measured. It is this fact, more than any other, which makes the experimental work quite tedious. Although most of the experimental work has been done with practically insoluble long-chain fatty acids and higher alcohols, it is nonetheless true that relatively soluble short-chain compounds also form dipolar monomolecular layers but with decreasing concentration into the bulk of the solution. This fact makes it impossible to skim off the impurities by a sweeping technique and impossible to achieve purity by allowing the impurities to float to the top of a vessel and then drawing the solution off from the bottom.

The Problem of Obtaining Reproducibility

Since, of the four potentials in the Volta potential measuring circuit, only the solution surface potential and the probe disk surface potential are subject to appreciable change, reproducibility of the Volta potential difference depends on the reproducibility of these surface potentials. Actually, since only the difference of two probe-solution Volta potential differences is of importance, it is sufficient that the surface potential of the probe disk remain constant during a series of measurements and during the repositioning of the probe from one solution to the other. There is no need for the surface potential of the probe disk to remain constant over a long duration or to be reproducible from one experimental set-up to another.

On the other hand, the difference of the surface potentials of the two solutions is an integral part of the solution-solution contact potential difference. Thus, to achieve C.P.D. reproducibility, the difference of the solution surface potentials must be reproducible. A priori, it would seem that the only practical way to assure the reproducibility of this difference is to have perfectly clean solution surfaces at all times. But this, needless to say, is easier said than done.

Toward the goal of achieving C.P.D. reproducibility, our first experimental project--and, indeed, the larger portion of the experimental work with the final apparatus--was to measure the C.P.D. between identical solutions. Naturally, the prime requirement for this is that organically pure water be obtained. Multiple distillation was carried out starting with a commercial tin-lined still and finishing with distillations from Pyrex flasks into Pyrex reservoirs. Triple distillation was abandoned early when it was found that no difference in reproducibility could be detected between triply and doubly distilled water. All vessels with which the water came into contact were carefully cleaned and given final rinses with Fisher "Certified" reagent acetone. Both 10^{-2} and 10^{-3}

N HCl solutions were measured but almost all of the early work was done with 10^{-3} N HCl. The solutions were made from distilled water and the appropriate amounts of a commercial 1.00 N HCl standard solution.

In this early work, no direct attempt was made to obtain zero C.P.D. but rather, use was made of the fact that the surface potential of a solution reaches a value after about three weeks which remains constant save for a slow fluctuation of one to five millivolts a day. Therefore, this "old" solution can conveniently serve as a reference potential against which the Volta potentials of the probe disk and the other solution can be compared. Thus, with this artifice, the labor involved in studying the reproducibility of solutions is about halved. This saving is considerable since the set-up time required--for disassembling parts of the apparatus, thoroughly cleaning them as well as diverse auxilliary equipment, and reassembling them with meticulous care in order to minimize organic contamination--is from two to three days of full-time work. After the reassembly is complete, the hood is replaced and about ten to twelve hours is required before the concentration of solution vapor in the hood reaches practical saturation, so that the surface potential of the probe disk remains essentially constant as the probe is moved from one solution to the other.

Measured against the "old" solution as a reference, the reproducibility of the Volta potential differences was extremely poor--roughly ±70 mv extreme variation about the mean of a set of six determinations. Each of the above measurements was taken about twelve hours after the trough was filled and the hood replaced. Three fillings were made from a single five-gallon carboy of the solution, then a new carboy was prepared and three more determinations were made. The time rates of change (after twelve hours) of the solution surface potentials were roughly equivalent so that their decay curves were roughly exponential and parallel. In every case the Volta potential of the solution became more positive with the passage of time and the initial time rate of change was roughly 4 mv/hr. As the solutions aged, the discrepancy among their surface potentials increased.

An interpretation that can be given is that dipolar organic compounds, such as fatty acids, are present in the water supply and that these are carried over with the steam during the successive distillations. Attempts were made at obtaining higher purity by letting the final distillate set for several days and then siphoning off the bottom two-thirds of the water. However, reproducibility was not conclusively improved.

It was then found that a commercial distilled water ("Shamrock doubly-distilled water from the Eureka Water Co. of Oklahoma City) significantly improved the reproducibility. This water has since been used in all of our experiments. With this "Shamrock" water nine determinations (three from each carboy) gave "initial" Volta potentials of +5, -2, +21; -19, -29, -14; +20, +5, +13 mv with respect to the mean of the nine readings. While in terms of extreme variation from the mean of the nine readings, this represents an improvement by only a factor of two, the extreme variation from the mean of each set of three is at most about ±15 mv. While the improvement in reproducibility is definite, it still falls far short of the ±0.5 mv which is needed for an accurate determination of the liquid junction emf.

Much later in our experimental work, after trying two other techniques to be discussed later, we returned to this problem and achieved considerably better results. This time, instead of using an "old" solution as a reference Volta potential, we cleaned both solution systems each time and refilled them with identical solutions from the carboys. An approach to identity of organic impurities was achieved by premixing two 5-gallon carboys together. Thus, since in this work only two fillings were obtained from each carboy, the data appears as two sets of four measurements--each set being drawn from two premixed carboys. The contact potential differences between the two "identical" solutions were +1.6, -1.9; +0.7, +2.5 mv and -4.2, -2.7; -0.4, -2.8 mv where the semicolons separate the readings from different but premixed carboys. The mean of the eight readings is about -1 mv but this is probably not significant. Thus, in these measurements, the extreme variation from zero C.P.D. is about 4 mv. The reason for this relatively large gain in reproducibility is not too clear: it might be due to the inclusion of a soaking and rinsing cycle of n-Heptane in the washing operation (which had not been done previously) or it might possibly be due to the fact that many months of washing and soaking have finally leached out organic impurities in the polyethylene troughs which were previously dissolving and floating to the surface. A small amount of reflection can conjure up many other possibilities but there is no point in stressing the obvious lack of complete control of the cleanliness parameters in this experiment. In each of the above measurements, the course of the Volta potential of each solution was followed for at least three days. For the first day or so in every case the Volta potential of each solution remained about the same or increased by at most 20 mv. After the first day, the

Volta potential became more positive at a rate of roughly 2 mv/hr; and after three days at the rate of about 1 mv/hr. But in every case, although the Volta potential of each solution may have increased by about 150 mv or so, the Volta potential difference between the solutions remained the same within 1 mv of its initial value for at least two days after filling. Indeed, in one case the contact potential difference was originally -1.9 mv, after five days was -3.2 mv, and after twenty-one days was -18.2 mv. (A study of the behavior of the Volta potential of the probe disk was also conducted during this time.) During this twenty-one day period the Volta potentials of the solutions increased about 500 mv.

In summary: it has been demonstrated that, by meticulous cleansing and handling, it is possible to attain a solution surface potential reproducibility of about ±3 mv. This is not to be construed to mean that near-organically-pure solution surfaces have been obtained. On the contrary, it is probable that each solution is at all times covered with a monomolecular organic film. What has been demonstrated here is that meticulous techniques can almost assure identical monomolecular layers on different solution troughs filled from the same vessel. Unfortunately, this ±3 mv reproducibility is not quite good enough to permit a determination of the liquid junction emf to within the ±0.5 mv necessary to make a really significant contribution to electrochemistry.

At this point, rather parenthetically, it might be mentioned that an evaluation of the constancy of the Volta potential of the probe disk was continually carried out during this research. Several methods have been used in this study but all depend on the greater constancy of the solution surface potentials than the probe disk surface potential during the short time between measurements. This criterion is adequately fulfilled during the first day and after the first week after filling. One technique in this study is to measure the Volta potential difference with the probe above one solution, then above the other, again above the first, then above the second, and so on with various periods of waiting in between. Another technique is to allow the probe disk to remain about two millimeters above one solution for an hour or longer or until a steady state of adsorption has occurred and then to raise it about five inches, immediately lower it again, and then redetermine the Volta potential difference. Another technique is to allow the probe disk to remain about five inches high in the general atmosphere in the hood and then to lower it into position above one of the solutions and determine the Volta potential difference as a function of time. This technique is also carried out with the hood removed so that the probe reaches adsorption equilibrium with the room air.

The several hundred measurements directed toward the evaluation of the behavior of the surface potential of the nickel-plated probe disk can be summarized as follows:

a) The short-term changes induced in the surface potential of the probe are usually rather completely reversible. This, undoubtedly, is correlated with the reversibility of water-vapor adsorption on the surface of the probe.

b) After it has attained adsorption equilibrium in an atmosphere of essentially 100 per cent relative humidity (and with HCl vapor), exposure to room air makes the probe 15 to 40 mv more negative.

c) After it has attained adsorption equilibrium at a distance of about two millimeters above a solution surface, raising the probe a distance of about five inches where a new equilibrium is established in an hour or less, causes the probe to become about 3 to 6 mv more negative when water vapor saturation is established within the main chamber.

d) Quickly raising the probe five inches above a solution and immediately lowering it again to the solution causes it to become 0.5 to 2 mv more negative.

e) Moving the probe from a position two millimeters above one solution to a like position above the other (as during an actual contact potential measurement) makes it 0.5 to 1.5 mv more negative _when the two solutions have the same concentration_ and when adsorption equilibrium had been established about two millimeters above the first solution.

The actual behavior of the probe disk surface potential depends somewhat on the "aging" of the probe--that is, on its overall time of exposure to the vapor from HCl solutions. During the first six weeks of operation of the instrument, the surface potential variations were about twice as large as indicated above.

It is, of course, condition (e) which is the most important for our contact potential work. When the two solutions are identical in concentration, a quick succession of measurements taken above the first solution, above the second, first, second, and so on, can reduce the uncertainty of the Volta potential of the probe disk to about 0.5 mv at most.

This is well within the reproducibility of the solution surface potentials which we have attained. Thus, to within about 0.5 mv, the difference of the probe-solution Volta potential differences is the solution-solution contact potential difference. In this connection it is noteworthy that reversing the interchangeable silver chloride electrodes in the junction chamber changes the probe-solution Volta potential difference by an amount which ranges from undetectable to about 0.6 mv depending on conditions. If the electrodes have been standing for a week or so in the same solution, the interchange potential difference is usually less than 0.3 mv. Moving the liquid switch and thus causing some relative motion between the E_0 silver chloride electrode and its solution, results in an initial change of Volta potential difference of about 1.5 mv. However, the change is self-reversing and after about two minutes the potential returns to its former value to within about ±0.2 mv. If the liquid switch is moved too abruptly, tiny air bubbles are admitted into the capillary tips. These cause large and random fluctuations in potential. However, no trouble arises if the switch is moved without large acceleration. Nonetheless, in some of our final work, the liquid switch was bypassed and contact was maintained between the potentiometer and both solutions at all times. This did not introduce any of the difficulties that had earlier been suspected.

In conclusion, we may say that with this apparatus it is possible to measure the contact potential difference between solutions of the same concentration to within at most ±0.5 mv uncertainty. Moreover, zero contact potential difference can be measured between ostensibly identical solutions with about ±3 mv extreme variation. Unfortunately, as we shall see later, the uncertainty in the contact potential difference measurement between solutions of different HCl concentration is somewhat greater.

Additional effort could be expended in an attempt to obtain organically purer water but, because of the large volume of solution required in the washing and filling operations, this would not be easy. More will be said about this approach at the end of this chapter. However, even if organically pure water could be obtained in sufficient quantity, the reproducibility would still be limited by organic impurity in the electrolytes. In order to have a non-zero junction emf, the two solutions must either have different solutes or different concentrations of the same solute. In either case, the solutions--even if made from water totally free from organic compounds--would have different amounts of organic impurities from the electrolytes used. Moreover, the techniques required to obtain organically pure electrolytes would be rather elaborate.

It was the consideration of these facts which led us to attempt to remove the organic film present by sweeping the surface and to attempt to annul the oriented-dipole double layer surface potentials by floating a film of a non-polar organic liquid on the solution surfaces. These techniques will now be described in the sections which follow.

The Sweeping Method

Langmuir and later Adam[1] perfected a technique for measuring the surface pressure exerted by a monomolecular film of an insoluble organic substance floating on an aqueous solution surface. The usual substances studied were long-chain fatty acids and alcohols of more than twelve car-

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[1] Adam, op. cit., p. 28.

bon atoms. The vessels were rectangular troughs usually made of glass and coated with paraffin wax. In order to obtain "clean" surfaces at the start of each experiment, the trough was filled brimful with the solution and its surface was swept by moving one or more paraffin-coated glass strips across it. Both the trough and the sweeping strips were recoated with paraffin before a new run was begun. The surface pressure of "clean" water (obtained by sweeping the surface with different paraffined strips several times in succession) was usually roughly a hundred times less than that of a monomolecular film.

As was described in the last chapter, the final apparatus was designed so that sweeping could be performed without removing the hoods and thus disturbing the water-vapor equilibrium. In the initial work the two identical sweeping assemblies (each consisting essentially of two vertically mounted Teflon strips) were drawn across the two identical polyethylene solution troughs which had been filled brimful and "heaping" with the solution. Prior to being mounted in the apparatus before each run, the sweeping assemblies were thoroughly cleaned with "Tide" brand detergent solutions, scrubbed and soaked in three separate solutions of ammonia in distilled water, and finally rinsed with reagent grade acetone. All handling, as also with other parts of the solution system, was done while wearing Neoprene gloves thoroughly cleaned and rinsed with acetone each time.

It was discovered that the sweeping process invariably produced static charging of the trough surfaces to such an extent that precise measurement was impossible for about twenty-four to thirty-six hours afterwards. Indeed, as had been noticed earlier, handling the troughs in the cleaning and remounting operations also caused static charging which normally required more than twelve hours to dissipate. This difficulty was obviated by exposing each trough after mounting and sweeping to eight milligrams of radium (surrounded by two centimeters of lead) at a distance of about six inches. The exposure time required to dissipate the static charge is about fifteen minutes.

Sweeping usually caused the Volta potentials of the solutions to become roughly 230 mv more negative but the reproducibility of different sweepings of "identical" solutions was only roughly ±30 mv in terms of extreme variation. Furthermore, the time rate of change of solution Volta potential after sweeping was in the neighborhood of 1 mv/min for the first hour or so and gradually declined to about 1 mv/hr after the first day. This rapid time rate of change limited the precision of the measurement rather severely. Usually, the first measurements were taken at the set time of forty-five minutes after the solution had been swept in order to allow time for charge dissipation from both troughs. Thereafter, the course of the potential was usually followed for a day or so through a change of roughly 300 mv.

Because of the very poor reproducibility, several minor modifications were tried in the cleaning and handling operations and in the height of solution in the troughs but no conclusive improvement was noted. It was then decided to try different materials as sweepers. Sweeping strips wrapped with waxed paper gave considerably poorer reproducibility. Polyethylene rods gave about the same reproducibility as before and, oddly enough, about the same static charging against the polyethylene troughs as Teflon did. Glass strips, however, gave a somewhat better reproducibility of ±12 mv extreme variation and somewhat less static charging but about the same post-sweeping time rate of change.

The poor reproducibility of the sweeping procedure in our work and the rapid post-sweeping time rate of change are likely due to re-spreading of an imperfectly removed insoluble surface film and/or to rediffusion of soluble organic compounds back to the solution surface after the sweepers have passed. There remains, of course, the possibility that the sweepers themselves were never perfectly free from organic compounds. The somewhat better performance of the glass sweepers could be due to the fact that the possibility of edge-leakage under the sweepers is minimized by the wettable nature of the glass surface.

Instead of devoting more time to refining the sweeping technique, we decided to try the totally different technique described in the next section. The prime reason for eschewing further attempts at sweeping is that more than an order-of-magnitude greater organic purity would be required and this would entail an almost prohibitive amount of labor, since about ten gallons of water are required for a single run when the sweeping assemblies must also be cleaned.

The Macroscopic Organic Film Method

Since the reproducibility and time stability of the sweeping method turned out to be rather poor, we decided to try a different tack in the course of our investigation. The essence of this method is to float a film of macroscopic thickness of some liquid organic substance of very low dielectric constant on the solution surfaces. The principles on which our hope for the success of this stratagem rest are the following:

Molecular orientation probably occurs at the solution-organic liquid phase boundary in the same manner as at the solution-air boundary. However, in the former case, ionic charge carriers can penetrate into the upper phase and thus thermodynamic equilibrium can, in time, be established across the phase boundary. It is this ionic equilibrium alone which determines the equilibrium potential difference between the two phases. Thus, if there be an initial potential difference across the interface due to the orientation of molecular dipoles, this dipolar potential difference should disappear in time due to the migration of the ions to form opposing ionic atmosphere double layers in both the aqueous and organic phases. At thermodynamic equilibrium, the Volta potential of the organic phase should be that of the pure aqueous phase plus the Galvani potential difference between the two phases. From the Nernst distribution law, this Galvani potential difference should, at least to approximation at low concentrations, be independent of concentration; but this must be checked by experiment. It should also be pointed out that the Volta potential of the organic phase is independent of dipole orientation only if no such orientation occurs at the organic phase-air boundary. This supposition seems reasonable in view of the 2:1 ratio of dielectric constants across this boundary compared with the 80:1 ratio across the solution-air boundary. Moreover, this ratio of about 40:1 probably appears exponentially in a Boltzmann-type distribution function.

The first organic liquid tried was "Nujol," a brand of highly purified mineral oil. Its spreading coefficient was so low that a lens of it had to be almost six millimeters thick before it would cover the solution (10^{-3} N HCl). The Nujol had previously been allowed to stand, with occasional agitation, in contact with the identical solution onto which it was to be poured for three days before it was used in order to allow it to come to solution equilibrium with the aqueous phase. The presence of the Nujol initially caused the Volta potential to be about 60 mv more negative and, after a day, about 40 mv more negative than it was in the absence of the Nujol. Thereafter, the Volta potential above the Nujol was a function of the position of the probe disk above it. If the probe disk was stored overnight at a distance of about three millimeters above the Nujol, the Volta potential of the latter was roughly what that of the solution had been before the Nujol was added. On the other hand, if the probe disk was stored totally away from the Nujol overnight, the Volta potential of the Nujol was about 110 mv more negative. Intermediate distances gave intermediate effects. Further investigation disclosed that the Volta potential of the Nujol would change approximately exponentially from one equilibrium to the other with the initial rate of about 30 mv/hr. The final equilibrium would be attained in about nine hours. Furthermore, during a period of almost three weeks, the phenomenon was approximately reversible and reproducible.

A possible explanation is that some volatile, dipolar impurity from the Nujol deposits on the probe disk whenever it is left close to the Nujol; but this is by no means certain. It is also possible that the potential of the Nujol layer changes due to the deposition of static charge on its surface whenever the probe disk is close. Presumably, natural radioactivity would be sufficient to carry the small amount of charge required across the air gap; the conductance across six millimeters of Nujol is extremely low. However, what is certain in any case is that Nujol films do not function in the way they must in order to be of value for our work.

A search was initiated for an organic liquid which would combine the necessary and the optimum qualities thought to be required for good performance. These qualities are:

Density less than that of water.

High spreading coefficient so that relatively thin films can be used.

Zero permanent dipole moment so that adsorption on the probe disk would be less likely to cause trouble and so the dielectric constant is very low.

Relative insolubility of it in water and water in it.

Low volatility.

No effect on polyethylene plastic.

Relatively inexpensive for the quantity and purity needed.

From data and information on more than a thousand compounds, only p-Xylene and the aliphatics from n-Octane to n-Tetradecane were found to meet these requirements.

For the initial work, p-Xylene was chosen since it is considerably less expensive than the aliphatics. In the experiments 200 ml of p-Xylene were poured onto each solution to form a layer about two millimeters thick. In the span of one day evaporation into the space of the inner hood decreased the film thickness to slightly under one millimeter. The vapor pressure of p-Xylene is about 9 mm of Hg at 25°C.

While shipment of p-Xylene was awaited, pure but mixed-isomer

Xylene was tried. This was found to make the Volta potential of the probe disk more negative by roughly 100 mv. Moreover, this probe disk potential depended severely on the "history" of the position of the disk with respect to the Xylene surfaces. This experimental aside served to emphasize the wisdom of using compounds with zero permanent dipole moment.

Addition of layers of p-Xylene to the solutions caused their Volta potentials to become more positive initially by about 190 mv. The Volta potential of the probe disk was not noticeably changed by the presence of p-Xylene vapor. The Volta potentials of the p-Xylene films slowly increased with time until they stabilized after about thirty hours at roughly 60 mv higher than initially where they remained with fluctuations of about ±10 mv for almost a week.

Altogether, seven attempts were made to measure zero C.P.D. between two 10^{-3} N HCl solutions drawn from the same carboy with 200 ml of 99 per cent pure p-Xylene poured onto their surfaces. These measurements were recorded after the Volta potential of the p-Xylene had essentially stabilized--that is, a day or so after the p-Xylene was poured on. These results are recorded below. The first row gives the solution-solution C.P.D. about one hour after filling and just before the p-Xylene was added. The second row gives the respective Xylene-Xylene Volta potential difference after stabilization (about a day later).

-0.8	-2.2	+6.5	+1.7	+4.9	-7.6	+3.0 mv
+7.3	+11.1	+3.8	-5.8	+0.6	+2.5	-1.4 mv

The mean of the seven solution-solution contact potential differences is +0.8 mv while that of the seven Xylene-Xylene Volta potential differences is +2.6 mv. The respective maximum variations from zero are about 8 and

11 mv. There does not seem to be any correlation between the Volta potential differences before and after adding the p-Xylene.

One attempt at using n-Heptane instead of p-Xylene was made. However, the two millimeter layer evaporated before stabilization of the Volta potential measurements occurred. (The vapor pressure of n-Heptane is about 46 mm of Hg at 25°C.)

It is apparent that the reproducibility of the p-Xylene measurements is somewhat inferior to that of the solution-solution C.P.D. The mean values of the respective sets are particularly discordant. However, on this basis alone, it is impossible to predict what the mean values would be if another set of measurements were taken. It is also difficult to point out the probable causes of the relatively poor reproducibility of the p-Xylene measurements. Dipolar impurities in the p-Xylene could be responsible. A better guess might be that, since long-chain dipolar molecules are preferentially soluble in the organic phase, these impurities from the aqueous phase diffuse into the p-Xylene and orient very slightly at the Xylene-air interface. If this latter conjecture is correct, then it is obvious that the macroscopic organic film technique is of no use at all for our purposes.

It was a pleasant surprise to find that the solution-solution C.P.D. reproducibility in the set of seven measurements was considerably better than the ±30 mv previously recorded. Perhaps the reason lies in our measuring the C.P.D. between two fresh solutions in this set of seven, whereas in the older set of nine the readings were taken fourteen hours after filling and were referred to the Volta potential of an "old" solution. Or, perhaps the reason lies in our including soaking with n-Heptane in the washing cycle used in the later work.

Because of this improved solution-solution C.P.D. reproducibility, we then decided to make a further, careful investigation of the possibility of measuring zero C.P.D. between solutions of identical concentration. In order to obtain more measurements from the same solution, we pre-mixed two 5-gallon carboys at a time. The data were taken forty-five minutes after filling (and after the static charge caused by handling the troughs had been dissipated by radium). These data are recorded in the previous section, "The Problem of Obtaining Reproducibility." These eight measurements have an extreme variation of about ±4 mv from zero C.P.D. If these eight are combined with the seven from the p-Xylene work, the mean of the set of fifteen is -0.35 mv. However, this near-zero mean may be fortuitous. Moreover, even if we assume that the mean of a set of twenty measurements would always give the correct solution-solution C.P.D., the prodigious amount of labor required reduces the practicality of the method. The great value of these measurements is that they unequivocally demonstrate that the apparatus functions properly as a whole and the appreciable extraneous contact potential field assymmetry in the main chamber does not exist. Therefore, interchange of solutions between the two troughs (when different concentrations are used) is not required.

A Determination of a HCl Concentration Junction Emf

Since it had been found that careful procedure and meticulous cleanliness could give about ±4 mv (extreme variation) reproducibility between solutions of identical concentration, we decided to attempt to measure the liquid junction emf between a solution of 10^{-3} N HCl and 10^{-2} N HCl. This solution pair was chosen since most of the previous work had been done at 10^{-3} N and since the emf is predicted to be relatively large (about 37 mv) so that the inaccuracy due to organic impurities would be relatively small.

However, much to our chagrin, the behavior of the Volta potential of the nickel-plated probe disk was found to be considerably less reliable and less predictable than when the solutions were identical so that the uncertainty caused by the probe is ±2 to ±3 mv. This variation of probe Volta potential is presumably due to different concentrations of HCl in the vapor immediately above the different solutions. To be more specific: if the probe disk is left for an hour or so at a distance of 2.5 mm above the 10^{-2} N HCl solution, it becomes about 17 mv more positive than when it is left for an hour or so at an equal distance above the 10^{-3} N HCl solution. The effect is approximately reversible. When the probe disk has been stored at 2.5 mm above the 10^{-3} N solution and then is positioned at the same distance above the 10^{-2} N solution, its Volta potential increases about 7 mv in six minutes and then slowly increases to the equilibrium value in about forty-five minutes. When the probe disk has been stored above the 10^{-2} N solution and then is positioned above the 10^{-3} N solution, the same phenomenon, but with reverse sign, occurs.

A way of minimizing this variation is to measure the solution-probe Volta potential differences as quickly as possible by taking a reading above one solution, above the second, again above the first, again above the second, and so on. In this manner the time between successive measurements over different solutions is about five minutes. After the third or fourth cycle of measurements, the Volta potential of the probe disk is quasi-stationary and the amplitude of its fluctuations is reduced to ±2 mv or, at worst, ±3 mv. This technique was used in taking the measurements recorded below.

In each case the junction between the solutions was formed in a porous plug of tightly-packed Pyrex glass wool in the junction cell described in Chapter VII. The junction was formed while the solution troughs were being irradiated with gamma radiation in order to dissipate static charge. The first measurements were taken forty-five minutes after the troughs had been filled and just after the hood on the main chamber was replaced. The course of the solution-solution C.P.D. was followed for at least two days thereafter. Five different experimental runs were carried out. The first two measurements were on solutions drawn from two carboys which were mixed before the respective quantities of 1.00 N HCl standard solution were added, the second two measurements from another pre-mixed pair of carboys, and the last measurement from yet another pre-mixed pair.

C.P.D. 45 min. after filling	45.2	39.4	39.3	35.7	38.0 mv
C.P.D. 3 hrs. after filling	48.1	38.6	42.7	36.9	37.7 mv
C.P.D. 20 hrs. after filling	56.3	40.9	40.0	37.4	39.2 mv
C.P.D. 2 days after filling	61.6	42.5	40.8	39.2	43.5 mv

The means of the sets of five measurements at the several times are 45 min., 39.5 mv; 3 hrs., 40.8 mv; 20 hrs., 42.8 mv; and 2 days, 45.5 mv. If we were to throw out the first run as spurious (as it possibly is), the apparent reproducibility would be considerably improved--however, there would be no possible justification for this. Since the unpredictability of the probe Volta potential amounts to about ±2 mv, the third digit in these data is really not significant. The calculated standard deviation of the sets of five measurements is about 3 mv and the probable error is about 2 mv. Thus, in the limited sense in which statistics can be applied to a set of only five measurements, we may say that our measurement of the contact potential difference between 10^{-3} N and 10^{-2} N HCl is 40 ±3 mv.

In Chapter III considerable discussion was devoted to methods of calculating the homosolute liquid junction emf E_j. From this discussion it follows that Method I and Method II are a priori about equally correct in the range from 10^{-3} N to 10^{-2} N. Table 1 of Chapter III presents the values which we calculated by the several methods. Method I gives for the above junction $E_j = 36.9$ mv while Method II gives 37.5 mv. We shall take the mean of these as the most probable theoretical value for E_j, that is, $E_j = 37.2$ mv. Of course, the accuracy of these calculations depends not only on the correctness of the theoretical concepts and on the approximations introduced, but also on the reliability of the empirical constants used. Fortunately, for HCl these constants are known with very good reliability. It is our conjecture that the uncertainty in the calculated value is no greater than ±0.5 mv. Thus, our measured value of 40 ±3 mv is to be compared with the calculated value of 37.2 ±0.5 mv.

Assuming for the moment that the correct value of E_j is 37 mv and that the measured value is exactly 40 mv, we might speculate on the causes of this "error." Three likely causes for this discrepancy could be advanced:

a) The different HCl concentrations in the vapor immediately above the different solutions could cause an assymmetry in the Volta potential of the probe in spite of the experimental technique used. The sign of the observed change of Volta potential with time when it is above the 10^{-2} N HCl solution is consonant with this hypothesis.

b) The different amounts of 1.00 N HCl standard solution used to make the working solutions will, of course, carry different quantities of organic impurities. These impurities could also account for the average increase of the discrepancy with time.

c) The difference of the surface potentials of two organically pure HCl solutions could be a not-exactly-zero function of concentration. Should this be so (even though the work of Görlich mentioned in Chapter V indicates otherwise), then it would mean that our method of determining E_j from C.P.D. measurements is not valid.

Of course, there is, in addition, always the possibility that our method of forming the junction or making the solutions is faulty. However, the concentration junction has long been celebrated as being foolproof. Nevertheless, and in a larger sense, none of these speculations should, at this stage of the work, be taken very seriously. After all, because of the regrettable lack of reproducibility, 40 ±3 mv is compatible with 37.2 ±0.5 mv.

Prospectus

At the completion of the present work, our thoughts naturally turn to ways in which it could have been done better and to ways for refining the techniques in the future. At the present time it seems that our method for determining the liquid junction emf from contact potential measurements is valid. However, before the determinations can be of great significance to the field of electrochemistry (and perhaps to the field of physiology) their reproducibility must be improved by ten-fold. This will not be an easy task. The best that one can do is to attempt to glean from the chaos of measurements some hint as to probable improvements in the technique.

In our final apparatus, polyethylene was chosen for the troughs because of its relative ease of fabrication, its high degree of chemical inertness, and its non-wettability. This latter characteristic was desirable so that the solution would not flow over the sides of the trough when it is swept. Low conductivity in the presence of water vapor and low dielectric constant are two secondary characteristics which were also regarded as important. With hindsight, we now realize that polyethylene troughs have two serious defects: it is impossible to make certain that they are organically clean and they are not dimensionally stable over a period of many months. Even the nominally one-inch thick troughs have deformed appreciably by plastic flow so that edge effects during sweeping become a serious problem. (Any additional supports for the troughs would have to be non-metallic in order to prevent contact charging.) The sweepers were made from Teflon for the same reasons as above plus the fact the low friction and the absence of stick-slip sliding are very desirable.

Now, however, we would recommend that both the solution troughs and the sweeping assemblies be made from "Vycor" brand, 96 per cent silica glass if this is economically feasible. Vycor is much more chemically inert than any other glass and does not exhibit plastic flow below 1000°C. The Vycor troughs and sweeping assemblies would be heated to around 700°C before the start of each run. Then the troughs would be installed in the apparatus and filled edge-to-edge full of solution. The sweepers would then be drawn across and the excess solution would run down the sides of the trough. Any organic film which did not adhere to the sweepers would presumably go along with the overflow solution. Heating to red incandescense would seem to be a fairly certain way of making sure that the surfaces of the troughs and wipers are free of organic impurities.

With this system of cleaning by incandescence, sweeping would not be necessary if organic-free water and electrolytes could be obtained. Perhaps organic-free water could be obtained by distillation from a concentrated solution of potassium hydroxide and potassium permanganate to which a salt of a heavy metal has been added in order to form a non-volatile soap from the fatty acid impurities. Two further distillations would then be caught in Vycor vessels previously heated to 700°C. If this technique proves to be insufficient, steam could be superheated to 700°C and then condensed.

In the case of crystalline electrolytes such as KCl, organic purity could probably best be achieved by heating the fused salt to incandescence. (Recrystallization would be a slow and uncertain technique complicated by adsorption on the surfaces of the crystals.) In the case of HCl it might be possible to achieve organic purity by simply boiling sulfuric acid (330°C) with sodium chloride and dissolving the effluent HCl gas in a flask of organically pure water. If this is not sufficient, then HCl gas could be heated to 700°C. However, the technical problem of finding an inert container for HCl at this temperature might not be easy.

Difficult as they may be, problems of organic impurity are not the only ones which must be solved before the reproducibility of solution-solution contact potential measurements can approach ±0.3 mv. The Volta potential of the probe disk must be made to be essentially independent of the position of the probe with respect to the solutions of different concentration or of different electrolytes. Admittedly, in investigating HCl solutions, we have probably encountered this problem at its worst. For non-volatile electrolytes such as KCl, it may well be that the Volta potential of the probe disk is as stable for different concentrations as it is between two identical HCl solutions although this question is moot since different concentrations of KCl have very slightly different vapor pressures which might significantly affect the adsorption potential.

It could be that the source of the difficulty in the case of the nickel probe is that it acts like an electrochemical electrode whenever it is in a saturated atmosphere. At saturation, metallic surfaces are covered with water films of nearly macroscopic thickness--indeed, water droplets of condensation were often observed on the shielding surrounding the probe disk. Nickel ions presumably dissolve in the adsorbed water film to form essentially the electrochemical nickel electrode, the emf of which is added to the surface potential of the adsorbed water. It is easy to see how the potential of this complex system could be a function of the HCl concentration of the vapor phase. If platinum were used instead of nickel, no metallic ions would dissolve in the adsorbed water film and it might eventuate that the probe Volta potential is less a function of position with respect to solutions of different concentrations. However, it could also easily be otherwise. The chief problem with platinum is that it would be economically impossible to also plate the large shielding surfaces with it.

It may turn out that all relatively inert metals behave about the same in an apparatus of this type. The main source of the difficulty with variable capacitance instruments may be that they require a small air gap in order to afford great enough sensitivity. The small air gap between the probe disk and the solutions during measurement predisposes the probe disk to small differences of vapor pressure and vapor composition above the two different solutions. If a large air gap could be made consistent with the sensitivity requirement, the Volta potential of the probe disk would be more independent of the position of the probe. At least, the time rate of change of the probe Volta potential would be diminished and this would result in negligible variation during and between measurements.

Thus, a way out of the dilemma might be to use the ionization method rather than our variable capacitance method to measure the solution-solution contact potential difference. Two great advantages attend the ionization method: elaborate shielding is not required and the probe-to-solution air gap may, with the help of modern instrumentation, be relatively large and yet afford sufficient sensitivity. We envision a platinum plated, polonium coated probe disk of around three-inch diameter about one inch above a solution of nine-inch diameter. The only shielding required would be a simple Faraday cage around the apparatus as a whole, since the range of the alpha particles from polonium is only four centimeters. The chief objection to this method is that the effects of alpha particle bombardment of the solution surfaces are largely unknown. However, since the advent of electrometer input tubes with grid currents in the neighborhood of 10^{-14} ampere and good stability in balanced-bridge type circuits, currents as small as 10^{-14} ampere can be easily and quickly measured. This great current sensitivity means that only relatively low ionization density is necessary between the probe and the solution for the required sensitivity. Thus, the measurement could probably be effected with negligibly small radiation-induced changes at the solution surfaces. And, with an air gap distance of one inch, the change in probe Volta potential due to differences in the vapor immediately above different solutions should be negligibly small during the minute or so required for the probe-solution Volta potential measurement. Our present apparatus could readily be adapted to the ionization method.

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APPENDIX

CONTACT CHARGING AT A METAL-PLASTIC INTERFACE

The Experiments

In the course of preliminary investigations, we hoped to make the metal Volta potential probe less susceptible to the changes caused by water-vapor adsorption by coating it with an acrylic plastic spray such as "Krylon." For this technique to be of use, it is, of course, mandatory that the plastic coating be electrically inert in order that the contact potential measurements be unaffected by its presence. Whether or not this might be so remained moot until ascertained empirically. Fortunately, the question could be settled by recourse to only relatively crude experiments but these, in turn, raised more and larger questions.

The experiments to be described here were performed with the exploratory apparatus described in the first part of Chapter VI. The system was essentially that diagrammed in Figure 1 of Chapter IV: the upper plate was of brass, the lower plate of aluminum, and the potential-change detector was a quadrant electrometer. (In later work the plates were plated with nickel and gold and a special vacuum-tube electrometer was used.

The plates were six inches in diameter and accurately plane. In the measurement process their separation was altered from about one-eighth inch to about five-eighths inch. The mechanism was so constructed that the gap, once set, would be reproduced every time.

To one side a vertical shaft, controlled in rotation and translation from below the housing, was provided in order to furnish a one-corner support for the plastic sheet to be swung in and out from between the plates. In its "out-of-the-way" position the plastic sheet was supported untouched in a sheet-metal niche in the housing which electrostatically shielded it from the condenser plates. The whole assembly was covered by an air-tight galvanized iron housing which, together with the aluminum base-plate, served as a Faraday cage. The experiments reported here were done in the normal air trapped within the housing.

With the quadrant electrometer the sensitivity of this apparatus (using an air-gap between the plates large enough to accommodate the plastic sheet) was about ±8 mv--that is, among about ten successive measurements, the total spread of values would be within 16 mv.

The first experiment was conducted with a 1/8x8x8 inch Lucite sheet supported at one corner by the rotatable vertical shaft so that it could be swung between the metal plate without removing the housing or touching the sheet against anything. The brass-aluminum (actually between the oxide and water-vapor coated surfaces) contact potential difference (brass negative) held fairly steady at about 0.850 volt with a maximum daily variation of 10 mv. When the Lucite sheet was first inserted between the plates, the apparent contact potential difference was so great that measurement was impossible. Since static charge was suspected, "flaming" the sheet was tried but with no success. Gamma bombardment from 8 mg of radium at about one foot distance for two days reduced the amount of static charge significantly but the apparent C.P.D. of 0.660 volt showed the probability of residual static charge. However, after four more days (without radiation) the static charge disappeared and henceforth for a week the C.P.D. with or without the presence of the Lucite sheet were always identical to within 10 mv. That semi-permanent polarization is not involved was demonstrated by the absence of any effect caused by storing the Lucite sheet overnight in various field strengths. Thus, save for the difficulty of dissipating the initial surface charge (which, incidentally, was always negative) this experiment indicated that a separately-supported Lucite sheet was indeed electrically neutral toward C.P.D. measurements.

The next question was whether or not a sheet of plastic in contact with one of the metal plates would also be electrically neutral. In order to increase the sensitivity by decreasing the dielectric gap between the plates, a carefully cleaned 1/16x8x8 inch Lucite sheet was used (instead of the former 1/8 inch) and was laid directly onto the lower (aluminum) plate. The metal-metal C.P.D. had now stabilized at 0.830 volt.

The same difficulty with static charge was encountered as before and again radium was of little help in getting rid of the last traces of charge. However, after four days the apparent C.P.D. seemed to stabilize at about 1.4 volts. Of course, since it was assumed that the difference between 0.830 volt and 1.4 volts was due to static charge, there was nothing to do but wait. (During all this time, between measurements and overnight, the plates were grounded at the least distance--about 3 mm--of separation.) For eight days the apparent C.P.D. remained approximately constant and the suspicion grew that something besides free surface static was involved. In order to determine whether semi-permanent polarization was involved, it was decided to change the "storage" field strength.

In order to ascertain the effect of various field strengths, measurements were limited to a given hour of each day and between measurements the apparatus was undisturbed. The field strength was varied either by changing the potentiometric potential difference between the plates or by changing their separation. The field strength experienced by the Lucite sheet (exclusive of that caused by the presence of the sheet) was simply calculated by dividing the metal-metal Volta potential difference by the separation distance of the plates.

The apparent C.P.D. had been stable at about 1.43 volts for eight days (both with and without gamma irradiation) in a field of roughly 3 volts/cm upward; then the Lucite sheet was kept (for 24 hour intervals as always unless otherwise stated) in a field of roughly 0.2 volt/cm upward. The next day the apparent C.P.D. was 0.64 volt and the succeeding day 0.23 volt. For another day the reading remained the same and then the field was changed back to 3 volts/cm upward. For two days the apparent C.P.D. rose at a rate of about 0.06 volt/6 hours and then the rate decreased slowly until after about two weeks the apparent C.P.D. stabilized at about 1.30 volts. After three days of relative stability (±0.02 volt) a field of 14 volts/cm upward was applied and the apparent C.P.D. started drifting upward again and stabilized about eighteen days later at 2.41 volts. The field was then reduced to about 0.2 volt/cm upward again. One day later the apparent C.P.D. was 0.53 volt. Another day reduced it to 0.18 volt where it remained stable for three days. The field was again set at 3 volts/cm upward and caused the apparent C.P.D. to rise in the same manner as before to a stable value of 1.22 volts in about twelve days. As before, reducing the field to 0.2 volt/cm upward caused the apparent C.P.D. to stabilize at 0.20 volt in two days.

Thereupon a new thing was tried: the sense of the field was reversed and the field was set at 19 volts/cm downward. The next day the apparent C.P.D. was -3.25 volts and the following day was -4.12 volts and it stabilized after three days at about -4.4 volts. Then the field was set at 1 volt/cm downward. In four days the apparent C.P.D. stabilized at -2.55 volts.

Then the field was reset to the former value of about 0.2 volt/cm upward. The readings on successive days were -0.16, +0.03, +0.12, +0.20, +0.23, +0.23, +0.24 volt. "Storage" fields of first 1 volt/cm upward and later 3 volts/cm downward were then applied. Table 2 records the results of these twelve different "runs" under the influence of the various field strengths.

Considering the crudity of the experiment, one may conclude that the reproducibility is fairly good. It is evident that the relationship between the applied "storage" field strength and the resultant asymptotic effective double-layer potential difference is not at all linear. While the data of Table 2 are insufficient to justify precise quantitative conclusions, they are amply sufficient to qualitatively demonstrate the effect of applied fields under these conditions. It is apparent that the oxide-Lucite double-layer spontaneously becomes negative in the absence of an applied field. An upward directed field causes the effective double-layer to become more positive while a downward directed field causes the effective double-layer to become more negative. Furthermore, it seems

TABLE 2

THE EFFECT OF VARIOUS APPLIED FIELD STRENGTHS ON THE APPARENT CONTACT POTENTIAL DIFFERENCE OF THE ALUMINUM-LUCITE-AIR-BRASS CONDENSER SYSTEM

Applied field strength (volts/cm)	Apparent C.P.D. of system (volts)		Effective double-layer potential diff. (apparent C.P.D. -C.P.D.) (volts)		Time required to reach asymptotic apparent C.P.D. (days)
	Beginning	Asymptotic (steady-state)	Beginning	Asymptotic	
14 up	1.30	2.41	0.5	1.6	18
3 up	....	1.43	...	0.6	..
3 up	0.23	1.30	-0.6	0.5	14
3 up	0.18	1.22	-0.6	0.4	12
1 up	0.24	0.97	-0.6	0.17	6
0.2 up	1.43	0.23	0.6	-0.6	2
0.2 up	2.41	0.18	1.6	-0.6	2
0.2 up	1.22	0.20	0.4	-0.6	2
0.2 up	-2.55	0.23	-3.3	-0.6	5
1 down	-4.4	-2.55	-5.2	-3.3	4
3 down	0.97	-3.8	0.17	-4.6	2
19 down	0.20	-4.4	-0.6	-5.2	3

that a field of a given magnitude has a greater and faster effect when it is directed downward rather than upward. In one case when the apparent C.P.D. was rising slowly under the influence of a field of 14 volts/cm upward, the field was dropped to 0.2 volt/cm upward for $3\frac{1}{2}$ hours. This caused the apparent C.P.D. to drop from 1.16 to 0.95 volt. After these field-strength experiments (which took three months) the Lucite sheet was removed and the metal-metal C.P.D. was found to be 0.74 volt.

In the absence of the Lucite sheet, the "storage" fields were varied as before in order to ascertain whether or not an effect would be found. If it existed at all, the effect without the presence of plastic was small--ten to fifteen millivolts at most. This variation, while suspiciously well correlated, is suspect since it is on the threshold of the sensitivity limit and is partially obscured by the small daily drift.

A $1\frac{1}{2}$ mm deep layer of vacuum-pump oil was then put on the lower (aluminum) plate. Its effect on the C.P.D. was at most 0.02 volt and was independent of field strength as was shown by experiments over a period of nine days.

Tentative Interpretations

The crudity of these experiments is apparent. While the Lucite sheet was plane to casual observation, its non-planarity was sufficient to restrict its intimate atomic-scale contact with the aluminum plate to probably less than 10 per cent of the apparent area. Thus there is no hope of quantitatively relating the C.P.D. deviation in these experiments to the actual double-layer potential difference. A "Krylon"-type plastic spray was not used, since with it there would be no way of ascertaining whether the intrinsic brass-aluminum C.P.D. remained sensibly constant or not because removal of the "Krylon" film would probably change the intrinsic C.P.D.

However, in spite of the preliminary character of these experiments, one conclusion can certainly be drawn: the apparent C.P.D. of the aluminum-Lucite-air-brass system varies markedly and rather reproducibly with the field strength to which it has been subjected prior to the measurement. This effect is probably not caused by semi-permanent polarization or electret-type behavior of the Lucite, since the experiment in which the Lucite sheet was supported independently of the plates showed that--after time had been allowed for static charge to dissipate--the insertion of the Lucite sheet between the plates did not measurably affect the C.P.D.

The interpretation of the C.P.D. discrepancy which seems most probable is that it is caused by the passage of electrons across the interface formed by the aluminum oxide and the Lucite. This diffusion of electrons occurs spontaneously from the metal into the plastic in the absence of an external field across the dielectric gap. The application of an external field of the order of a few volts per centimeter biases the diffusion of the electrons so that the plastic can be made more positive or negative at will. A kind of rectifying action exists at the boundary, since the electrons move into the plastic several times more rapidly than they move out of the plastic under the influence of fields of opposite senses but of roughly the same magnitude. Not all dielectrics exhibit contact charging against metal oxide. In the one other case studied--vacuum pump oil--contact charging was not evident. Perhaps the fact that the volume conductivity of the oil is roughly a thousand times that of Lucite is of importance here.

More specifically, since the C.P.D. in the absence of plastic was about 0.8 volt on the average, an apparent C.P.D. of greater than 0.8 volt indicates a net positive charge on the plastic while an apparent C.P.D. of less than 0.8 volt indicates a net negative charge on the plastic. Thus, since in the absence of appreciable external field the apparent C.P.D. comes to equilibrium at about 0.2 volt, it follows that the oxide-plastic interface has the effect of a double-layer of 0.6 volt negative outward. This does not mean, however, that the actual oxide-plastic interface comes to a spontaneous potential difference of -0.6 volt since the areas of actual contact constitute only a small fraction of the area of the aluminum plate. All that can be said is that the negative potential difference of the actual double-layer is considerably greater than 0.6 volt.

A further conclusion that can be drawn from the variation of apparent C.P.D. with the "storage" field strength is that at some field intermediate between 0.2 volt/cm and 1 volt/cm upward--probably nearer 1 volt/cm--no contact charging of the Lucite would occur. This field-induced annulment of contact charging could conceivably be of technical importance in industry (particularly in the textile industries) where contact charging has proved to be a refractory problem not usually soluble by ionization techniques.

After this work had been terminated, it was discovered that a previous study had unambiguously demonstrated the existence of metal-insulator contact charging. Utilizing a technique totally different from that herein described, Peterson[1] and Loeb conducted a thorough study of contact charging by rolling small spheres of borosilicate glass and fused quartz on a nickel surface and measuring the charge thereby acquired by the spheres. Besides being a function of surface conditions including the surface conductivity of the "non-conducting" sphere, the maximum charge acquired is limited by gaseous discharge to the metal and thus is markedly dependent on gas pressure in the system. As was also found in our experiment, the spontaneous charging gave the dielectric a negative charge. Because of the nature of the experiment only the charge (not the potential) could be measured. It is likely that the charge equilibrium thus measured on a rolling sphere is considerably different--possibly different in nature--from the long-duration charge equilibrium measured in our experiment. There is, moreover, an interesting discrepancy between the results of Peterson's experiment and those of ours: Peterson finds that electrostatic fields of about 1000 volts/cm normal to the nickel surface cause significant changes in the maximum charge of the sphere (approximately proportional to the field strength) _but only in the presence of high relative humidity_. (This effect is ascribed to the concomitant variation of surface conductivity.) Moreover, the magnitude of the effect at ±1000 volts/cm is smaller than in our experiment at ±3 volts/cm. It is possible that the two experiments measure different things, since the time scales differ by a factor of roughly 10^5. Moreover, it must also be kept in mind that rather different dielectric materials were studied by these two distinct techniques.

It appears that our modified contact potential technique could be

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[1] J. W. Peterson, J. App. Phys. _25_ 501 (1954); _25_ 907 (1954).

developed into a valuable complement to the rolling-sphere technique. If the plastic were applied to the metal from solution, there seems to be good reason to believe that our technique could determine the actual oxide-plastic double-layer potential difference as a function of field strength and time. Provision should certainly be made for evacuating the apparatus and for varying the field strength over several orders of magnitude.