THE ELECTRICAL DOUBLE LAYER AND THE THEORY OF ELECTROCAPILLARITY[1]

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The theory of the electrical double layer is discussed with particular reference to those aspects of the subject usually included under the heading "electrocapillarity". Modern values for the thermodynamic properties of the double layer are presented for typical substances, and references are given to that part of the literature which is likely to be of interest in connection with the problems here discussed.

CONTENTS

I. INTRODUCTION

The review[3] which follows deals with the theory of electrocapillarity and its relation to the problems of elucidating the structure of the electrical double layer. The theory of electrokinetic phenomena is not discussed.

[2] Publication of this paper was delayed by the loss of the original manuscript in transit.

[3] The symbols used in this paper are listed below. All capacities and charges are per square centimeter of interface.

C = differential capacity of the electrical double layer

C^d = differential capacity of the diffuse double layer

C^o = differential capacity of the region between a metallic surface and the outer Helmholtz plane

C_i = differential capacity of the region between a metallic surface and the inner Helmholtz plane

D = dielectric constant

D_0 = diabattivity of free space ($= 4\pi \times$ permittivity of free space)

E = electrical potential difference at an ideal polarized electrode as read on the potential-fixing potentiometer

$\mathbf{E}$ = electrical potential difference at an ideal polarized electrode relative to the potential of the electrocapillary maximum

$\mathcal{E}$ = electrical potential difference at an ideal polarized electrode as read on the potential-fixing potentiometer when the reference electrode is a normal calo-

The terms "electrocapillarity" and "electrical double layer" are not commonly well understood. A satisfactory definition of the first must await a discussion of the ideal polarized electrode, another unfamiliar term, but we may state meanwhile that electrocapillarity is the study of the surface tension of metals in contact with inert salt solutions, together with the study of all of the effects with which this is connected. The term "electrocapillarity" arises from the fact that most of the early studies in the field were done with the Lippmann capillary electrometer.

The electrical double layer is the array of charged particles and oriented dipoles which is thought to exist at every interface. Very often the term is used in a narrower sense to mean the array of charges and dipoles between two immiscible media when one is a salt solution. It is in this narrower sense that the term is here used.

The concept of the electrical double layer is due to Quincke (80), although that term was not used by him. The double layer was thought to consist of two layers of charge, one positive and one negative, situated at the interface. Today the

mel electrode and when liquid-junction potentials have been eliminated as well as possible

$E^-(E^+)$ = electrical potential difference E when the reference electrode is simply reversible to the anion (cation) of a salt solution

F = Faraday's constant

K = integral capacity of the electrical double layer

K^d = integral capacity of the diffuse double layer

K^o = integral capacity of the region to which C^o refers

K^i = integral capacity of the region to which C^i refers

k = Boltzmann's constant

M = molar concentration of a solution

m = molal concentration of a solution

n_{0i} = number of ions of type X_i in unit volume of solution measured at a point remote from the double layer

n_i = number of ions of type X_i in unit volume of solution measured at a point within the double layer

q = electronic charge of the electrical double layer

r = radius of an adsorbed anion or distance from the interface to the inner Helmholtz plane

T = absolute temperature

w_i = work required to move an ion of type X_i from the interior of a designated position within the double layer

X_i = an ion or neutral molecule of type designated by the subscript i

x = distances measured from the physical interface

z = absolute value of the valence of an ion

$z_-(z_+)$ = valence of an anion (cation) including sign

z^i = maximum number of ions of type X_i which can be adsorbed at 1 sq. cm. of an interface

z_{0i} = maximum number of ions of type X_i for which there is space in 1 cc. of solution

α = the metallic phase of an ideal polarized electrode

β = the non-metallic phase of an ideal polarized electrode

Γ_i = superficial density of a component of type X_i as involved in the Gibbs adsorption equation

point of view is somewhat more complicated, although the name persists even in those cases where it is plainly inappropriate.

Briefly the electrical double layer may consist of a layer of electrons (if the non-electrolytic phase is a metal or electronic conductor), a layer of adsorbed ions, and a *diffuse* double layer consisting of an ionic atmosphere in which ions of one sign are in excess of their normal concentrations whereas those of the other sign are in defect. This atmosphere of abnormal concentrations of ions falls off rapidly as one recedes from the surface, the half-thickness of the charge density being seldom over 100 Ångströms and usually much less. Finally, there may exist at the interface a thin (often monomolecular) layer of neutral molecules which, whether they are oriented or not, exert an influence on the thermodynamic properties of the interface. Diagrams of the electrical double layer are given later (figures 17–19), after the theory upon which they are based has been presented.

Metal–solution interfaces lend themselves to the exact study of the double layer better than other types because of the possibility of varying the potential differ-

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$\Gamma_+(\Gamma_-)$ = superficial density of cations (anions)

Γ_s = superficial density of entropy at an interface

γ = mean activity coefficient of the ions of a strong electrolyte

ϵ = charge on a single univalent cation

η = total charge of the solution phase of the electrical double layer $(= -q)$

η^d = charge of the diffuse double layer

$\eta_-^d(\eta_+^d)$ = contribution of any excess or deficiency of anions (cations) to the charge of the diffuse double layer

η^i = charge of the compact (adsorbed) part of the double layer

$\eta_-^i(\eta_+^i)$ = charge of the compact part of the double layer when the adsorbed ions are anions (cations)

κ = a measure of the reciprocal thickness of the diffuse double layer defined by equation 57

μ = chemical potential of a neutral molecular species

$\mu_-(\mu_+)$ = chemical potential of an anion (cation)

μ_i = chemical potential of a component X_i

$\nu_+(\nu_-)$ = number of cations (anions) furnished by the dissociation of one molecule of a salt

$\nu = \nu_+ + \nu_-$

ρ = charge density (charge per unit volume)

σ = interfacial tension

ϕ_-^i = specific adsorption potential of an anion

ψ = electrical potential at any point within the double layer relative to the interior of the solution phase

ψ^r = rational potential difference between dissimilar phases

ψ^o = electrical potential of outer Helmholtz plane relative to the interior of the solution phase

ψ^i = electrical potential of inner Helmholtz plane relative to the interior of the solution phase

$\psi^\alpha(\psi^\beta)$ = cavity potential (i.e., electrostatic potential) of the metallic (non-metallic) phase

ψ^I = cavity potential of a copper wire attached to the metallic phase

ψ^{II} = cavity potential of a copper wire attached to the reference electrode

MAX = subscript or superscript referring to the electrocapillary maximum

ence between the phases without varying the composition of the solution. This is done through the use of a reference electrode and a potentiometer which fixes the potential difference in question. In favorable cases there is a range of potentials for which a current does not flow across the interface in a system of this kind, the interface being electrically similar to a condenser of large specific capacity. The capacity of this condenser gives a fairly direct measure of the electronic charge on the metallic surface, and this, in turn, leads to other information about the double layer. No such convenient and informative procedure is possible with other types of interfaces, a fact which explains the preoccupation with such systems in the present review.

Of the metals which might be used for the purpose outlined, mercury is preëminent. Being a liquid, its surface is readily cleaned, it is free from mechanical strains, and its interfacial tension is readily measured. In addition, mercury is distinguished by its low chemical activity and high hydrogen overvoltage. The latter characteristic makes it possible to work at potentials which would otherwise be objectionable because of a rapid evolution of hydrogen from the reduction of the solvent. Nearly everything one desires to know about the electrical double layer is ascertainable with mercury surfaces if it is ascertainable at all.

II. THE IDEAL POLARIZED ELECTRODE

For an understanding of electrocapillary phenomena, an understanding of the ideal polarized electrode is prerequisite. This type of electrode is observed only with high-overvoltage metals, and then only in approximation. It is a type very different from the reversible electrodes with which one deals in thermodynamic discussions of galvanic cells, yet it is reversible and at equilibrium.[4] Its importance rests upon the fact that it can be treated by exact thermodynamic means.

The rigorous definition of an ideal polarized electrode is as follows (46): It is a system composed of a metal in contact with an electrolytic solution for which, at equilibrium, the concentration of every charged component is finite in one phase *only*. As applied to electrons, this statement is to be taken to mean that there exists in the solution phase no finite amount of any component which can take up or give up finite amounts of electricity from the metallic phase.

This definition calls for some amplification. In the first place it is necessary to state what are regarded as charged components. The metallic phase is thought of as composed of two charged components, electrons and metallic ions. The solution phase is thought of as composed of neutral solvent molecules and of ions of whatever sort may be present. These ions are the charged components of the phase. If dissolved hydrogen is present and if its equilibrium with hydronium ions is to be considered, this is regarded as consisting of protons and electrons, both of which are charged components. Hydrogen ions are regarded as hydrated protons. Dissolved oxygen is thought of as oxide ions plus electrons. Hydroxyl ions are similarly thought of as hydrated oxide ions. In general, if two substances are present which can be converted into one another

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[4] The latter point is not always conceded. It is discussed in what follows.

by the addition or removal of charge, these two forms are regarded as forms of the same basic component, the more reduced form of which is composed of electrons plus the other. The reason for this procedure concerning the choice of components is that it makes it easier to develop the thermodynamic theory of electrocapillarity in a rigorous manner.

The definition of an ideal polarized electrode is chosen so that passage of charge across the interface shall not take place spontaneously at equilibrium. More exactly stated, when the potential difference between the phases is altered slightly, no finite amount of charge must cross the interface of an ideal polarized electrode during the reëstablishment of equilibrium. This is a corollary of the definition, because if charge did cross the interface, finite amounts of some charged component would then be present in both phases, contradicting the requirement of the definition. Experimentally, the ideal polarized electrode is an electrode which behaves like an electrical condenser without leakage. Its capacity arises from the fact that charges may approach or recede from the interface, though they do not cross it.

This definition of an ideal polarized electrode is too strict ever to be fully realized in the laboratory, but close approximations to it are possible, and, what is more important, the deviations which are unavoidable are of negligible effect, as will presently be shown.

An example will serve to illustrate the definition and also to bring out additional points of importance. Consider a clean mercury electrode in an aqueous 1 M potassium chloride solution (completely deaërated) into which is immersed a normal calomel electrode. Between the mercury in the calomel electrode and the clean mercury electrode there is inserted a potentiometer and, optionally, a galvanometer. The clean mercury electrode is attached to the negative end of the potentiometer. No continuous current flows through the circuit if the potential is not made too large. This system may have any number of conditions of equilibrium, depending upon the setting of the potentiometer. For definiteness, consider that $-E$, the potentiometer reading, is 0.556 volt, in which case q, the electronic charge on the mercury surface, will be zero,[5] as we shall show later. Under these circumstances the following reactions are all conceivable, any one of which would result in transferring charged particles from one phase to the other in violation of our definition of an ideal polarized electrode.

Reaction	Equilibrium concentration
$2Hg \rightarrow Hg_2^{++} + 2e^-$	$c_{Hg_2^{++}} = 10^{-36}$ moles per liter
$K^+(aq) + e^- \rightarrow K$ (in Hg)	$N_K = 10^{-45}$ moles per mole
$2Cl^- \rightarrow Cl_2 + 2e^-$	$p_{Cl_2} = 10^{-28}$ atm.
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$p_{H_2} = 4 \times 10^{-3}$ atm.

If the electrode is ideally polarized, all of these reactions must produce only negligible quantities of their products at equilibrium. The calculation of these quantities is straightforward and gives the results indicated on the right. N_K is

[5] This does not imply that the potential difference between the phases is zero. a question to be discussed below.

the mole fraction of potassium in mercury, assuming a perfect solution. The first three concentrations are negligible, as demanded by the definition, but the pressure of hydrogen required for equilibrium is not. An appreciable amount of charge would therefore move from the mercury to the solution in the course of building up this equilibrium concentration.

As a practical matter, the high hydrogen overvoltage of mercury causes the attainment of complete equilibrium to be very slow compared to the rate of attainment of ionic equilibrium within the double layer.[6] In all such cases, which are extremely common in thermodynamic practice, the slow reaction may be ignored. Occasionally the secondary effects need to be considered. Thus the current flow accompanying the process may have electrical effects of an undesired nature, or the products of the reaction may build up to significant concentrations. But these are practical matters which can be minimized by careful design.

At lower values of $|E|$ the equilibrium partial pressure of hydrogen goes down, and values of E can be found for which all of the equilibrium concentrations are negligible. At higher potentials no complications are observed in practice until $E = -2.0$ volts or thereabouts, although the equilibrium partial pressure of hydrogen is then about 10^{22} atm. The hydrogen overvoltage of mercury, of course, makes this possible.

Other slow reactions may be experienced because of imperfections of the experimental arrangement. Thus it is inconceivable that the mercurous-ion concentration could be kept down to 10^{-36} moles per liter, since the solubility of calomel allows it to rise to about 10^{-18} moles per liter. More important, particles of colloidal calomel may find their way to the surface and react according to the equation

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$
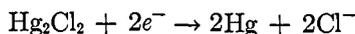
thus transferring charge across the interface. This reaction is again of no consequence, since it does not affect the equilibrium of the double layer.

There was a wholly erroneous opinion held at one time to the effect that the properties of the double layer at a mercury interface were fixed by the concentration of the mercurous ion (the so-called potential-determining ion). Since the latter is present at equilibrium in amounts so small as to be meaningless except in a statistical sense, and since in any case the concentration of mercurous ions will generally exceed the equilibrium value because of experimental imperfections, it should be evident that the concentration of this ion is of no importance provided it is small. The old practice of adding mercurous ions to systems to be investigated was unnecessary and escaped being harmful only because the diffusion of such ions to the interface was slow compared to the rate of establishment of equilibrium within the double layer. Those mercurous ions which reached the interface were promptly removed by electrolysis.

We may now define electrocapillarity as the study of ideal polarized electrodes

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[6] Equilibrium is attained in a matter of microseconds or milliseconds, depending upon the geometrical distribution of the electrodes (see Section IX).

and of electrodes which behave like ideal polarized electrodes. The term has sometimes been used to include the field of electrokinetics, but this practice is not recommended by the writer.

The potential of an ideal polarized electrode is fixed by an external source of E.M.F., or if there be no such, then by the charge which happens to be present at the interface. In the latter case the potential of a stationary electrode will rapidly drift to that of a calomel electrode (assuming the solution is a chloride), owing to the action of colloidal calomel or other reducible matter.

If an isolated reservoir of mercury is allowed to flow in a fine stream through a deaërated solution of an inert electrolyte, it will very rapidly come to a potential of zero electronic charge (19, 53, 73). This is so because each droplet of mercury which falls carries with it a large part[7] of any residual charge which might have been present on the isolated reservoir initially. If negative ions are adsorbed on the mercury after electronic equilibrium is attained, positive ions are carried along in equivalent amounts, leaving the surface uncharged as far as electrons are concerned. Even slow-dropping mercury (3 sec. per drop) comes to a state of zero charge if oxygen and other reducible substances are very rigorously excluded (42, 61, 62). The potential of zero charge is also the potential of the electrocapillary maximum, as is well known and as we shall subsequently prove.

It was thought at one time that the potential of the isolated reservoir in the experiment described above must be identical with that of the solution, it being assumed that zero charge corresponded to zero potential difference. Such an assumption is easily proved false by comparing different solutions (84), but it is apparent anyway that zero charge does not necessarily imply zero potential difference. For example, a layer of oriented dipoles will produce a difference of potential on its two sides, although its net charge is zero. Such layers of oriented dipoles are very common,[8] and it is not at all certain that even water molecules are not oriented at a mercury surface, producing a potential difference which cannot be measured.

III. THE ELECTROCAPILLARY CURVE AND A DEFINITION OF THE POTENTIAL SCALES EMPLOYED

It has been known for a long time that the interfacial tension of mercury in an ideal polarized electrode varies with the potential difference imposed across the interface. Numerical data are given by many authors (22, 25, 54, 58, 59, 67, 68, 70, 93), the work of Gouy being the most extensive and of high accuracy (36, 38). Curves representing this variation are called electrocapillary curves, and are often almost parabolic in shape (63) (figure 1). Nevertheless one makes

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[7] The capacity of the droplet relative to the solution is much greater than the self-capacity of the reservoir; hence virtually all of any excess charge accumulates on the surface of the mercury droplet.

[8] An adsorbed anion, together with a non-adsorbed cation, may be regarded as a dipole. It is in this sense that layers of oriented dipoles are most common, although layers of oriented polar molecules are also common enough.

a serious error in assuming them to be exactly so, for the deviations from parabolic form are thermodynamically related to the interesting properties of the double layer. Because these deviations are small, other methods of obtaining the same information are more commonly employed (27, 42, 78, 79).

The right-hand end of the curves in figure 1 and in all of the curves to follow corresponds to the largest negative potential imposed upon the mercury from the external source. A point corresponding to a potential more negative than the electrocapillary maximum is said to lie on the cathodic branch of the curve in question and to represent negative polarization. Potentials more positive than the electrocapillary maximum correspond to the anodic branch and represent
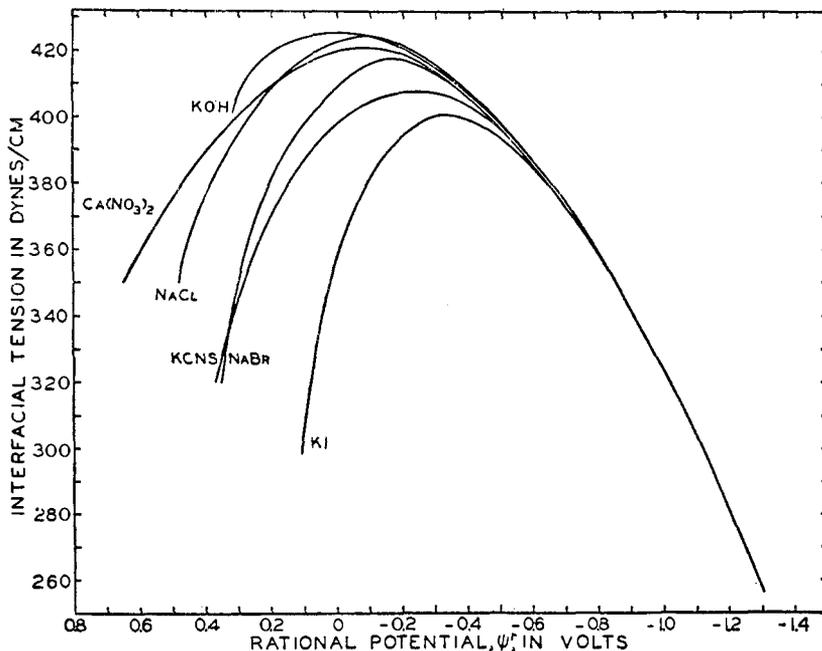

FIG. 1. Interfacial tension of mercury in contact with aqueous solutions of the salts named. $T = 18°C$. Abscissas are measured relative to a "rational" scale in which the potential difference between the mercury and a capillary-inactive electrolyte is arbitrarily set equal to zero at the electrocapillary maximum.

positive polarization. (As used by other authors, positive polarization often means that E, the observed potential, is positive.)

Until the thermodynamic theory of electrocapillarity has been discussed, there is not much to be learned from the electrocapillary curves in figure 1. There are two features of these curves worthy of remark at this point, however. The shape and position of the curves do not depend significantly upon the cation employed, except that hydronium ion and very large cations, such as tetramethylammonium ion, give somewhat different results. The differences observed with hydronium ion are probably attributable to the effects of that ion on the anions present.

Regardless of the anion present, the curves become nearly coincident on the right-hand side corresponding to negative polarization. This is understandable, since the negative charge of the mercury repels anions under these circumstances, making close contact of mercury and anion rare.

There are several kinds of electrical potential difference with which one has to deal in discussing the electrical double layer. The "absolute" or "true" potential difference between dissimilar phases is an undefined concept, and no attempt will be made to use it in this paper. The question is further discussed in Section VIII, however.

The potential of a point within a macroscopic cavity in an isotropic conductor is a definite quantity which can in principle be measured.[9] It will be called the cavity potential and is equal to what is sometimes called the electrostatic potential of the medium (1), the potential of a point "just outside" the surface. The only reason for introducing a new term is that the term "electrostatic potential"
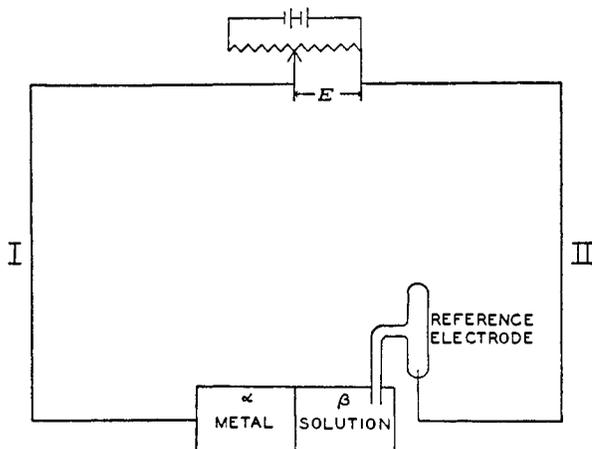

FIG. 2. Schematic representation of the system to which the equations refer

has been so often misused that it has largely lost its meaning. The term "cavity potential", on the other hand, can hardly be misunderstood.

The cavity potential *difference* between metals in contact is the Volta or contact potential. It is discussed in Section VIII.

Consider the system illustrated in figure 2. I and II are wires of the same metallic substance, say copper. α is the metallic phase of an ideal polarized electrode in contact with the electrolytic solution β. The reference electrode may be supposed to contain the electrolyte β, so that liquid-junction potentials will be absent. Designating by ψ^I, ψ^{II}, ψ^α, and ψ^β the cavity potentials of the several phases, it is evident that

$$E + (\psi^\alpha - \psi^I) + (\psi^\beta - \psi^\alpha) + (\psi^{II} - \psi^\beta) = 0 \tag{1}$$

[9] Actually, one can only measure differences of potential, but this is an unimportant distinction, since differences are all one ever really needs to know.

The potentiometer reading, E, is regarded as $\psi^I - \psi^{II}$. It will most often be negative in electrocapillary measurements.

In the discussions to follow, α, the metallic phase, will not be altered in composition (a more general case is discussed by Koenig (60)), so that $\psi^\alpha - \psi^I$ is a constant and we may write:

$$d(\psi^\beta - \psi^\alpha) = -dE - d(\psi^{II} - \psi^\beta) \tag{2}$$

This equation is used below in the derivation of an important thermodynamic result.

In the discussion of the *kinetic* theory of the double layer which is to be presented it is necessary to depart from the strict thermodynamic definition of potentials. Even so, it is not necessary to talk about "true" potential differences of dissimilar phases, except that liquid-junction potentials of aqueous solutions will be regarded as defined. The exact sense in which this term is used is stated in Section VIII. It is to be noted that liquid-junction potentials do not enter into the thermodynamic treatment, however.

One of the most convenient points of reference in discussing the potential difference between mercury and solutions is the potential of the electrocapillary maximum, the point of zero electronic charge. This point of reference may be determined simply and accurately by means of the mercury stream technique described in Section II. Potentials measured relative to this potential will be represented by **E**, and negative values of **E** will correspond to negative polarization. Because so many authors have spoken of the potential defined in this way as if it were at least an approximation to the "true" potential difference between the phases of an ideal polarized electrode, it is probably well to repeat that no such idea is here entertained.

Very often a normal calomel electrode is employed in measuring electrocapillary curves and the like. If the solution in question is not potassium chloride of the same concentration, this has the disadvantage of introducing liquid-junction potentials. One can eliminate the uncertainty by reporting the results in terms of **E**, the potential relative to the electrocapillary maximum. Very often one wishes to know also, however, how the potential of the electrocapillary maximum varies with concentration or from electrolyte to electrolyte. At present this information does not serve any exact thermodynamic purpose, so that the introduction of small liquid-junction potentials in this case cannot be criticized, particularly since it is unavoidable. The directly observed potential (called the electron potential in Section VIII) of the metallic phase of an ideal polarized electrode relative to the mercury in a *normal calomel electrode* connected with the solution phase of the polarized electrode will be called $\mathfrak{E}$. The connection of the calomel electrode to the solution is supposed to be made in a manner which eliminates liquid-junction potentials. In practice this means that a correction will be made as well as possible for whatever liquid-junction potentials are present.

The value of $\mathfrak{E}$ at the electrocapillary maximum of a number of electrolytes is given in column 3 of table 1. The departure from a constant value is attrib-

uted to an adsorption of anions by the mercury. From independent evidence (equation 21, *vide infra*), one knows that adsorption is small or negligible for alkali carbonates, sulfates, and hydroxides. There is also good reason to believe that alkali fluorides are not adsorbed, although the necessary data for proving

TABLE 1

Properties of the electrical double layer at the potential of the electrocapillary maximum
(36, 45, 90)

ELECTROLYTE	CONCENTRATION	$\mathcal{E}^{MAX}$	ψ^r_{MAX}	Γ^{MAX}_{SALT}
	M	*volts*	*volts*	μ *coul./cm.*^{2}
NaF..................	1.0	−0.472	0.008	
	0.1	−0.472	0.008	
	0.01	−0.480	0.000	
	0.001	−0.482	−0.002	
NaCl.................	1.0	−0.556	−0.076	3.6
	0.3	−0.524	−0.044	1.8
	0.1	−0.505	−0.025	1.1
KBr................	1.0	−0.65	−0.17	10.6
	0.1	−0.58	−0.10	3.5
	0.01	−0.54	−0.06	0.6
KI.....................	1.0	−0.82	−0.34	15.2
	0.1	−0.72	−0.24	9.1
	0.01	−0.66	−0.18	4.8
	0.001	−0.59	−0.11	1.3
NaCNS...............	1.0	−0.72	−0.24	14.0
	0.1	−0.62	−0.14	6.3
	0.01	−0.59	−0.11	1.3
K_2CO_3...............	0.5	−0.48	0.00	−2.2
NaOH...............	1.0	−0.48	0.00	Small
Na_2SO_4..............	0.5	−0.48	0.00	Small
KNO_3.................	1.0	−0.56	−0.08	5.5
	0.1	−0.52	−0.04	2.0
	0.01	−0.52 (?)	(?)	

this conclusively are not yet available. It is found that values of $-\mathcal{E}^{MAX}$ all lie close together in the neighborhood of 0.47–0.48 volt for these salts.

The "best" value for $\mathcal{E}^{MAX}$ in the absence of adsorption of anions and cations is close to −0.480 volt.[10] If it were not for possible water orientation at the interface and unknown electrical effects at the mercury surface itself (such as an

[10] Heretofore a value of −0.52 or −0.50 volt has been commonly used.

"overshoot" of electrons, for instance), one would possibly be justified in thinking of this as a "true" potential difference between the phases of a normal calomel electrode. What it is, rather, is the "rational" potential difference between these phases,—rational because it accounts for all the factors which are susceptible to measurement and ignores those which are neither susceptible to measurement nor significant in the interpretation of results. The rational potential difference, ψ^r, is defined by the equation:

$$\psi^r = \mathcal{E} + 0.480 \text{ volt} \tag{3}$$

It is not a thermodynamic quantity because liquid-junction potentials enter into its measurement.

There is at least one circumstance in which the rational potential must be used with care. In non-aqueous systems, the orientation of solvent molecules affects the observed potentials (23). All that can be observed is the difference between the effects of water orientation and of another solvent's orientation. Frumkin's results (23) indicate that such solvents as methanol, ethanol, and acetone are oriented with their positive (hydrocarbon) ends toward the mercury, at least more so than water. This result hardly helps one even to guess, however, how water molecules are oriented at a mercury surface, if indeed they are. Use of the rational potential as defined by equation 3 with non-aqueous systems amounts to assuming that any shifts in the value of $\mathcal{E}$ at the electrocapillary maximum in the absence of ion adsorption are to be attributed to orientation of the non-aqueous solvent molecules at the interface.

IV. THE THERMODYNAMIC THEORY OF ELECTROCAPILLARITY (23, 25, 33, 41, 46, 53, 60, 68, 77, 86, 89)

The thermodynamic theory of electrocapillarity may be derived from the Gibbs adsorption equation (Gibbs' equation 508, reference 33), according to which

$$d\sigma = -\Gamma_s dT - \Sigma \Gamma_i \, d\mu_i \tag{4}$$

In this equation σ is the interfacial tension of two immiscible phases, μ_i is the chemical potential (partial molal free energy at constant temperature and pressure) of a component X_i, Γ_i is the excess of that component, in moles per unit area of interface, over that which would be present in the system if each phase were of uniform composition, with the composition of the interior of the phase, up to a plane drawn parallel to but not necessarily coincident with the physical interface. The actual position of this plane is arbitrary except for the dictates of convenience. Curved surfaces may be considered essentially plane until the thickness of the region of inhomogeneity approaches the radius of curvature of the interface (51). The summation in equation 4 extends over all the independent components of the system, which were always thought of as neutral substances.[11] Γ_s is a quantity expressing the excess of entropy in the system

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[11] This statement applies explicitly only to the derivation of Gibbs' equation 508 (our equation 4).

in a manner exactly analogous to the definition of Γ_i. A simple but rigorous derivation of equation 4 is given by N. K. Adam (2).

The adaptation of equation 4 to the problems of electrocapillarity has been subject to much dispute. The difficulty has been partly associated with a failure to understand the properties of the ideal polarized electrode, which is continually confused with non-polarizable electrodes which form the more usual subject of thermodynamic discussions of electrodes. A further difficulty has arisen because of the fact that polarized electrodes are seldom actually at equilibrium, although this is purely a practical matter and influences the experimental results almost not at all. Finally one must inquire closely into the validity of using equation 4 with charged components serving as independent components.

The early treatments of this problem are characterized by what the present writer regards as an unnecessarily obscure point of view. A typical exposition is that of Frumkin (23). The electrons are omitted from the summation and the "potential-determining" ion, Me^{+z}, the ionic component of the metallic phase, is regarded as a component of the solution, although its equilibrium concentration is vanishingly small. The potential difference between the phases is then related to the concentration of this ion, and the electronic charge is regarded as represented by an excess or deficiency of this ion at the interface. It is not surprising that this theory has not been generally endorsed, although a very careful analysis shows that it is basically correct and leads to the correct results.

An apparently rigorous treatment is given by Gouy (41), who does not employ the Gibbs adsorption theorem but proceeds from a thermodynamic analysis of the whole system, including the reference electrode and the external source of potential. The difficulty of following his analysis has apparently impeded its general acceptance, although it appears that if it were couched in modern terminology, it would be no more difficult than those treatments which employ the Gibbs equation.

A relatively simple approach is that of Koenig (60), who achieved the correct results by means of two rather improbable assumptions. He assumed, first, that equilibrium does not subsist at the interface and secondly, that there exists at the interface a barrier impermeable to charged particles. In spite of these assumptions, Koenig has given a complete and in other respects very satisfactory derivation of the equations of electrocapillarity.

Grahame and Whitney (46) have shown how it is possible to achieve Koenig's results without making his assumptions. Charged particles fail to cross the interface, not because of the presence of any barrier but because of a lack of any tendency to do so. At equilibrium, each charged particle is content to stay on its own side of the fence. The exceptions are those charged particles which react so slowly that their presence leaves the double layer virtually undisturbed.

Because of the differences in the initial assumptions, there is a slight difference in the interpretation of the symbols employed by Koenig and by Grahame and Whitney, although the equations are identical in form. In the treatment by the latter, the symbols have the same meanings as already defined for the Gibbs equation.

The basic equation, applicable to any ideal polarized electrode at constant temperature and pressure and derived from equation 4 (46 or 60), is

$$d\sigma = q\,d(\psi^\beta - \psi^\alpha) - \Sigma\Gamma_i d\mu_i \tag{5}$$

or by equation 2

$$d\sigma = -q\,dE - q\,d(\psi^{II} - \psi^\beta) - \Sigma\Gamma_i\,d\mu_i \tag{6}$$

where q is the surface charge density of electricity[12] on the metallic phase. Equation 6 is restricted through the use of equation 2 to systems in which the composition of the metallic phase remains unaltered.

The components of the system over which the summations in equations 5 and 6 extend are the *charged* components and the neutral molecules which do not dissociate appreciably. In principle the summation includes the components of both phases, but since we are considering that the composition of the metallic phase is to remain unaltered, the chemical potentials of the components of that phase, including the electrons, are unchanged and $d\mu_i = 0$ for each such component. Thus in effect the summation includes only the components of the non-metallic phase.

The definition of q used in the derivation of equation 5 is

$$q = -F\sum^\beta \Gamma_i z_i$$

where the summation is limited to the ions of the non-metallic phase. q is therefore equal to the total charge of the ions of the double layer with signs reversed. F is the Faraday. z_i is the valence of X_i, including sign.

It might appear at first sight that the value of q would depend upon the position of the surface of reference relative to which the values of Γ_i are reckoned. This is easily proved to be not so. Let the surface of reference be placed at A and let N_+^A and N_-^A be the numbers of equivalents of cations and of anions, respectively, which *would be* present in the system if the phases were uniform with the compositions of their interiors right up to the surface A. Let N_+ and N_- be the numbers of equivalents of cations and of anions which *actually are* present. Then from the definition of q

$$q = -F(N_+ - N_+^A) + F(N_- - N_-^A)$$

Because the interior of the phase is electrically neutral

$$N_+^A = N_-^A$$

and therefore

$$q = -F(N_+ - N_-)$$

This last equation shows that q does not depend upon the position of the surface of reference. If the extent of the interface is extended by 1 sq. cm., keeping

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[12] By this we mean to include only electronic charge. Adsorbed ions are explicitly excluded from the definition of q.

the intensive variables constant, the net work required is σ and the total charge which flows through the external circuit connecting the phases is q. This makes it plain why σ and q do not depend upon the position of the surface of reference. On the other hand, the amount of one of the components which must be added to maintain the composition constant is not so unambiguously specified, since the concentration may be increased by removing appropriate amounts of the *other* components or by adding the component in question. Specifying that the surface of reference is to be fixed by setting Γ for some one component equal to zero amounts to specifying that the composition is to be adjusted, after expanding the surface, by adding or removing the other components only.

An interesting question arises concerning the interpretation of μ_i, the chemical potential, when the component in question is charged. This is the familiar problem of individual ionic activity coefficients, and it turns out, as always, that the particular combinations which arise in any actual experiment are determinate. As an example we may refer ahead to equation 17, where the chemical potential of the salt finally replaces the chemical potentials of the individual ionic types.

The first and simplest application of equation 6 is to an ideal polarized electrode at constant composition (designated by the subscript μ). Each term in the summation is zero, and so also is $d(\psi^{II} - \psi^{\beta})$. Therefore

$$(d\sigma/dE)_{\mu} = -q \tag{7}$$

This is the well-known Lippmann equation (67, 68). It states that the slope of the electrocapillary curve is equal to the electric charge density of the metallic surface. Experimental results verifying this and the equations to follow will be given in the next section.

It follows from equation 7 that at the potential of the electrocapillary maximum $q = 0$, as stated previously. It may be noted that the reference electrode employed in the application of equation 7 need not be one which can be joined to the solution without liquid junctions, since on the assumption merely that the liquid-junction potential does not change during an experiment carried out at constant composition,

$$dE = d\mathbf{E} = d\psi^r = d\mathcal{E}$$

and equation 7 is valid regardless of the kind of potential considered. The rate of change of the slope of the electrocapillary curve is, from equation 7,

$$(d^2\sigma/dE^2)_{\mu} = -(dq/dE)_{\mu} = C \tag{8}$$

where C is the *differential capacity* of the double layer. The distinction between the differential capacity, $-dq/dE$, and all other kinds of capacity is of particular importance because of the fact that q is not proportional to $\mathbf{E}$. For the sake of clarity we may introduce a new type of capacity, K, designated as the static or integral capacity, and defined as

$$K = -q/\mathbf{E} \tag{9}$$

This is an appropriate definition, since $q = 0$ when $E = 0$, but unlike ordinary condensers, the ratio of q to E in the double layer is not constant. In figure 3, showing q as a function of E for some typical cases, the differential capacity is the slope of the curve at a given point, but the integral capacity is the slope of the *chord* drawn from the origin to the point. Except in special cases, the differen-
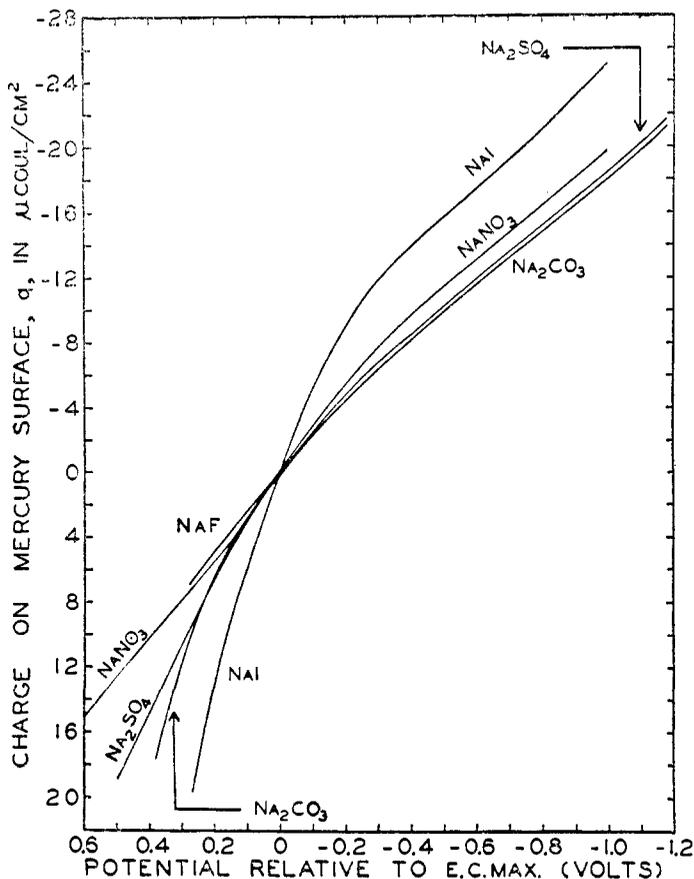

Fig. 3. Electronic charge on mercury surface in contact with uninormal aqueous solutions of the salts named. $T = 25°C$. Curves would coincide at the right if "rational" potential scale had been chosen.

tial capacity is the more significant quantity, but the integral capacity is very useful as an intermediate function in the making of calculations and as a means of representing data.

If one measures the capacity of a condenser or of the electrical double layer by means of an impedance bridge, it is always the differential capacity which is obtained. Unlike ordinary condensers, the capacity of the double layer varies with the D.C. potential imposed across it. A number of plots of the differential capacity as a function of the voltage are given in the next section.

The charge q can be obtained from differential capacity curves by graphical integration, since from equation 8

$$q = -\int_0^{\mathbf{E}} C \, d\mathbf{E} \tag{10}$$

The limits are as shown because $q = 0$ when $\mathbf{E} = 0$. By a further integration (of q with respect to $\mathbf{E}$) one can obtain the shape of the electrocapillary curve (equation 7), but the constant of integration cannot in this instance be ascertained other than by direct measurement of the interfacial tension at some one point.

The integral capacity is easily calculated from the differential capacity through equations 10 and 9. The differential capacity can be obtained from the integral capacity through the following equation (obtained from equations 8 and 9):

$$C = K + \mathbf{E}\left(\frac{dK}{d\mathbf{E}}\right)_\mu \tag{11}$$

It will be noted that at the electrocapillary maximum $C = K$.

We turn now to a consideration of the effects of varying the composition of the electrolyte. For these cases it becomes necessary to specify the nature of the reference electrode more closely. Liquid-junction potentials are to be avoided, which requires that the reference electrode must change as the electrolyte changes. There are two possible types of electrodes which may then be considered, those which are simply reversible to one of the anions and those which are simply reversible to one of the cations. The observed electromotive force E, *as read on the potentiometer*, will be designated by E_j^- or E_j^+ in the two types, respectively. If the reference electrode is simply reversible to one of the anions, for example, equation 6 will read:

$$d\sigma = -q \, dE_j^- - \Sigma\Gamma_i d\mu_i - q \, d(\psi^{II} - \psi^\beta) \tag{12}$$

From this point on it will be supposed in this section that only one anionic type and one cationic type are present. The surface of reference with respect to which the Γ_i's are reckoned will be so chosen that $\Gamma_{SOLVENT} = 0$. This latter choice is discussed further below. The presence of only a single anionic and a single cationic type makes the subscript j superfluous. Equation 12 now reads (if the reference electrode is reversible to the anion)

$$d\sigma = -q \, dE^- - \Gamma_+ d\mu_+ - \Gamma_- d\mu_- - q \, d(\psi^{II} - \psi^\beta) \tag{13}$$

where the $+$ and $-$ subscripts refer to cations and anions. From the definition of chemical potentials it follows that

$$d\mu = \nu_- d\mu_- + \nu_+ d\mu_+ \tag{14}$$

where μ is the chemical potential of the neutral salt and ν_+ and ν_- are the numbers of cations and anions, respectively, formed by the dissociation of one molecule of salt.

The potential $\psi^{II} - \psi^\beta$ varies with the chemical potential of the anion, if the

reference electrode is simply reversible to the anion, according to the equation

$$z_- F\, d(\psi^{II} - \psi^{\beta}) = d\mu_-$$ (15)

From the definition of q (or from the electroneutrality requirement)

$$q + z_+ \Gamma_+ F + z_- \Gamma_- F = 0$$ (16)

When equations 14, 15, and 16 are introduced into equation 13, and noting that $z_+/z_- = -\nu_-/\nu_+$, the following simple and important result is obtained:

$$d\sigma = -q\, dE^- - \frac{\Gamma_+}{\nu_+} d\mu$$ (17)

If the reference electrode is reversible to the cation, one obtains by an exactly analogous procedure:

$$d\sigma = -q\, dE^+ - \frac{\Gamma_-}{\nu_-} d\mu$$ (18)

These equations and also those which follow may be put in forms more suitable for computation by the introduction of the relation

$$d\mu = \nu RT\, d \ln\{m\gamma(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}\} = \nu RT\, d \ln m_{\pm}\gamma = \nu RT\, d \ln m\gamma$$ (19)

The nomenclature is essentially that of Lewis and Randall. γ is the mean activity coefficient, m is the molality, and $m_{\pm}$ is the mean molality, defined by the relation $m_{\pm} = m(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}$. ν is the sum of ν_+ and ν_-.

At constant composition equations 17 and 18 reduce to the Lippmann equation. At the electrocapillary maximum, where $q = 0$, one has

$$d\sigma^{MAX}/d\mu = -\Gamma_+^{MAX}/\nu_+ = -\Gamma_-^{MAX}/\nu_-$$ (20)

The symbol $d\sigma^{MAX}/d\mu$ means that the differentiation occurs at $q = 0$.

The quantities on the right are equal to Γ_{SALT}^{MAX}, the number of moles of neutral salt adsorbed per unit area of interface at the electrocapillary maximum. Therefore

$$d\sigma^{MAX}/d\mu = -\Gamma_{SALT}^{MAX}$$ (21)

Values of Γ_{SALT}^{MAX} computed from this equation are listed in table 1. Unfortunately the accuracy with which σ^{MAX} can be ascertained is not as great as one would wish for this purpose. The equation itself, however, suffers from no known restrictions other than those appropriate to the Gibbs adsorption equation itself.

At constant E^- or E^+ equations 16 and 17 give

$$-\nu_+(d\sigma/d\mu)_{E^-} = \Gamma_+ \quad \text{and} \quad -\nu_-(d\sigma/d\mu)_{E^+} = \Gamma_-$$ (22)

These results indicate that Γ_+ or Γ_- can be obtained at any point on the electrocapillary curve by measuring the rate of change of interfacial tension with composition at constant imposed potential, E^+ or E^-. (The potentiometer reading is the thing to be held constant, not any ill-defined quantity.) It has not been very generally realized that Γ_+ and Γ_- could be calculated separately without the introduction of non-thermodynamic assumptions. Some results obtained with these equations will be presented in the next section.

Very convenient alternate forms of equation 22 are obtained by dividing through by equation 7 (with E^- or E^+ for E)

$$- \nu_+ q (dE^-/d\mu)_\sigma = \Gamma_+ \qquad (23)$$

and

$$- \nu_- q (dE^+/d\mu)_\sigma = \Gamma_- \qquad (24)$$

In obtaining these results the identity $(d\sigma/d\mu)_E (d\mu/dE)_\sigma (dE/d\sigma)_\mu = -1$ has been used. Differentiation of equation 22 gives:

$$- \nu_+ (\partial^2\sigma/\partial\mu\partial E^-) = \partial\Gamma_+/\partial E^- \text{ and } - \nu_- (\partial^2\sigma/\partial\mu\partial E^+) = \partial\Gamma_-/\partial E^+ \quad (25)$$

Since the order of differentiation is immaterial, the left-hand members may be rewritten, with the aid of the Lippmann equation (7), as

$$\nu_+ (dq/d\mu)_{E^-} = (d\Gamma_+/dE^-)_\mu \text{ and } \nu_- (dq/d\mu)_{E^+} = (d\Gamma_-/dE^+)_\mu \qquad (26)[13]$$

Graphical integration of the left-hand members of these equations with respect to E^- or E^+ gives $\Gamma_\pm$ as a function of $E^\mp$ except for the constant of integration. Since q can be obtained from capacity data (equation 10), Γ_+ and Γ_- can be obtained from capacity data, except for the constant of integration. The latter can be evaluated through the use of equation 20 or 21, but this requires accurate interfacial tension data which may not be available. Alternative methods of fair accuracy but not of strictly thermodynamic character will be discussed later.

The evaluation of Γ_+ and Γ_- for electrocapillary systems of many kinds is an important task so far barely begun. The chief difficulty has been the lack of accurate experimental data and unclear ideas concerning the meaning of the thermodynamic equations.

We may now consider the reasons for the assumption made earlier that $\Gamma_{\text{SOLVENT}} = 0$. Basically, the justification is that of simplicity. The equations take their simplest form when this assumption is made. But nothing is lost thereby, since it is only a stoichiometric calculation to find the amount by which any Γ changes for a shift in the position of the surface of reference through a given distance. Moreover, this is all the information which can be obtained by thermodynamic means, since if one chooses to set $\Gamma_{\text{Me}^+s} = 0$, the only convenient alternative, one obtains equations having exactly the same physical significance.[14]

As a matter of convenience, Γ_+ and Γ_- will frequently be expressed in units of charge per unit area in spite of the fact that their definitions are in terms of moles per unit area. It is believed that this inconsistency will cause no confusion.

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[13] These equations could have been obtained by inspection from equations 17 and 18 by noting that $d\sigma$ is an exact differential. Equations 26 are the reciprocity relations satisfied by the line integral of an exact differential.

[14] More explicitly, one obtains the equations given by Koenig (60). An example will serve to illustrate the truth of the assertion that these equations are equivalent to those here derived. Instead of our equation 21, Koenig gives

$$\frac{d\sigma^{\text{MAX}}}{d\mu} = -\Gamma_{\text{SALT}}^{\text{MAX}} + \frac{N^\beta}{N_0} \Gamma_{\text{SOLVENT}}$$

V. VERIFICATION AND APPLICATION OF THE THERMODYNAMIC THEORY OF ELECTROCAPILLARITY

The two principal kinds of equations developed in the thermodynamic theory of electrocapillarity are those which deal with variations of electrical potential and those which deal with changes of composition. The first class has been extensively verified, the second not at all. There is no serious doubt about the correctness of either class, however.

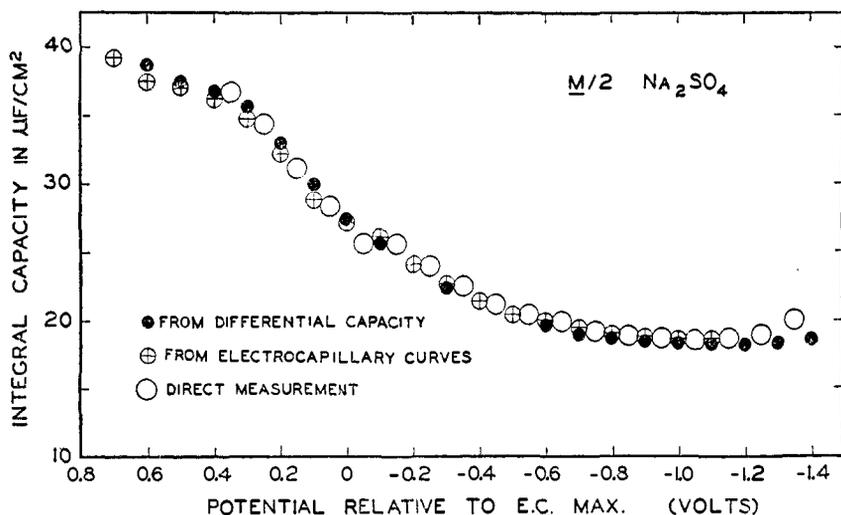A three-way check of the first class of equations is shown in figure 4. For con-

FIG. 4. Three-way check of the Lippmann equation. Crossed circles computed from data by Gouy (36).

venience the integral capacity is plotted. The three types of points represent (a) an evaluation of K from differential capacity data using equation 10, (b) an evaluation of K from interfacial tension data using equation 7, and (c) an evaluation of q from direct measurements of the charge carried by falling mercury droplets of known surface area. In the case cited, all three types of data were known with exceptional accuracy. There are no arbitrary constants in these data. Other verifications of the first class of equations are given by Frumkin (23), by Proskurnin and Frumkin (78), by Borissova and Proskurnin (9), by Craxford (14), and by Grahame (42). Proskurnin and Frumkin pointed

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where N_0 is the mole fraction of solvent and N^β is the mole fraction of solute within the solution. But this equation can be derived from equation 21, for if $\Gamma_{SOLVENT} = y$ at some arbitrarily chosen interface and zero at the interface to which equation 21 refers, then Γ_{SALT}^{MAX} will change by exactly $N^\beta y / N_0$ when the surface of reference is moved from one position to the other. When this is added to equation 21, Koenig's equation results. It is to be noted that $d\sigma^{MAX}/d\mu$ has a fixed value independent of the position of the surface of reference.

out in 1935 (78) that contamination of the metallic surface by traces of capillary-active substances had rendered earlier measurements of the differential capacity so inaccurate that the demands of equation 8 had seemed not to be satisfied. This difficulty is overcome nowadays either by extraordinary care in the purification of solutions and metallic surfaces (9) or by the use of a dropping electrode technique (42, 43).

Differential capacity data for representative types of the solutions which have been investigated are given in figures 5–6.[15] Other data of the same kind are given by Gouy (36), by the Russian group of workers (9, 27, 78, 87, 88), and by Grahame (42, 43).

The characteristics of the differential capacity curves in figures 5–6 depend very greatly upon the anion and almost not at all upon the cation, except the hydronium ion, provided it is of fairly low molecular weight. This was to be expected, of course, from the fact that the electrocapillary curves show such behavior. An explanation of many of the characteristics of these curves will be evident from the mathematical development of the kinetic theory to follow, although not all of the details are fully understood. For instance, there is still some difficulty in explaining the difference between the behavior of hydroxides and fluorides under negative polarization, since both of these anions have large hydration energies (7) and would be expected to be as much alike as two univalent cations. The "humps" which appear near the electrocapillary maximum of most curves are not correctly predicted by any theory and are believed by the present author to arise from the mutual electrostatic repulsion of ions in the double layer in directions parallel to the interface.

The second type of thermodynamic equation of electrocapillarity deals with the effects of varying the composition. In figure 7 there are presented data by Gouy on the interfacial tension at the electrocapillary maximum of several electrolytes (36). Many more data are contained in the original paper. According to equation 21, the slope of these curves measures the amount of electrolyte adsorbed at the interface. Values calculated in this way are included in table 1. There has been no experimental verification of these results by independent means, although such verification is theoretically possible. There is no real doubt, however, concerning the validity of the equation from which they are derived.

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[15] These data by the author disagree somewhat with similar data by Vorsina and Frumkin (87, 88). The disagreement is not serious except at small negative values of E with dilute solutions. In plots of q vs. E one observes two roughly linear regions connected by a non-linear region near $E = 0$ (6; 10, p. 74; 13, 76). Since the slope of these curves gives the differential capacity, the impression has grown up that there are two "characteristic" values of capacity corresponding to positive and negative polarization, respectively. This impression is not borne out by the differential capacity curves themselves, which do not approach a constant value over any considerable range of potentials with positive polarization. The appearance of the q vs. E curves is somewhat misleading, since very considerable changes of slope may go unnoticed or pass as experimental error. Even with negative polarization the differential capacity does not approach a constant value but has a flat minimum.

Values of Γ_{SALT}^{MAX} have been plotted against ψ_{MAX}^r in figure 8. A few discordant values have been omitted (0.01 M sodium thiocyanate; 0.1 M sodium chloride;
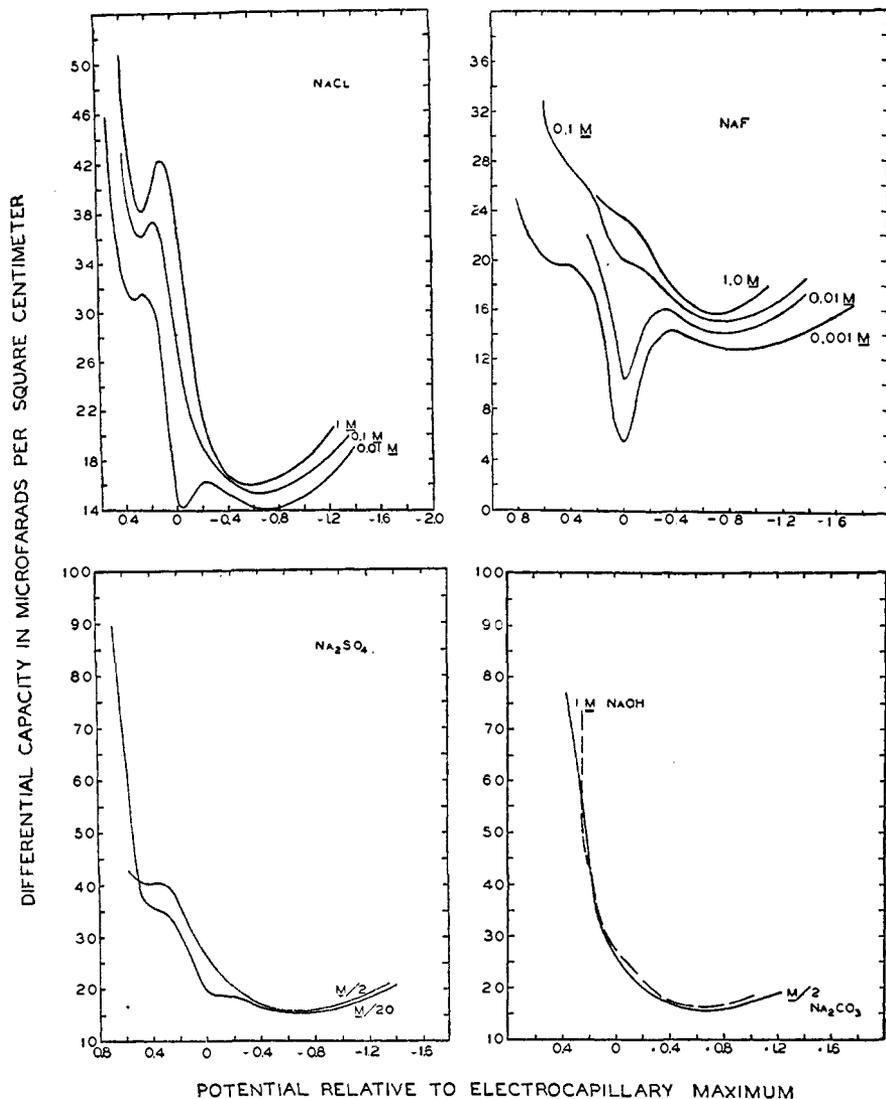

FIG. 5. Differential capacity of the electrical double layer between mercury and aqueous solutions of the salts named. $T = 25°C$.

0.1 M potassium nitrate). Except for the omitted points, the curves at a given concentration are consistent enough to serve as a starting point for estimating Γ_{SALT}^{MAX} from ψ_{MAX}^r. The latter is so much easier to measure that in many instances

the values taken from the curve are likely to be more accurate than the measured values. Thus for 0.01 M sodium thiocyanate and 0.1 M sodium chloride the
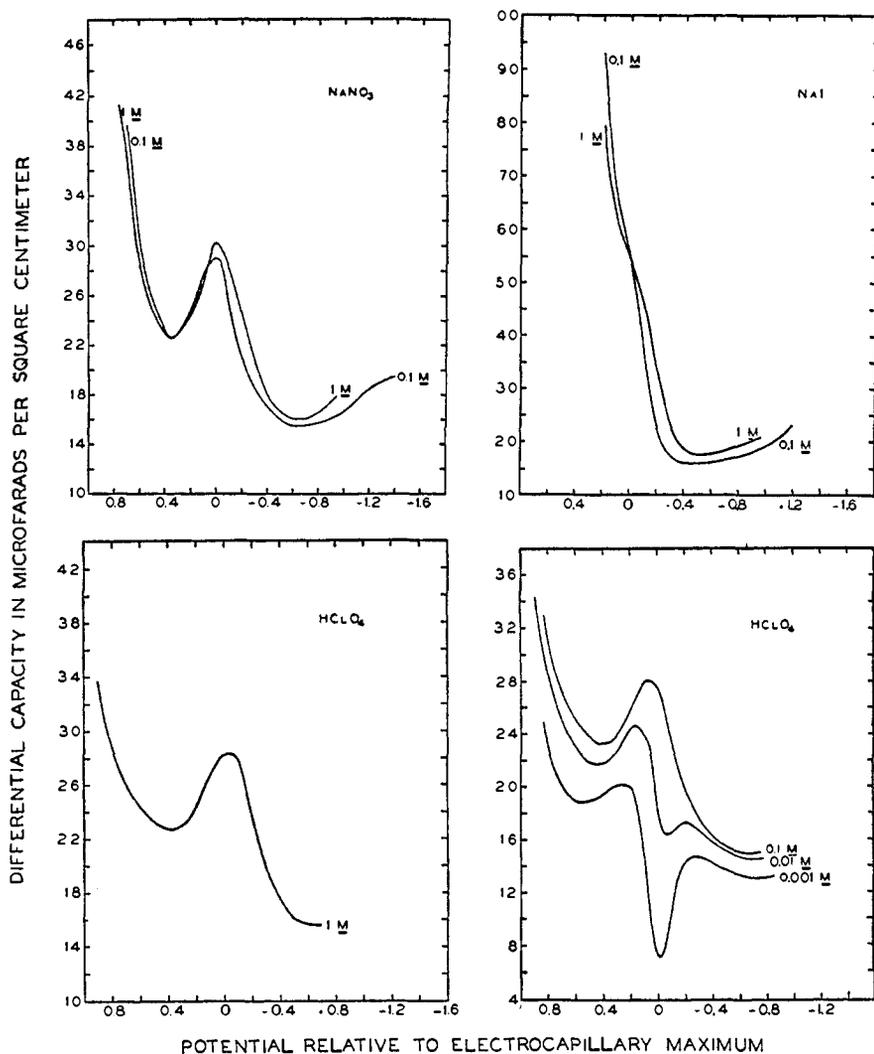

FIG. 6. Differential capacity of the electrical double layer between mercury and aqueous solutions of the salts named. $T = 25°C$.

observed values are probably in error. On the other hand, all of the observed values for nitrates are a little higher than the curve would suggest, a result which is correlated with the dissimilarity of the cathodic branches of the differential capacity curves of halides and nitrates.
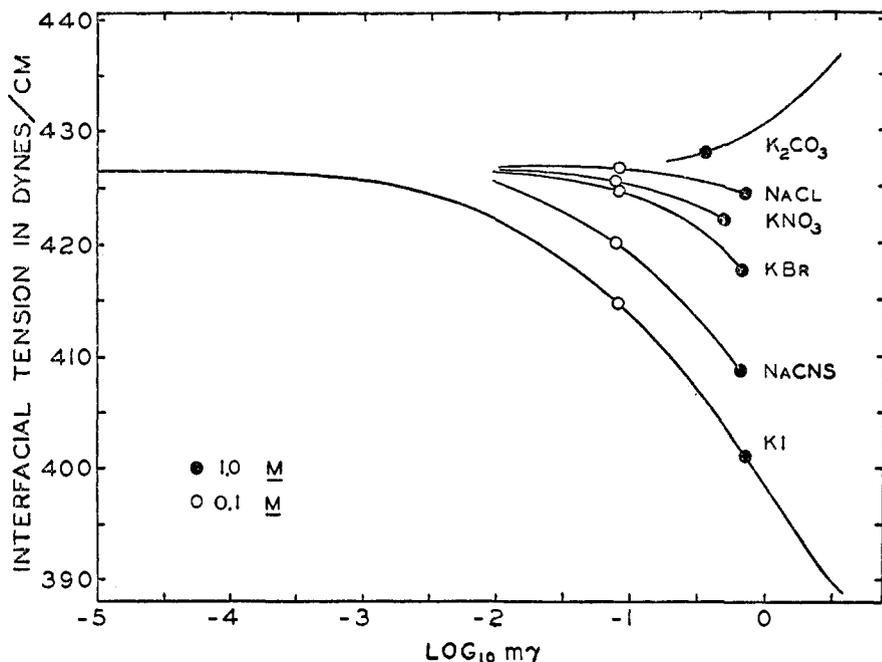
Fig. 7. Maximum interfacial tension of mercury in contact with aqueous solutions of the salts named. $T = 18°C$. Data by Gouy (36). The slope measures the amount of salt adsorbed (equations 19 and 21). (Additional points not shown were used in the construction of the figure.)
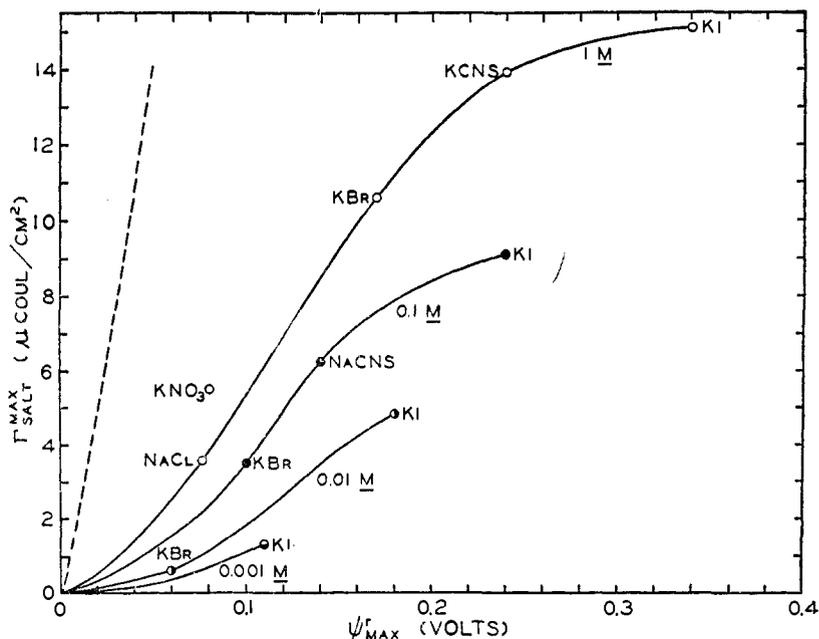

Fig. 8. Salt adsorption on a mercury surface at the potential of the electrocapillary maximum. Lines connect points of same concentration. Ordinates represent shift of the potential of the electrocapillary maximum caused by the salt. The dotted line shows calculated values for unimolar solutions based upon the erroneous assumption that $\psi^o = \psi^i$.

Curves of Γ_+ *vs.* E^- can be obtained in two ways, through equation 22[16] or through equation 26. In the latter case only the shape of the curve is ascertained, the constant of integration being unknown. If the curves are made to coincide at one point, the agreement at other points constitutes a partial check on the validity of equations 22 and 26. Such a check is shown in figure 9,
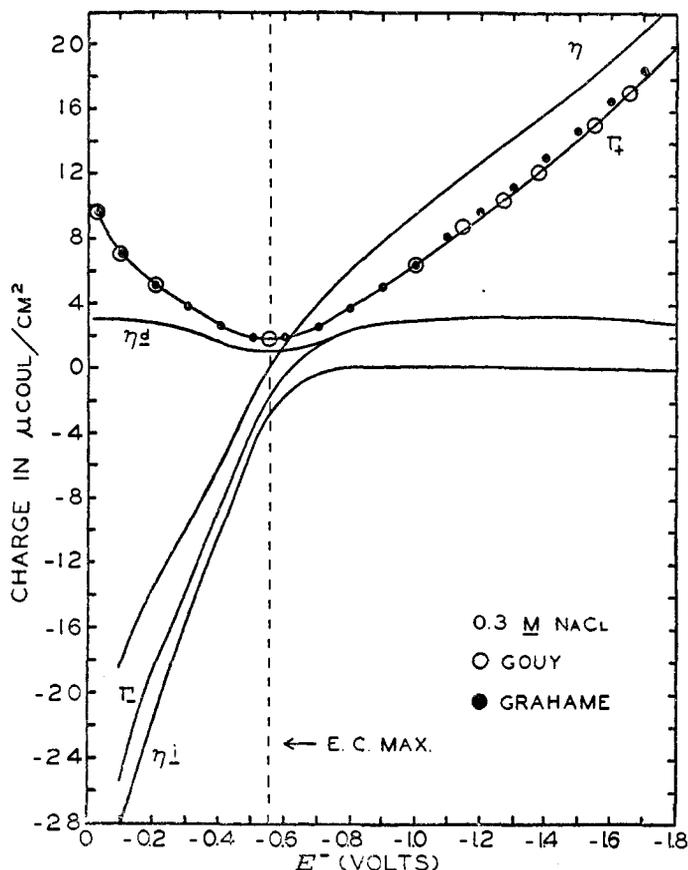

FIG. 9. Components of charge of the double layer between mercury and aqueous 0.3 M sodium chloride solution. $T = 25°C$. Open circles computed from data by Gouy (36). η is total charge. Γ_+ is charge attributable to cations in the double layer; η_-^d is charge attributable to anions repelled from the diffuse double layer; η_-^i is charge attributable to anions adsorbed on mercury surface. Γ_- is the sum of these two. Potentials measured relative to 0.3 M sodium chloride–calomel electrode.

where Γ_+ (expressed in μ coul./cm.^{2}) has been calculated for 0.3 M aqueous sodium chloride by means of each of the two equations mentioned. The agreement obtained has more to do with the accuracy of the experiments than with the accuracy of the equations, however, since equation 26 is derived from equation

[16] Other values of Γ_+ and Γ_- obtained through the use of equation 22 are given by Iofa, Frumkin, Ustinskiĭ, and Ĕlman (54, 55).

22. Again it would be possible to verify these results by direct analytical means,[17] but such verification has not been attempted.[18]

In figure 9 there are also plotted Γ_- and $-q$ (labeled η in conformity with the nomenclature of the next section) obtained from equations 26 and 10, respectively, and also two other quantities, η_-^i and η_-^d, to be defined later. These are components of Γ_- and are obtained by non-thermodynamic means as explained below.

Figure 10 gives similar data for another concentration of sodium chloride. These data are not of the highest possible accuracy, and will probably need some revision when recently discovered techniques (43, 79) have been more widely applied.

Γ_+ shows the interesting property of being positive even on positive polarization. On positive polarization, the mercury surface holds anions not only by coulombic forces but also by covalent bonding. The resulting binding is known as a specific adsorption because it is specific to the various anions. As a result of specific adsorption, more anions are held on the mercury surface than corresponds to the positive charge on the mercury. Consequently the net charge of the two layers is negative and cations are attracted. The specific adsorption observed at the electrocapillary maximum is only a special case of this phenomenon.

We turn now to the application of the above results to problems which cannot be settled by thermodynamic means alone. The assumptions we are about to make are in better agreement with the experimental data than any others of which we know. Part of the evidence has been given by Whitney and Grahame (90) and is repeated in Section VI in somewhat different form.

Ions which are held to the mercury surface by covalent bonds are certainly not separated from the surface of the metal by water molecules. Ions which are held to the mercury surface by van der Waals forces are also assumed not to be separated from the surface by solvent molecules. Ions which are *not* held to the mercury surface by covalent bonds or by van der Waals forces will be assumed to be separated from that surface by a solvent sheath, at least when the solvent is water. This amounts to assuming that the work needed to displace the solvent on the side of the ion nearest the interface is not negligible compared to the work needed to move the ion up to the nearest point of approach not in-

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[17] One could allow a stream of mercury to flow through a column of solution while maintaining the potential at a fixed value and measuring the current flow and the time. An analysis of the top and bottom "compartments" would give the amount of neutral salt transferred. Knowing the integral capacity as a function of E, one could compute q and therefore the area of the mercury surface. From the total charge transferred and the known transference numbers, one could then compute the amounts of each ion moved from one compartment to the other by transference. These data would be sufficient to determine Γ_+ and Γ_-. The difficulty, of course, lies in the difficulty of avoiding convection currents during the experiment. The experiment is interesting primarily in that it shows that Γ_+ and Γ_- are measurable magnitudes apart from considerations of interfacial tension.

[18] Such measurements as have been made have been done with non-polarized electrodes (66, 74, 75, 83).

volving such solvent displacement. The locus of the electrical centers of a layer of adsorbed ions, whether adsorbed by covalent bonds or van der Waals forces or both, will be called the *inner* Helmholtz plane. The locus of the electrical centers of hydrated or solvated ions in contact with the mercury surface will be called the *outer* Helmholtz plane. It is assumed that the *outer* Helmholtz plane is the same for all ions, even for anions, although the latter are generally more easily
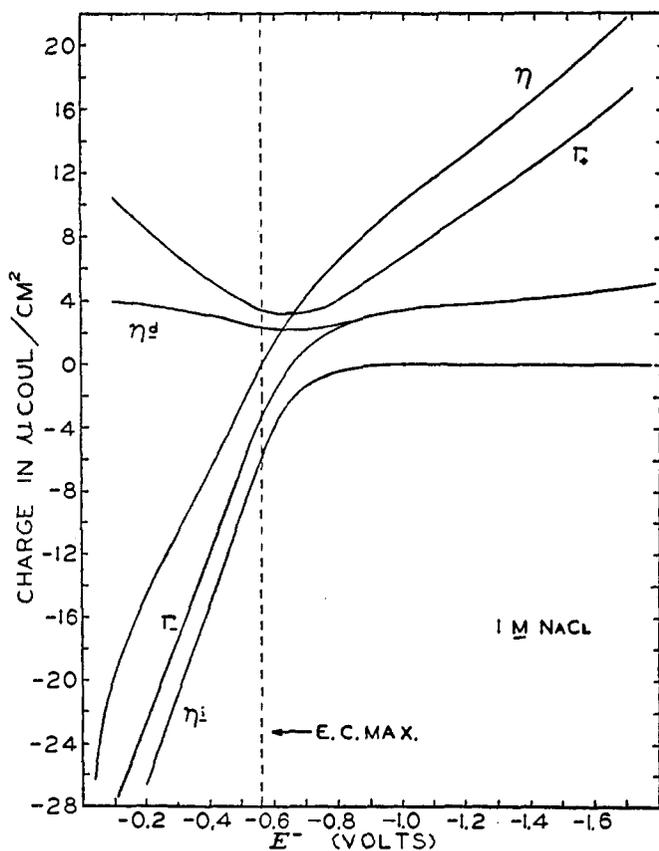

FIG. 10. Components of charge of the double layer between mercury and aqueous 1 M sodium chloride solutions. $T = 25°C$. See legend of figure 9. Potentials measured relative to 1.0 M sodium chloride-calomel electrode.

dehydrated. It should be noted that we do not speak of a *layer* of ions at the outer Helmholtz plane, since the forces which act there are long-range forces and serve only to produce an ionic atmosphere. Except in the case of very large adsorbed ions, it is to be expected that the outer Helmholtz plane will lie farther from the surface than the inner.

The great similarity of the electrocapillary properties of low-molecular-weight cations leads one to believe that they do not populate the inner Helmholtz plane, where their various radii would lead to varying results. If this

conclusion be accepted (and additional evidence for it will be presented at the end of Section VI), it follows that Γ_+ is determined solely by the condition of the double layer from the outer Helmholtz plane out into the solution. Therefore if one compares two points having the same value of Γ_+ on a curve such as that in figure 9, one expects that the potential of the outer Helmholtz plane will be the same in the two cases and that a "map" of the double layer showing concentrations and potentials would be the same for the two cases from this point out. Moreover, even on comparing different solutions of the same valence type and of the same concentration, if the cation is the same or behaves the same, the difference of anion should make little difference, and a "map" of the double layer for a condition corresponding to the same value of Γ_+ should be the same for both. This principle will be subject to experimental verification when more data of sufficient accuracy became available. Meanwhile it may be used as a guide in the absence of such information.

The differential capacity of the region between the mercury surface and the inner Helmholtz plane will be designated as C^i and defined by the equation

$$C^i = dq/d(\psi^r - \psi^i) \tag{27}$$

ψ^i is the potential of the inner Helmholtz plane. Its meaning is discussed in Section VII. The integral capacity of this region will be designated by K^i and defined by the equation

$$K^i = q/(\psi^r - \psi^i) \tag{28}$$

From these two equations it follows that[18a]

$$K^i = \frac{1}{\psi^r - \psi^i} \int_0^{\psi^r - \psi^i} C^i \, d(\psi^r - \psi^i) \tag{29}$$

This equation is used below for the evaluation of K^i.

The potential at which Γ_+ is a minimum, the Γ_+^{MIN}-potential, is one of special interest.[19] At this point a small change in the imposed over-all potential causes no change in the value of Γ_+ and therefore no change in the potential of the outer Helmholtz plane, ψ^o. The potential of the inner Helmholtz plane, ψ^i, must also remain unchanged, since it controls ψ^o. Therefore the differential capacity of the whole double layer is equal to the differential capacity of the region between the mercury surface and the inner Helmholtz plane, C^i. This capacity is nearly the same at the Γ_+^{MIN}-potentials of each of the sodium chloride concentrations studied. It lies between 32 and 34 $\mu f/cm.^2$ and its constancy leads one to suppose that it is constant under a wide range of conditions. If it is constant, it follows from equation 29 that it is equal to the integral capacity of the same region. Thus

$$C^i = K^i \tag{30}$$

[18a] The limits of integration are set by noting from elementary electrostatics that when $q = 0$, $\psi^r = \psi^i$.

[19] Note that Γ_+^{MIN} is the minimum value of Γ_+, whereas Γ_+^{MAX} is the value of Γ_+ at the electrocapillary maximum. The subscript or superscript MAX always refers to the electrocapillary maximum in this paper.

This equation is important in that it gives a means of calculating K^i and therefore ψ^i, the potential of the inner Helmholtz plane, from experimentally observable results. The results will be accurate near the Γ_+^{MIN}-potential and probably also elsewhere.

Equation 28 is one of the Stern equations (85), of which we shall speak later. There is one important difference, however, in that ψ^i is not here regarded as identical with ψ^o. Stern recognized the desirability of distinguishing between these quantities, but underestimated the necessity for doing so. At the electrocapillary maximum of 0.3 M sodium chloride, for instance, $\psi^i = -0.044$ volt, whereas $\psi^o = -0.022$ volt according to a later estimate which is probably not greatly in error.

It is evident from figures 9 and 10 that the adsorptive forces are becoming stronger as the mercury becomes more highly charged positively.[20] It has not always been recognized that this is not simply the result of an increased coulombic attraction in a simple sense but represents a strengthening of the covalent bond by which the anions are held to the mercury surface. This result is to be expected on any theory of chemical binding. The positive charge enhances the stability of the electron-pair which binds the atoms. This same phenomenon is apparent in the chemical behavior of simple inorganic salts. When two such salts are compared, differing only in the charge on the cation, the more highly charged cation binds the anions much more strongly. Comparing ferrous and ferric chlorides, for instance, the latter dissociates much less than one would anticipate from interionic attraction theory. Ferrous and ferric hydroxides display the same behavior, the greater insolubility of the latter corresponding to far greater bond strength. Salts of tin, lead, mercury, manganese, and cobalt exhibit this behavior in marked degree. Salts of copper appear to constitute an exception, for which some reason can perhaps be found. The nitrates, perchlorates, and bisulfates of the metals do not show the phenomenon, no doubt because these ions are not bound to metallic ions by covalent bonds to any marked extent. It is interesting to note that nitrate, perchlorate, and bisulfate ions show little or no specific adsorption on mercury of the type associated with covalent-bond formation until the mercury is strongly positively charged. The fluoride ion, which behaves differently from all of these ions, is probably unique because its strong electronegativity hinders the formation of covalent bonds with cations to a large degree.

It would be desirable to be able to set down rigid rules for the experimental recognition of the presence or absence of adsorption of ions. This we cannot do in general, since the concept is not a purely thermodynamic one. Certain nonthermodynamic considerations are possible, however. We restrict our attention first to the electrocapillary maximum.

One is tempted to say that if $\Gamma_{SALT}^{MAX} = 0$ at the electrocapillary maximum, ion adsorption is absent, and this is nearly true. But it is found that in very

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[20] The increasing values of Γ_+ show this, since Γ_+ would not even be positive if adsorptive forces were absent. The calculations leading to figure 15 (see Section VII) give a quantitative measure of the effect.

concentrated solutions of salts whose ions are believed to be unadsorbed, Γ_{SALT}^{MAX} becomes negative (table 1 or figure 7). This effect may be thought of as being caused by a small constant adsorption of solvent which results in the displacement of larger amounts of solute in concentrated than in dilute solutions. Other explanations which could be given are essentially equivalent to this. Because of this effect, Γ_{SALT}^{MAX} is negative in the absence of ionic adsorption. Positive values of Γ_{SALT}^{MAX} indicate adsorption, but zero or negative values do not guarantee its absence.

At potentials different from that of the electrocapillary maximum, the situation is likewise complicated. If Γ_+ is positive on positive polarization, anion adsorption is indicated. If Γ_- is negative on negative polarization, cation adsorption is indicated. If Γ_+ is negative on positive polarization, anion adsorption is probably absent. If Γ_- is positive on negative polarization, cation adsorption is probably absent.

When more data are available for capillary-inactive electrolytes such as sodium fluoride, it will probably be possible to say with more exactitude what Γ_+ and Γ_- must be in any given case if adsorption is to be deemed absent.

The term "*specific* adsorption" is used in cases where it seems probable that covalent-bond formation is responsible for an observed adsorption. Otherwise the less explicit term "adsorption" is used. Iodide ion is almost certainly held to the mercury surface by covalent bonds, an effect which also limits the ionizability of mercurous and mercuric iodides. There is a considerable correlation between the specific adsorbability of anions on mercury and the ionizability (or solubility) of the corresponding mercury salts, but because of the exceptions and special cases, this correlation cannot be made very convincing without extensive discussion. The nitrates constitute the most glaring discrepancy, since nitrate ion shows greater adsorbability than chloride ion. van der Waals (dispersion) forces suggest themselves at once in this and similar cases (e.g., perchlorates), but the situation is by no means clear.

VI. THE KINETIC THEORY OF THE DIFFUSE DOUBLE LAYER (8, 11, 16, 20, 21, 39, 40, 72)

The kinetic theory of the diffuse double layer deals with that part of the double layer which lies at or beyond the outer Helmholtz plane. At distances closer to the interface than this, the assumptions break down and other methods of treatment are necessary. These other methods are discussed in the next section.

There are three equations upon which the theory to be developed rests, and since it is possible to proceed from these without further approximations or assumptions directly to experimentally significant results, it is evident that any faults in the theory must be faults of the original equations. The three equations to which we refer are: (*1*) the Poisson equation for a system whose potential varies in only one direction

$$d^2\psi/dx^2 = -4\pi\rho/DD_0 \qquad (31)$$

(*2*) the Boltzmann equation

$$n_i = n_{0i}e^{-w_i/kT} \qquad (32)$$

and (*3*) an equation expressing the work w_i needed to bring an ion of type X_i from the interior of the solution to the point in question:

$$w_i = z_i \epsilon \psi \tag{33}$$

In these equations ψ is the electrical potential (relative to the interior of the solution) at a point within the double layer (discussed below); ρ is the electric density (charge per unit volume) at the point in question; x is the distance of this point from the surface of discontinuity, positive values of x corresponding to points within the solution; D is the dielectric constant of the solution; D_0 is 4π times the permittivity of free space (discussed below); n_i is the number of ions of type X_i per unit of volume at a point whose potential is such that an amount of work w_i is needed to bring an ion of this type from the interior of the solution to the point in question; n_{0i} is the number of ions of type X_i per unit of volume within the body of the solution; k is the Boltzmann constant; T is the absolute temperature; z_i is the valence number including sign; and $z_i \epsilon$ is the charge of an ion X_i. Most of these quantities call for further comment.

The potential at a point within the double layer is not a wholly unambiguous quantity, particularly when the "point" in question is really a region as large as the solvated ion. For the present the best solution to the difficulty is to regard equation 33 as a definition of ψ. This procedure is not a complete solution to the problem, however, for it assumes that all of the work w_i is electrical work, and it assumes that the same value of ψ will be obtained whatever ion is used for the test ion. The other kinds of work neglected by this procedure are (*1*) the work involved in displacing polar solvent molecules from a region of high field strength (8), (*2*) the work involved in pushing all of the other ions in the region a little closer together (the crowding effect), and (*3*) the work involved in distorting or displacing the solvent sheath of a solvated ion as a result of a too close approach of the ion to the metallic surface. The first-named effect is almost certainly very small compared to other errors in the theory. The second effect has been considered in a quantitative manner by Bikerman (8), but it is unfortunately true that the introduction of factors intended to account for this effect in the fundamental equations leads to a differential equation which cannot be integrated without assuming that the potential is very small, so small that the results have a very limited range of validity. Within this range, however, the crowding effect is almost certainly of minor consequence. Even if the mathematical difficulties could be overcome, it is still not certain how the effects of crowding should be introduced. One may treat the problem as a volume effect, the ions having a lesser probability of entering a region already partly filled, or one may treat the problem as an electrostatic effect, computing the work required to make a place for the test ion. Both types of calculation are subject to great uncertainties. It will be shown presently that the double layer is not more crowded than a moderately concentrated solution, so that the error introduced by the neglect of crowding is probably not so serious as to make the entire treatment fictitious. Nevertheless, the neglect of crowding is likely to prove to be the most serious defect of the kinetic theories of the diffuse double layer now in vogue.

The third effect listed above, the work required to displace the solvent sheath of an ion on the side of the metallic phase, is certainly not small enough to justify its neglect in aqueous solutions.[21]   The equations to be developed in this section may not be applied, therefore, to ions whose centers lie closer to the interface than the outer Helmholtz plane.   This is a point which has sometimes been overlooked or ignored.

The dielectric constant D is dimensionless.   We shall use the value 78.49 for water at 25°C. (17).   The propriety of using the dielectric constant of the solvent in equation 31 and in the equations to be derived from it is discussed below.

The constant D_0 is introduced in order to avoid the confusion which accompanies attempts to make the dielectric constant other than a dimensionless constant.   A discussion of this problem is given by Wood (94) and also by Guggenheim (50). D_0 may be defined by the equation

$$f = \frac{q_1 q_2}{r^2 D_0}$$

where f is the force acting between charges q_1 and q_2 *in a vacuum* at a distance r. In practical units D_0 has the value $10^9/c^2 = 1.112 \times 10^{-12}$ coul.-volt^{-1}-cm.$^{-1}$ A similar quantity, κ_0, called the permittivity of free space, has been introduced by Harnwell (52), who gives a clear discussion of the reasons for the introduction of such a constant.   We have chosen to introduce D_0, equal to $4\pi\kappa_0$, in order to make our equations more closely resemble those which have appeared in previous treatments of the kinetic theory of the electrical double layer.   Thus DD_0 in our treatment is identical with what has been simply called D heretofore.   It is suggested that D_0 be called the diabattivity of free space, from $\delta\iota\alpha\beta\alpha\tau\delta\varsigma$, passable.

The largest value of Γ_+ ordinarily observed is about 20 μ coul./cm.^{2} This is the value found on extreme cathodic polarization of a mercury surface in 0.3 M aqueous sodium chloride, for instance (figure 9).   Under these conditions the cations will be expected to lie in a very compact layer, essentially a monolayer, although still formally a diffuse layer.   The average spacing of the ions of the double layer will then be about 9.0 A. from center to center.   This calculation includes an approximate correction for the ions normally present in that region from the solution and also takes into account the fact that there is a deficiency of anions amounting to about 3 μ coul./cm.^{2} in the double layer under these conditions.   For comparison, the average spacing of ions in a 1.0 M solution of a z-z valent electrolyte is about 10.6 A., only a little greater than the figure named above.   These considerations offer some justification for the assumption that the neglect of crowding effects does not invalidate the entire treatment.   At the same time, they indicate that the results to be obtained cannot be accepted without some reservation.

The assumption is made through the use of equation 31 that the potential is a function only of x.   This assumption has been questioned (88, p. 262) on the

[21] If any one of the ionic types present in the solution at an appreciable concentration has a large solvation energy this statement is valid, for the development requires that equation 33 be valid for every ionic type in the solution.

grounds that the electric charge density at a given value of x is by no means constant on a microscopic scale. On the other hand, if the potential be defined by means of equation 33, as suggested, then since the work w_i has a definite value for each value of x, the value of the corresponding potentials will suffer from no uncertainty on this account.

It has become evident in recent years (e.g., reference 27) that the values of ψ encountered in the diffuse double layer are a good deal smaller than had commonly been supposed, and that the same is true of $d\psi/dx$, the field strength. It is the latter consideration which makes it reasonable to use the dielectric constant of the solvent in the calculations which follow, while the former avoids a difficulty associated with the use of equations 32 and 33. Thus at a potential of 0.3 volt, once considered easily attainable in unimolar solutions, equations 32 and 33 lead to the result that the concentration of the more abundant ion, assumed univalent, is about 10^5 times greater than in the interior of the solution. This is manifestly impossible in all but very dilute solutions, and if such potentials were actually possible in unimolar solutions, then the theory would necessarily be very greatly in error. It may appear that image forces are neglected in the following treatment. This is not so, since the effects of the "image" charges in the metallic surface are taken account of implicitly by giving a non-zero value to ψ at one boundary (see reference 72). Combination of equations 32 and 33 gives:

$$n_i = n_{0i}e^{-z_i\epsilon\psi/kT} \tag{34}$$

The charge density at any point is the sum of the charge densities of the individual ionic types, or

$$\rho = \Sigma\, n_i z_i \epsilon = \Sigma\, n_{0i} z_i\, \epsilon e^{-z_i\epsilon\psi/kT} \tag{35}$$

Substituting this in equation 31 gives the fundamental differential equation:

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\epsilon}{DD_0} \Sigma\, n_{0i} z_i e^{-z_i\epsilon\psi/kT} \tag{36}$$

This can be integrated once by introducing the identity

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

which after substitution and integration gives:

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi kT}{DD_0} \Sigma\, n_{0i}\,(e^{-z_i\epsilon\psi/kT} - 1) \tag{37}$$

The constant of integration has been evaluated by noting that in the interior of the solution $d\psi/dx = 0$ and $\psi = 0$.

For many purposes it is not necessary to integrate this equation further. According to Gauss' law (which may here be regarded as an integrated form of equation 31)

$$d\psi/dx = 4\pi\eta^d/DD_0 \tag{38}$$

where

$$\eta^d = \int_x^\infty \rho \, dx \qquad (39)$$

According to equation 39 η^d is the *surface* charge density, the total charge in a column of liquid of unit cross section extending from the plane in question (the one to which $d\psi/dx$ refers) on into the body of the solution where $\psi = 0$. Equation 38 is only valid when the dielectric constant is constant from $x = x$ to $x = \infty$. Since this assumption was already made in integrating equation 36, no new approximations are involved in the use of equation 38. The superscript d in η^d refers to the *diffuse* double layer.

Combining equations 37 and 38 gives η^d as a function of ψ.

$$\eta^d = \pm \sqrt{\frac{DD_0 kT}{2\pi} \Sigma n_{0i} (e^{-z_i \epsilon \psi / kT} - 1)} \qquad (40)$$

Let

$$A = \frac{DD_0 kT n_{0i}}{2\pi}$$

For a *z-z* valent electrolyte equation 40 can be simplified to:

$$\eta^d = -A \sqrt{\exp(z\epsilon\psi/kT) + \exp(-z\epsilon\psi/kT) - 2} \qquad (41)$$

$$= -A[\exp(z\epsilon\psi/2kT) - \exp(-z\epsilon\psi/2kT)] \qquad (42)$$

$$= -2A \sinh z\epsilon\psi/2kT \qquad (43)$$

$$= -11.72 \sqrt{c_i} \sinh 19.46 \, z\psi \quad \mu \text{ coul./cm.}^2 \qquad (44)$$

The negative sign is chosen because η^d is positive when ψ is negative and *vice versa*. Equation 44 is evaluated for aqueous solutions at 25°C. c_i is the concentration in moles per liter and ψ is in volts.

Up to this point in the treatment of the kinetic theory of the electrical double layer the equations refer to values of ψ anywhere within the diffuse double layer. If one substitutes for ψ in equation 44 the potential of the *outer Helmholtz plane*, designated by ψ^o, one obtains the value of η^d for the *entire* diffuse double layer. From here on the symbol η^d will sometimes have this special meaning. It will be clear from the context which meaning is intended in any given case.

There are two kinds of capacity of the *diffuse* double layer to be considered, the differential capacity C^d and the integral capacity K^d. These are defined in terms of the potential of the *outer* Helmholtz plane, ψ^o, as follows:

$$K^d = -\eta^d/\psi^o \quad \text{and} \quad C^d = -d\eta^d/d\psi^o \qquad (45)$$

$$K^d = \frac{2A}{\psi^o} \sinh z\epsilon\psi^o/2kT \qquad (46)$$

$$C^d = \frac{z\epsilon A}{kT} \cosh z\epsilon\psi^o/2kT \qquad (47)$$

$$= 228.5 z\sqrt{c_i} \cosh 19.46 \, z\psi^o \quad \mu f/cm.^2 \text{ at } 25°C. \qquad (48)$$

At low values of ψ^o, the hyperbolic cosine is almost unity and both C^d and K^d (to which it is then equal) are constant, but this constancy does not extend to values of ψ^o comparable to those found in practice. Table 2 shows how K^d and C^d compare and also how they vary with ψ^o. Values in parentheses correspond to values of ψ^o beyond what can easily be achieved in practice. It will be noted that the maximum attainable value of ψ^o goes up with decreasing concentration, while the maximum value of C^d decreases slowly. Even in $10^{-3} M$ solution, however, this maximum value is very large ($\sim 300 \ \mu f/cm.^2$), which means, according to equations to be developed later (52 and 53), that the capacity of the diffuse double layer exerts little influence on the observed over-all capacity at large positive or negative polarizing potentials. This fact is in some respects fortunate, since it is exactly under these conditions that the postulates of the theory are

TABLE 2

Calculated differential and integral capacities, C^d and K^d, of the diffuse double layer for z-z valent electrolytes in aqueous solution at 25°C.

Capacities are in $\mu f/cm.^2$

CONCENTRA- TION		CHARGE × POTENTIAL OF OUTER HELMHOLTZ PLANE, $z\psi^o$						
		0.0 v	0.02 v	0.04 v	0.06 v	0.08 v	0.10 v	0.12 v
M								
1	K^d.......	228	235	252	285	(334)	(403)	(502)
	C^d........	228	246	302	403	(568)	(820)	(1200)
0.1	K^d.......	72.2	74.3	79.9	90.0	105	128	159
	C^d........	72.2	77.8	95.5	127	180	259	378
		0.12 v	0.14 v	0.16 v	0.18 v	0.20 v	0.22 v	0.24 v
0.01	K^d.......	50.2	63.9	82.9	109	(145)	(194)	(263)
	C^d........	120	176	259	383	(565)	(835)	(1233)
0.001	K^d.......	15.9	20.2	26.2	34.4	45.8	61.5	83.2
	C^d........	37.8	55.6	82.2	121	179	264	390

most unreliable. Even a very large error in the theory, percentagewise, will lead to only small errors in the expected properties of the double layer.

K^d and C^d are sometimes mistaken for the capacities of the whole double layer, which is quite erroneous because the potential ψ^o, to which the calculations refer, is very different from any potential one might think to use for a calculation of the over-all capacity. Moreover it is not true that $d\psi^o = dE$, which seems to be the assumption sometimes made.

The relation between the capacity of the whole double layer, in the absence of adsorbed ions, and the capacity of the *diffuse* double layer is found as follows: Let C^o and K^o be the differential and integral capacities of the region from the mercury surface to the outer Helmholtz plane. Then from electrostatic considerations alone (or as a definition of K^o)

$$- \eta^d = K^o(\psi^r - \psi^o) \tag{49}$$

Remembering that K° is not necessarily a constant, one writes also, as a definition of C°:

$$- \mathrm{d}\eta^d = C^\circ \mathrm{d}(\psi^r - \psi^\circ) \tag{50}$$

If ionic adsorption is assumed absent,[22] the charge on the diffuse double layer, η^d, is identical (except for sign) with the charge on the metallic surface, q, and ψ^r is identical with E. Therefore from equations 8 and 9:

$$- \eta^d = K\psi^r \text{ and } - \mathrm{d}\eta^d = C \, \mathrm{d}\psi^r \tag{51}$$

Combining equations 45, 49, 50, and 51 one has

$$K = K^\circ K^d/(K^\circ + K^d) \tag{52}$$

and

$$C = C^\circ C^d/(C^\circ + C^d) \tag{53}$$

Therefore the integral capacity of the whole double layer is equal to the capacity of two condensers of capacities K° and K^d connected in series; an analogous statement applies to the differential capacity.

The reasonableness of this result becomes apparent if one imagines two layers of charge placed at the outer Helmholtz plane, one equal to the charge on the mercury surface, the other of the same magnitude but of opposite sign. Such a system is readily seen to have a capacity given by equation 52 or 53.

For the theoretical evaluation of K and C, one needs to know K° and C°, which are not given by the theory and represent an as yet unsolved theoretical problem.

To judge from the appearance of the differential capacity curves (figure 5), fluorides show less ionic adsorption at ordinary potentials than any other salts.[23] This is presumed to be a consequence of the fact that the fluoride ion is hydrated (7) and that fluoride ion does not readily form covalent bonds with mercury. For the experimental evaluation of K° and C°, therefore, solutions of fluorides would seem to be particularly suitable. Concentrated solutions are more suitable than dilute, since K^d and C^d are then so large that their effect on K and C is minimized (equations 52 and 53). As a test of the theory so far developed the writer has calculated K° and C° from differential capacity data obtained with 1 M sodium fluoride, using the relations 52 and 53 together with equations 46 and 47 which had little effect. These values of K° and C° are shown in figure 11. It was assumed, then, that K° and C° depended only upon q (or η^d), and with the aid of this assumption and the equations named, the differential

[22] Adsorbed ions populate the inner Helmholtz plane. Hence the absence of ionic adsorption insures that all of the ionic charge is accounted for in the diffuse double layer. Since cation adsorption is assumed negligible in any case, the values of Γ_+ already found and plotted in figures 9 and 10 represent the contribution of the cations to η^d. This quantity will later be designated as η^d_+. The sum of η^d_+ and η^d_- (plotted in the figures) then gives η^d.

[23] This fact will be subject to experimental verification when more accurate capacity data become available.

capacity C of more dilute solutions of sodium fluoride was calculated. The results are presented in figures 12, 13, and 14.[24]

Although the agreement is not perfect, it is better than one would expect in view of the uncertain character of the theory of the diffuse double layer. Generally, the observed capacities on the cathodic side are lower than the calculated. The significance of this result cannot yet be stated with any assurance.

The minimum capacity at the electrocapillary maximum of dilute solutions arises from the greater average distance of the ions of the diffuse layer under these conditions. The maxima at small cathodic potentials[25] arise from the fact that
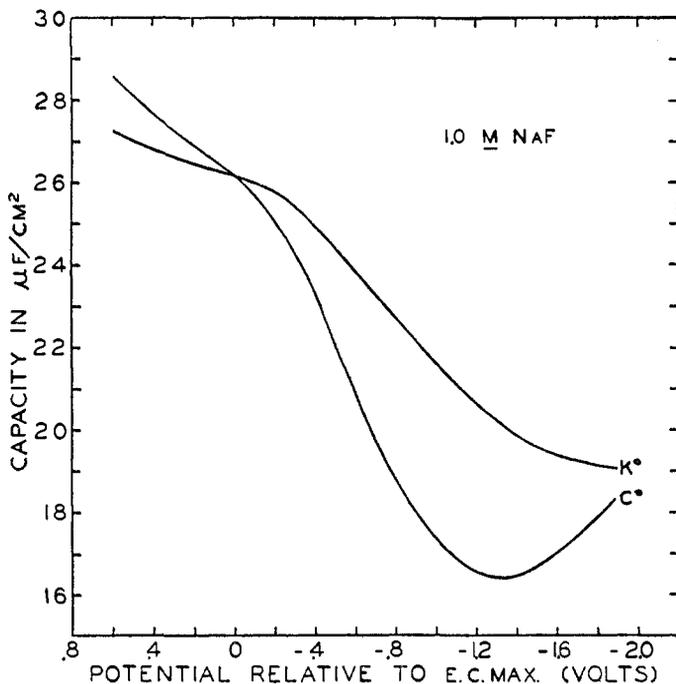
FIG. 11. Integral and differential capacities of the non-diffuse part of the double layer, calculated from data for 1 M aqueous sodium fluoride. This capacity is in series with the capacity of the diffuse double layer (table 2).

C^o is decreasing while C^d is increasing. The calculations are not extended to large values of positive polarization, because it was felt that the assumed absence of ion adsorption would not then be justified. The conclusion which we draw from these results is that the theory of the diffuse double layer is accurate enough to be useful in spite of the dubious character of the assumptions upon which it is based.

[24] The values here given are of a preliminary nature, since the experimental data were not of the best.

[25] Vorsina and Frumkin (88) do not observe the effect except in the presence of polyvalent cations (see footnote 15).
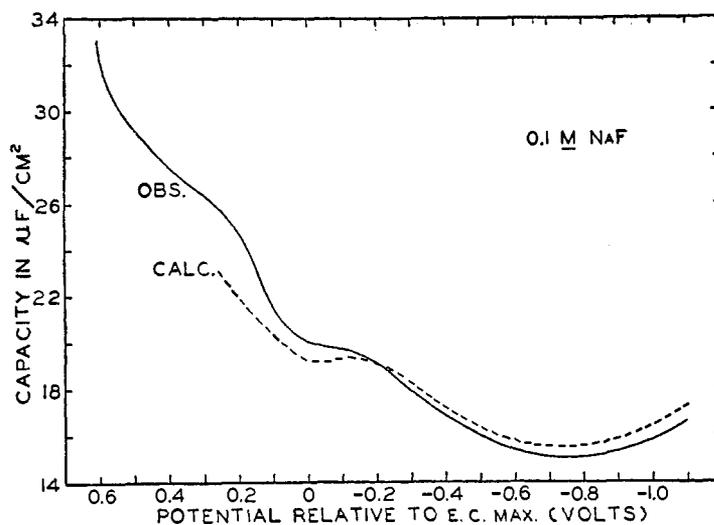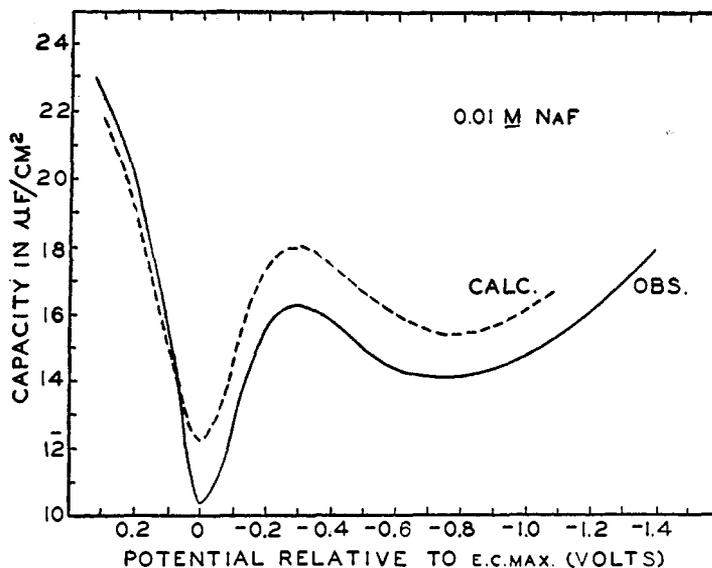
FIG. 12. Calculated and observed differential capacity of mercury in contact with 0.1 M sodium fluoride. $T = 25°C$. Experimental data obtained with 1.0 M sodium fluoride enter into the calculated values.

FIG. 13. Calculated and observed differential capacity of mercury in contact with 0.01 M sodium fluoride. $T = 25°C$. Experimental data obtained with 1.0 M sodium fluoride enter into these calculations.

The variation of $K°$ and $C°$ with E (figure 11) is probably due in part to the effect of crowding at the interface. Usually it is explained that anions, because of their greater polarizability, are more compressible, hence move closer to the interface, and therefore have a greater intrinsic capacity in a monolayer. Such

an effect would cause the values of K° and C° to vary as anions replace cations in the double layer. But this explanation is hardly applicable to the fluoride ion, whose polarizability is about the same as that of a typical cation. Moreover, it ignores the fact that the polarizability of the cation plays no rôle. Thus potassium and sodium ions give almost the same values of C° and K°, in spite of having very different polarizabilities. It is probably true, however, that large polarizability of anions makes for high specific adsorption, which in turn produces large over-all capacity C. This effect presumably accounts for the large increase of capacity always observed on strong positive polarization.
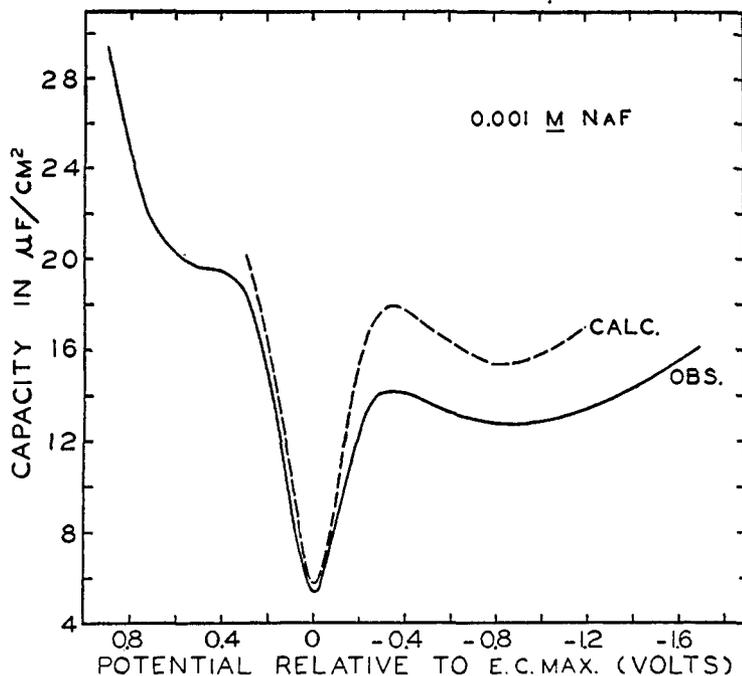

Fig. 14. Calculated and observed differential capacity of mercury in contact with 0.001 M sodium fluoride. $T = 25\,^\circ\mathrm{C}$. Experimental data obtained with 1.0 M sodium fluoride enter into these calculations.

Values of K° and C° depend very strikingly upon the anion present, even in the absence of specific adsorption. Thus the hydroxide ion, which is hydrated and not specifically adsorbed under negative polarization, differs greatly in its electrocapillary properties from the fluoride ion, which it would be expected to resemble. The investigation of problems such as this remains for the future.

It is now desired to find the manner in which ψ varies with x. Combining equations 43 and 38 gives:

$$dx = -\sqrt{\frac{DD_0}{32\pi kT n_{0i}}}\ \operatorname{csch}\frac{z\epsilon\psi}{2Kt}\ d\psi \tag{54}$$

It should be recalled that this equation is restricted, through use of equation 43, to symmetrical valence types. It can be integrated through the identity

$$\int \text{csch } \theta \, d\theta = \ln \tanh \left| \frac{\theta}{2} \right| + \text{const.} \tag{55}$$

whereupon

$$x - x_\infty = x' = -\sqrt{\frac{DD_0 kT}{8\pi n_{0i} \varepsilon^2}} \ln \tanh \left| \frac{z\epsilon\psi}{4kT} \right| \tag{56}$$

The constant of integration is x_∞. It is the value of x for which, if the differential equation were valid at all values of x, $\tanh z\epsilon\psi/4kT$ would become unity and ψ would become infinite. $x - x_\infty$ is therefore the distance of a point from this hypothetical plane of infinite potential, a distance designated by x'. Differences in x' are physically significant, although x' itself is not.

A new quantity, κ, is defined as

$$\kappa = \sqrt{\frac{8\pi \varepsilon^2 \epsilon^2 n_{0i}}{DD_0 kT}} \tag{57}$$

$$= 3.28 \times 10^7 \, z\sqrt{c_i} \quad \text{cm.}^{-1} \text{ at } 25°\text{C.}$$

and equation 56 takes the more compact form

$$x' = -\frac{1}{\kappa} \ln \tanh \left| \frac{z\epsilon\psi}{4kT} \right| \tag{58}$$

or

$$\psi = \pm \frac{4kT}{z\epsilon} \tanh^{-1} e^{-\kappa x'} \tag{59}$$

Equation 59 gives ψ as a function of x'. For small values of $e^{-\kappa x'}$ (large values of x'),

$$\tanh^{-1} \theta \sim \theta \qquad (\theta \ll 1) \tag{60}$$

and

$$\psi \sim \pm \frac{4kT}{z\epsilon} e^{-\kappa x'} \tag{61}$$

This result shows that at sufficiently large values of x', ψ is an exponential function of x' with a half-thickness of $\ln 2/\kappa$ or $2.11 \times 10^{-8}/z\sqrt{c_i}$ cm. at 25°C. For 1-1 electrolytes at unimolar concentration, the half-thickness is therefore of the order of magnitude of the ionic radius of the non-solvated ion. This small half-thickness points up the difficulty of defining potentials within the double layer. At lower ionic concentrations the half-thickness is greater, and the theory may be presumed to be more reliable.

The maximum value of the potential gradient may be calculated from equation 38. Numerical substitution shows that in aqueous solution at 25°C.

$$\frac{d\psi}{dx} = 0.1614 \times 10^6 \eta^d \text{ volts/cm.} \tag{62}$$

where η^d is expressed in μ coul./cm.^{2}

η^d seldom exceeds 20 μ coul./cm.^{2}, a value which corresponds to about 3×10^6 volts/cm. This is not as large a field strength as previous calculations (of much greater complexity) had indicated (72). It is not certain whether or not the dielectric constant of water is greatly different from its usual value at this field strength. Malsch (69, 70, 71; see also 15 and 17, p. 358) finds the dielectric constant of water to be down 0.7 per cent at 250,000 volts/cm., the percentage change being proportional to the square of the field strength. By extrapolation, this would lead one to expect a very low dielectric constant at 3×10^6 volts/cm., but such a long extrapolation is obviously not to be given much weight. The whole argument is a little pointless in any case, since the practice of treating the electrical double layer as a continuum is presumably unsound for high values of η^d. One carries out the calculations primarily to obtain orders of magnitude and to investigate the reasonableness of the mathematical treatment.

The calculated maximum field strength is almost independent of the concentration and of ionic charge, because the maximum value of η^d is found to be almost independent of these.

It is often desirable to calculate the contribution to the charge of the diffuse layer made by the cations or anions individually. We define these quantities, termed η^d_+ and η^d_-, through the equations:

$$\eta^d_+ = \int_x^\infty (\rho_+ - n_{0i} z\epsilon)\, dx \tag{63}$$

$$\eta^d_- = \int_x^\infty (\rho_- + n_{0i} z\epsilon)\, dx \tag{64}$$

ρ_+ and ρ_- are the charge densities of cations and anions, respectively, both of which are assumed to have valences of absolute value z. The sum of η^d_+ and η^d_- is η^d.

$$\eta^d_+ + \eta^d_- = \int_x^\infty (\rho_+ + \rho_-)\, dx = \int_x^\infty \rho\, dx = \eta^d \tag{65}$$

Equation 35 gives for ρ_+

$$\rho_+ = n_{0i} z\epsilon e^{-\Psi} \tag{66}$$

where $\Psi = z\epsilon\psi/kT$. From equation 63

$$\eta^d_+ = n_{0i} z\epsilon \int (e^{-\Psi} - 1)\, dx \tag{67}$$

In this equation and in those which immediately follow, the limits of integration are from $x = x$ to $x = \infty$. Taking the square root of the square of the quantity in parentheses gives:

$$\eta^d_+ = n_{0i} z\epsilon \int \sqrt{e^{-2\Psi} - 2e^{-\Psi} + 1}\, dx \tag{68}$$

$$= n_{0i} z\epsilon \int \sqrt{(e^{\Psi} + e^{-\Psi} - 2)e^{-\Psi}}\, dx \tag{69}$$

Introducing equations 41 and 38 in succession gives:

$$\eta_+^d = z\epsilon \int \eta^d \sqrt{\frac{2\pi n_{0i}}{DD_0 kT} e^{-\Psi}} \, dx \qquad (70)$$

$$= z\epsilon \int \sqrt{\frac{DD_0 n_{0i}}{8\pi kT} e^{-\Psi}} \, d\psi \qquad (71)$$

This can be integrated to give:

$$\eta_+^d = A(e^{-\Psi/2} - 1) \qquad (72)$$

Similarly one has that

$$\eta_-^d = -A(e^{\Psi/2} - 1) \qquad (73)$$

The signs in equations 72 and 73 are chosen as they were for equation 41. By division one obtains the ratio of η_+^d to η_-^d, a ratio which depends only upon Ψ.

$$\eta_+^d/\eta_-^d = -\,(e^{-\Psi/2} - 1)/(e^{\Psi/2} - 1) \qquad (74)$$

For low values of ψ, $\eta_+^d/\eta_-^d \sim -1$. For large values of $|\psi|$, η_+^d or $-\eta_-^d$ increased indefinitely, whereas the other quantity tends to the limit

$$\lim \text{ of } \eta_\pm^d = A \qquad (75)$$

$$= 5.86\sqrt{c_i} \ \mu \text{ coul./cm.}^2 \text{ at } 25°C.$$

For a 0.3 M solution of z-z valent electrolyte, this gives as a limit of η_-^d the value 3.2 μ coul./cm.^{2} The observed limiting value of Γ_- in figure 9 is identical with this result, although the agreement is doubtless fortuitous. The largest observed value of Γ_- in unimolar sodium chloride is about 5.5 μ coul./cm.^{2}, which may be compared with 5.86 μ coul./cm.^{2} predicted by equation 75. This agreement lends some support to the kinetic theory of the diffuse double layer, although it is probable that these results make the theory look better than it really is.

Γ_- is composed of two parts representing the charge attributable to the adsorption of anions, η_-^i, and the charge attributable to repelled anions η_-^d. Then

$$z_-F\Gamma_- = \eta_-^i + \eta_-^d \qquad (76)$$

η_-^i will always be negative or zero, and η_-^d will nearly always be positive or zero. Equation 72 can be used to evaluate Ψ for a given experimental value of η_+^d (taken to be identical with Γ_+). This value of Ψ can be used in equation 73 to evaluate the corresponding value of η_-^d. Since Γ_- is also known experimentally, one can evaluate η_-^i by equation 76. This procedure has been carried out for the evaluation of η_-^i represented in figures 9 and 10. There is relatively little uncertainty in this procedure, because η_-^d is small at potentials where η_-^i is appreciably different from zero.

Rice (81) has considered the nature of the diffuse double layer of electrons to be expected within the metallic phase itself. The treatment is similar to that

here outlined for ions. By using a low value for the dielectric constant of mercury, Rice obtained values for the capacity of the diffuse double layer in mercury comparable to those observed for the whole double layer. It is more usual to regard the dielectric constant of an electronic conductor as sensibly infinite, however, in which case the calculated capacity of the diffuse double layer in the metallic phase is also sensibly infinite, and its capacity, being in series with the rest of the double layer, exerts no effect. This amounts to saying that in classical electrostatics no appreciable part of the potential drop occurs within the metallic phase itself. If it were otherwise, in fact, the nature and concentration of the electrolyte would not be expected to exert so decisive an influence on the properties of the double layer.

If one assumes (erroneously) that ψ^o and ψ^i are identical, it becomes possible to calculate Γ_{SALT}^{MAX} (or η_+^d, which is the same thing at the electrocapillary maximum) from the theory of the diffuse double layer. The results of the calculation are in violent disagreement with experiment and also with any reasonable conception of the double layer. As an example, consider 0.1 M potassium iodide at the electrocapillary maximum. ψ^i, which is identical with ψ^r at the electrocapillary maximum, is observed to be -0.24 volt (table 1). If one assumes that this is also the value of ψ^o, then equation 72 gives for η_+^d a value of 192 μ coul./cm.^{2} (an impossible result). This is to be compared with the experimental value of 9.1 μ coul./cm.^{2} At higher concentrations the disagreement is even worse and the calculated value even more impossible (4300 μ coul./cm.^{2} at 1 M). These results illustrate the necessity of distinguishing between ψ^i and ψ^o, and also illustrate that ψ^o must be the smaller of the two absolute magnitudes. It is these considerations which have led us to assume throughout the non-thermodynamic parts of this paper that the diffuse double layer does not extend to the inner Helmholtz plane and that low-molecular-weight cations, which are not specifically adsorbed, do not populate that plane.

The dotted line in figure 8 gives the values of Γ_{SALT}^{MAX} calculated in this manner for unimolar solutions. The disagreement reflects the fundamental nature of the error implicit in the assumption that $\psi^o = \psi^i$.

VII. THE THEORY OF THE COMPACT DOUBLE LAYER (8, 85, 87, 92)

In Section VI ionic adsorption has been assumed absent, meaning that no ions come closer to the interface than the outer Helmholtz plane. This assumption is probably satisfied to a good approximation on negative polarization of mercury in solutions of capillary-inactive electrolytes and even in solutions of capillary-active electrolytes when the active substance is an anion and when the polarization is great enough to repel these anions from the interface. Under most other conditions it is to be expected that an adsorption of ions occurs and that these adsorbed ions lie closer to the interface than unadsorbed ions. The layer of adsorbed ions is called the compact double layer or, better, the compact *part* of the double layer. The double layer is now a triple layer, but it is not generally so called.

Stern (85) worked out a theory of the compact part of the double layer based

upon the Boltzmann distribution law. In spite of some defects, that theory still has much to recommend it. The central part of the theory will be here presented together with an indication of its limitations and the manner in which they may be removed.

Stern did not distinguish between what we have called the inner and outer Helmholtz layers, although he mentioned the possibility that such a distinction might be necessary. In the discussion which follows, this distinction will be made from the first.

Following Stern, let n^i be the number of adsorbed ions per square centimeter, n_{0i} the number of the same type of ion per cubic centimeter of solution, z^i the maximum number of ions that can be on 1 sq. cm. of surface, and z_{0i} the maximum number of ions for which there is space in 1 cc. of solution. If the course of a single ion is followed for some time, it will be found for a fraction of the time u^i at the interface and for a fraction of time u_{0i} in the solution. If no work were required to move an ion from the interior of the solution to a place at the inner Helmholtz plane, u^i/u_{0i} would be the ratio of the number of free places on the surface to those in the solution.

$$u^i/u_{0i} = (z^i - n^i)/(z_{0i} - n_{0i}) \tag{77}$$

If one considers not one ion but all the ions of a given type, it is evident that

$$u^i/u_{0i} = n^i/n_{0i} \tag{78}$$

If, finally, the amount of work w_i needed to move an ion from the interior of the solution to a free place at the interface is not zero, the right-hand term of equation 77 must be multiplied by the Boltzmann factor so that, with equation 78:

$$n^i/n_{0i} = (z^i - n^i)/(z_{0i} - n_{0i})e^{-w_i/kT} \tag{79}$$

Except in very concentrated solutions, n_{0i} is negligible relative to z_{0i}. With this simplification, equation 79 can be solved for n^i to give:

$$n^i = z^i \left/ \left(1 + \frac{z_{0i}}{n_{0i}} e^{w_i/kT} \right) \right. \tag{80}$$

Stern identifies n_{0i}/z_{0i} with the mole fraction, which is admittedly only an approximation at best, and he also changes the number 1 in the numerator to 2. This latter change is made in order that n^i shall reach the limit $z^i/2$ when w_i has large negative values, it being assumed that nearly equal numbers of cations and anions will be adsorbed, in which case the monolayer cannot be more than half filled with ions of a given type. The logic here is not compelling, particularly if one distinguishes between the inner and outer Helmholtz planes, in which case ions of only a single type need populate the inner Helmholtz plane.

Experimentally it is found that the compact part of the double layer is not usually near to a complete monolayer. Thus a charge of 30 μ coul./cm.[2] of chloride ions is about as large an adsorbed charge as one can conveniently deal with experimentally, and represents about 25 per cent of a complete monolayer.

Under these circumstances the unity in the denominator of equation 80 is small compared to $(z_{0i}/n_{0i})e^{w_i/kT}$, and one may write the equation in the form:

$$n^i = \frac{z^i}{z_{0i}} n_{0i} e^{-w_i/kT} \tag{81}$$

$$= 2r n_{0i} e^{-w_i/kT} \tag{82}$$

In equation 82, r is the radius of the non-solvated ion. The quantity z^i/z_{0i} has been set equal to $2r$, because the thickness of the region in question is to the thickness of a centimeter cube as $2r$ is to 1.

Equation 82 could have been derived directly by a consideration of the ratio of the probability that an ion would be in the solution to the probability that it would be in the interface. The numerical coefficient in equation 82 would then be 1 or 2, depending upon whether the mean free path of the ions is large or small compared to r. If the mean free path is short, spatial considerations are all that matter and the coefficient is 2; if the mean free path is long, the fact that ions can enter from only one side reduces the number of ions at the interface by one-half.

The work w_i may be divided up formally into a chemical and an electrostatic work term:

$$w_i = z_-\epsilon(\psi^i - \phi^i_-) \tag{83}$$

In this equation ψ^i is the electrical potential of the inner Helmholtz plane as before, and ϕ^i_- is an adsorption potential of the anions. It is only under special circumstances that this division has any physical significance, as explained below. Equation 83 differs slightly in form from Stern's equation because we find it more convenient to express ϕ^i_- in units of electrical potential, but the physical meaning is the same. Stern considered the possibility that both positive and negative ions might be adsorbed simultaneously, but since this case is experimentally rare and theoretically very complicated, we prefer to assume that only one type of ion is adsorbed. For cation adsorption equation 83 would be replaced by

$$w_i = z_+\epsilon(\psi^i + \phi^i_+) \tag{83'}$$

There is no general experimentally unambiguous procedure for dividing up w_i in this manner. The potential of the inner Helmholtz plane, ψ^i, may be calculated from equation 28 if one assumes that K^i is a constant. Although K^i does appear to be nearly constant under the conditions for which it can be evaluated (the Γ_+^{MIN}-potential), it is only on this assumption that ψ^i can be evaluated in general. At the electrocapillary maximum, however, ψ^i is known regardless of K^i (it is equal to ψ^r), and one can say in that case at least that ϕ^i is defined unambiguously by equation 83 or 83'. The equations given in this section, together with equations 43 and 28 and the identity

$$\eta = -q = \eta^i + \eta^d \tag{84}$$

constitute the essential parts of the Stern theory.

There are not sufficient equations in the Stern theory as here outlined to permit the calculation of the properties of the double layer without recourse to experimental data. The most significant use of the theory which can be made at present is the calculation of ϕ^i_- from equations 82 and 83 taken together with experimental data like that shown in figure 9. Values of ϕ^i_- obtained in this way are plotted in figure 15. The principal result of this calculation is the fact that ϕ^i_- varies with q. As the mercury becomes more positive, the chemical binding energy becomes greater. As already explained, this result is attributable
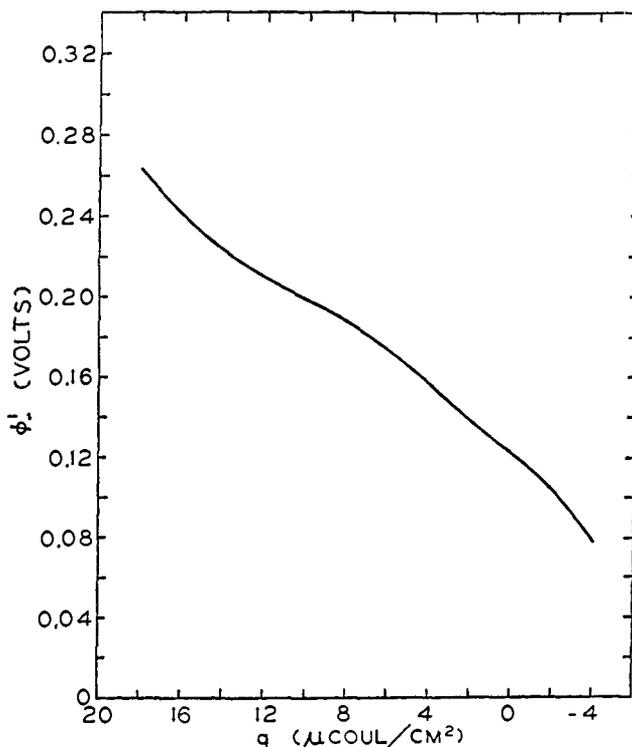
FIG. 15. Specific absorption potential, ϕ^i_-, for chloride ion on mercury as a function of q, the electronic charge on the metallic surface. Computed from data presented in figure 9.

to the increased stability of the electron-pair in a covalent bond in the presence of a positive charge.

In the original Stern theory it was implied that in the absence of ionic adsorption, ϕ^i_+ and ϕ^i_- were zero. This is not quite right in terms of our present concepts, for the work required to move an ion from the interior of the solution to a place on the interface would not then be zero but would be positive, owing to the work needed to displace the solvent sheath on the side of the interface. As a result of this, ϕ^i_- is positive and η^i would be nearly zero when ψ^i is zero, a result which differs from the prediction of the original Stern theory but which agrees

with the physical picture we have here adopted, i.e., the inner Helmholtz layer should not be populated appreciably in the absence of specific adsorption.

Although equation 82 was derived upon the assumption that the monolayer of adsorbed ions was far from complete, it is possible to interpret w_i in such a manner that the equation retains its validity at all ion densities. If w_i is regarded not merely as the energy needed to move the ion into a previously vacant space but as the energy needed to make a vacancy and to move the ion into it, it will be evident that n^i cannot exceed a monolayer even according to equation 82. In this sense equation 82 is no less reliable than equation 80.

Equation 82 may be combined with equation 83 and rewritten in terms of charge to make it more suitable for calculation.

$$\eta^i = 2z_- \epsilon r n_{0i} \exp\left\{-z_- \epsilon(\psi^i - \phi_-^i)/kT\right\} \tag{85}$$

$$= 3.86 c_i z_- \exp\left\{-38.92 z_-(\psi^i - \phi_-^i)\right\} \mu \text{ coul./cm.}^2 \text{ at } 25°C. \text{ if } r = 2 \text{ A.} \tag{86}$$

In these equations, as in those of preceding sections, z_- is the valence number, including sign, of the anion which is adsorbed. Cation adsorption is assumed absent.

We conclude this section with figures designed to illustrate the structure of the electrical double layer.

Figure 16 shows the potentials within the double layer calculated from equations 28, 43, 59, and 72, together with the experimental data represented in figure 9. A distance of 3 A. from the interface has been assumed in plotting the potential of the outer Helmholtz plane, but this number does not enter into the calculations. It is only an accident that the Γ_+^{min}-potential coincides with the potential of the electrocapillary maximum in this case. Perhaps the most significant feature of figure 16 is the fact that the potential of the inner Helmholtz plane reaches a maximum, a result which might have been anticipated from the fact that Γ_+ reaches a minimum.

Figures 17–19 show schematic representations of the electrical double layer under various conditions of polarization. Large circles represent an excess of an ion type assumed to be solvated. Dotted circles represent a deficiency of an ion type. Small circles represent an excess of a non-solvated ion; minus or plus signs not surrounded by circles represent electrons or a deficiency of electrons. The manner in which the potential varies with distance is indicated in the box in each figure. The magnitude of ψ^o is exaggerated in order to bring out the character of the variation of ψ with x in the diffuse double layer.

VIII. POTENTIAL DIFFERENCES BETWEEN DISSIMILAR PHASES (3, 47, 48, 49)

Progress in the study of the electrical double layer calls for a very clear understanding of the term "electrical potential difference" as applied to dissimilar media. In the discussion here given the author has refrained from introducing any new concepts. There is not much room for real disagreement in this subject nowadays, except in regard to terminology and conventions. It is hoped that

the treatment here given will make it possible for future authors to discuss the subject accurately without prolonged explanations.
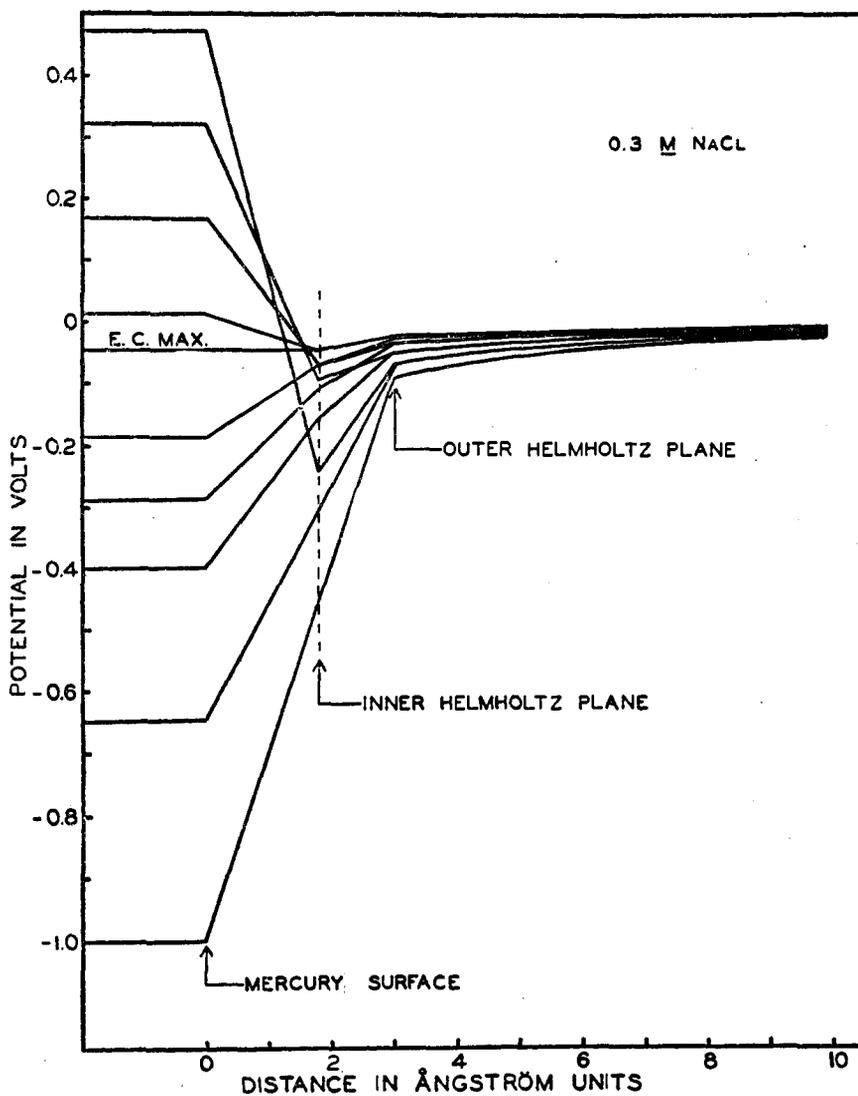

FIG. 16. Potentials in the electrical double layer between mercury and aqueous 0.3 M sodium chloride solutions at 25°C. at various polarizing potentials. Values calculated from data in figure 9. The potentials are "rational" in the sense defined in the text. Note that the potential of the inner Helmholtz plane reaches a maximum as the polarizing potential is varied from one extreme to the other.

Guggenheim in 1929 wrote a classic paper (47) in which it was demonstrated that absolute or "true" potential differences between dissimilar phases are unmeasurable because they are not defined. Moreover, it was pointed out that

attempts to define an absolute potential difference are unnecessary, since it is possible to describe all actual experimental observations in terms of potential differences of the types already known. In a subsequent paper (48) Guggenheim allowed that it was possible to define new types of potential difference which might prove to be convenient for some purposes, but the important point remained that there was no necessity for doing so.
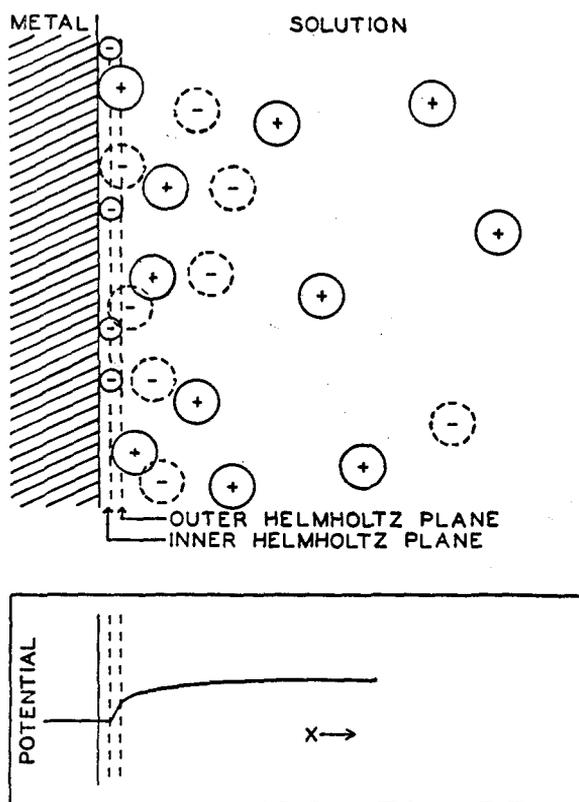

FIG. 17. Schematic representation of the electrical double layer at the potential of the electrocapillary maximum. Small circles represent adsorbed ions. Large circles represent solvated ions. Dotted circles represent "ghosts", ions which would be present if the double layer were not there.

In a third, seemingly little-known paper (49), Guggenheim suggested a definition of the activity coefficient of individual ionic species. The definition also serves to define the potential difference between dissimilar salt solutions in contact, or between two concentrations of the same salt solution. There was no contention that the suggested definition gave values of an "absolute" potential difference except with infinitely dilute solutions, where the quantity was defined anyway. The only advantage claimed was one of convenience and, all important, the advantage of not conflicting in any way with established thermodynamic

usage. The basis of the definition was an assumption that the ratio of the individual ionic activity coefficients in a salt solution is given by the Debye–Hückel limiting law. This much can be assumed without thermodynamic contradiction. Its chief virtue is that it makes it possible to talk about individual ionic activities and liquid-junction potentials without ambiguity. There is also a certain advantage in that it makes it possible to calculate liquid-junction potentials with less confusion of thought than had been the case formerly. If the idea is firmly
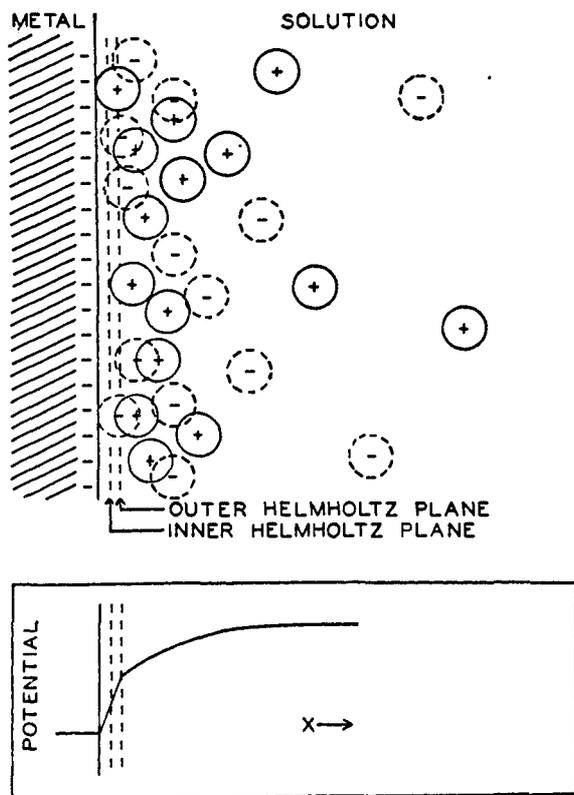
FIG. 18. Schematic representation of the electrical double layer with negative polarization. Note absence of adsorbed ions and increased concentration of positive ions as compared with figure 17. The concentration of "ghosts" is also increased.

grasped that the potential differences in question are not "absolute", there can be a great gain in clarity of exposition and of thought in Guggenheim's proposal.

Where liquid-junction potentials have been mentioned or used in the preceding parts of this review, Guggenheim's definition has been assumed.

The potential difference between immiscible phases is not defined by Guggenheim's assumption. Again it is convenient to have a working definition, provided one can keep clear of any suspicion of having proposed a definition of absolute potential difference. The rational potential difference, ψ^r, defined in Section III, is an example of a useful working definition.

The potential difference between two dissimilar isotropic metals in contact has been frequently misunderstood. There are two kinds of potential difference between dissimilar metals in contact which are measurable, the Volta or contact potential difference and what may be called the electron potential difference. The former can be measured only with very clean surfaces; it is the work required to move unit electric charge from the interior of a macroscopic cavity in one metal to the interior of a macroscopic cavity in the other. The walls of the cavities are assumed to be clean, in which case the work involved is a definite quantity which can be measured in a variety of ways (4). It is, for instance, the difference
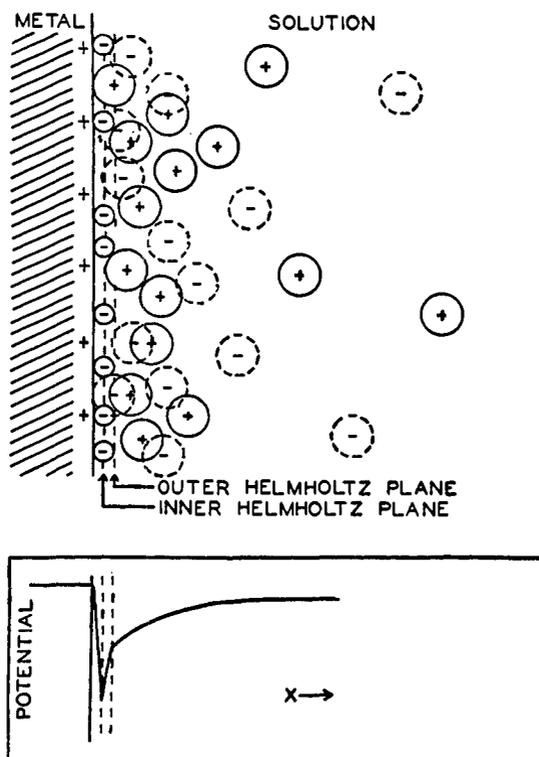

FIG. 19. Schematic representation of the electrical double layer with positive polarization. Note presence of adsorbed anions. Diffuse double layer is identical with that depicted in figure 18.

in the work functions of the metals, or minus the potential difference which must be put in series with the wire connecting the two metals in order to permit their clean surfaces to be moved toward or away from one another without a flow of electric current through the connecting wire. A constant temperature throughout the system is assumed.

The Volta potential difference between metals in contact is not affected by contamination of the metals at the point of junction, because any number of electronic conductors can be inserted between two metals without altering the electronic equilibrium of the metals. Thus as long as the contact is electronic

(not ionic), the Volta potential difference does not depend upon the cleanliness of the junction. The surfaces at which the *measurement* is made, however, must be clean.

The Volta potential difference is similar in magnitude to the E.M.F. established when the two metals are made the electrodes in a galvanic cell containing solutions of their salts. This is because the electron affinity of the uncharged metal atoms is a major controlling factor in both. Zinc has a lower electron affinity than copper; hence zinc in contact with copper loses electrons until it becomes positively charged, the copper becoming negatively charged. Because of its lesser electron affinity, zinc lies higher in the electromotive series than copper,[26] and its behavior in galvanic cells therefore depends upon one of the same factors as does its Volta potential.

It was supposed at one time that the similarity of Volta potentials and electrode potentials indicated the presence of a film of moisture between metals in contact. Today such a supposition appears unthinkable on any grounds, not the least of which is that the sign of the potential difference is wrong.

The *electron* potential difference between two metals will be defined as the work required to transfer an electron (not an idealized charge) from one phase to the other. If the metals concerned are in contact and at uniform temperature, this work will evidently be zero.[27] The electron potential difference is what is measured by all voltmeters, potentiometers, and the like, including electrometers.

If the ends of a uniform bar of metal are maintained at different temperatures, the electron potential at the two ends is not the same, as is evidenced by the existence of the thermoelectric effect. It is customary to explain this effect as arising from differences in the contact potentials at the two junction temperatures, but this explanation is misleading since it ignores the facts (a) that contact (i.e., cavity) potential differences must also be presumed to exist between two parts of a uniform bar of metal at different temperatures and (b) that what is measured is not a contact potential but an electron potential difference. Although it is undoubtedly true that contact potentials do depend upon temperature, the connection between this fact and the thermoelectric effect is remote. It is much more satisfactory to explain it as the difference in the electron potential differences generated by dissimilar metals maintained at the same terminal temperatures.

Since contact (Volta) potentials are a measure of the work required to move a unit charge from a point in the vicinity of one surface to a point in the vicinity of another, it is to be expected that all methods of measuring Volta potentials should be extremely sensitive to changes in the cleanliness or character of the surfaces in question, as is found to be the case. This fact is sometimes useful in deciding what kind of potential a given experiment measures. As mentioned above, however, the contact potential of electronic conductors does not of itself depend upon the cleanliness of the surface. It is only in the *measurement* of contact potentials that surface cleanliness becomes important.

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[26] The position of a metal in the electromotive series also depends upon the hydration energy of the ion formed, but this effect is not dominant.

[27] This statement assumed no continuous current flow from one phase to the other.

The potential of the electrocapillary maximum, $-\mathcal{E}^{MAX}$, observed with dilute amalgams or with metals other than mercury leads to interesting results. Thus an amalgam containing 0.004 per cent of cadmium gives with normal potassium chloride a value of 0.625 volt (12) instead of the 0.56 volt observed with pure mercury. Somewhat similar results are obtained with thallium amalgams in sodium sulfate solutions (30), and it is noteworthy that metallic gallium gives a value of about 0.9 volt in potassium chloride solutions (29). These variations can be accounted for in part by specific adsorption of anions and in part, perhaps, by reorientation of solvent molecules, but it is also true that the contact potential which arises when the mercury in the reference electrode is joined to the other metal composing the polarized electrode shifts the potential of the electrocapillary maximum by an equal amount (26).

There is a long-standing argument concerning the question of where the potential difference of a galvanic cell arises. The question can be answered correctly once it is accurately stated. To the question—Where does the electron potential difference arise?—there can be but one answer. It arises wholly within the cell. Since the electron potential of the solution is undefined, one cannot be more explicit. If one asks instead—Where does the cavity potential difference (the electrostatic potential difference) arise?—the answer is likewise unambiguous. It arises partly at the electrodes and partly at the junction between the metals which compose the electrodes. Since electromotive force is a form of electron potential difference, no part of the E.M.F. of a cell can be said to arise from the contact potential of the metallic electrodes.

Cavity potential differences between mercury and potassium chloride solutions have been measured by Klein and Lange (57), the junction between the two phases being made by means of a calomel electrode. In this way it was hoped to measure a "true" potential difference of the calomel electrode, but it is now evident that what was measured was only a little different from the potential of the electrocapillary maximum. The effects of the specific adsorption of anions on mercury were surely eliminated, but not the effects of different ionic hydration energies, which build up what are known as surface potentials (*vide infra*). Moreover, and even more serious, the method does not eliminate the effects of water orientation on the mercury, for water vapor was of necessity in contact with the mercury. Even if all of these effects could have been eliminated, no "true" potential difference would have been measured, since one knows nothing about the potential gradients which may exist at a clean surface of mercury. This all amounts to saying again that "true" potential differences cannot be measured because they are not defined.

The "true" potential difference between a metal and a solution has sometimes been defined as the work required to move an ion of the metal from the interior of the metal to the interior of the solution. It is not reasonable to call this the "true" potential difference, for at the very least one would have to correct for the hydration energy of the ion in solution and the "solvent" effect of the metal on the metallic ion. A metal in equilibrium with a solution of one of its salts reaches a state such that no work is needed to move the ion of the metal from one

phase to the other. But no one would suggest that the true potential difference in all such cases is zero.

Cavity potential differences have been measured for dissimilar solutions joined by salt bridges (24, 32). These measurements yield "surface potentials", a good approximation of the work required to move a test ion out through one interface and back through another. The second solution is so dilute that ionic accumulation at its interface may be ignored, and since the solvent effects on the test ion presumably cancel, what one has is an approximate measure of the work done in moving an idealized electric charge through any potential gradients set up by the presence of ions in the air–solution double layer of the more concentrated solution. It is found that the hydration energies of the ions are the controlling factor. Those ions (generally anions) which are least readily hydrated seek positions in the surface, making the surface negative to the interior of the solution. The order of the effectiveness of the anions in this regard is similar to that of the Hofmeister series, being $CNS^- > ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > OH^- > F^-$ (32).

Much larger surface potentials are observed with surface layers of neutral but polar molecules (1, p. 133). These layers of molecules also occur at the electrical double layer between mercury and salt solutions containing small amounts of sparingly soluble organic substances (31, 34, 35, 37, 38). Although these layers are most often monolayers, the experimental evidence of Gorodetskaya and Frumkin (31, 35) indicates that polymolecular layers may form when the surface layers are compressed. If the potential of the mercury is made strongly positive or strongly negative, the attraction of the surface for ions exceeds its attraction for the polar molecules, and the latter are displaced. This displacement phenomenon sometimes occurs over a small range of potentials and gives rise to sudden changes in the charge of the double layer. This leads to large values of the differential capacity and more or less abrupt changes of slope of the electrocapillary curves. This behavior is exhibited by solutions of heptyl alcohol in an inert electrolyte, for instance, as is shown by figures 20 and 21. The capacity is almost uninfluenced by the frequency of the current used in the measurement, but the apparent electrical resistance of the adsorbed layer increases with decreasing frequency. This phenomenon has been studied and explained by the author as arising from the fact that the true resistance of the adsorbed layer is not the directly measured resistance minus the resistance of the solution because the resistance of the solution is in series with the capacity of the double layer, whereas the resistance of the adsorbed layer is in parallel with its capacity (43).

IX. TIME LAG AND POLARIZATION RESISTANCE AT AN IDEAL POLARIZED ELECTRODE

It is frequently observed that the establishment of complete equilibrium at an interface may be a slow process requiring times of the order of seconds or more. Thus it is well known that the surface tension of some types of solutions changes with time after the formation of a fresh surface (5, 18). The E.M.F. of galvanic cells frequently reaches equilibrium only slowly, and the attainment of stable electrokinetic potentials may be a matter of days (95). In the two latter cases

a slow step can be postulated which does not demand that the actual orientation of ions in the double layer be slow. Thus the slow approach to a state of equilibrium in a calomel cell is undoubtedly to be attributed to the fact that a solid substance, mercurous chloride, is involved in the reaction by which equilibrium is attained:
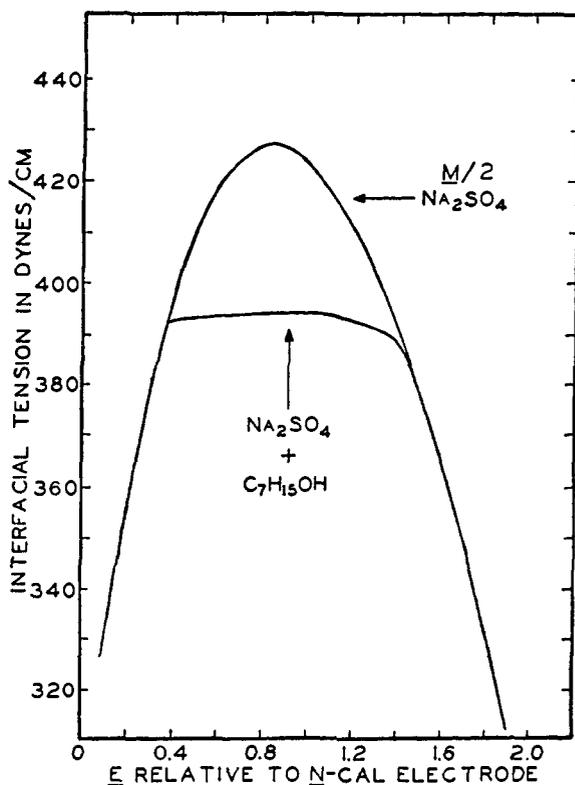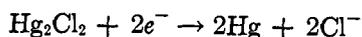
$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$

Fig. 20. Interfacial tension of mercury–aqueous sodium sulfate solutions with and without the addition of n-heptyl alcohol. Data by Gouy (38).

This reaction can proceed only when a mercurous chloride molecule is lying next to the mercury surface with the mercury ion favorably situated to receive the charge. This reaction does not necessarily take place instantaneously and in the amounts required by Faraday's law when a small current is passed through a calomel cell, since the capacity of the double layer is sufficient to supply a large charge with only a small change of potential. The above reaction then slowly restores the system to its equilibrium potential.

The slow attainment of equilibrium in the setting up of certain electrokinetic potentials is most probably associated with a slow change in the character of the surface (95). The slow change of surface tension exhibited by certain types of

solutions is not yet satisfactorily explained, but is probably not attributable to a time lag in the formation of the double layer, once the necessary particles arrive at the surface.

An upper limit may be set to the time required to establish *ionic* equilibrium in the double layer at a mercury surface. According to measurements made by the author (43), a 1 sq. cm. mercury surface in a solution of 1 M sodium
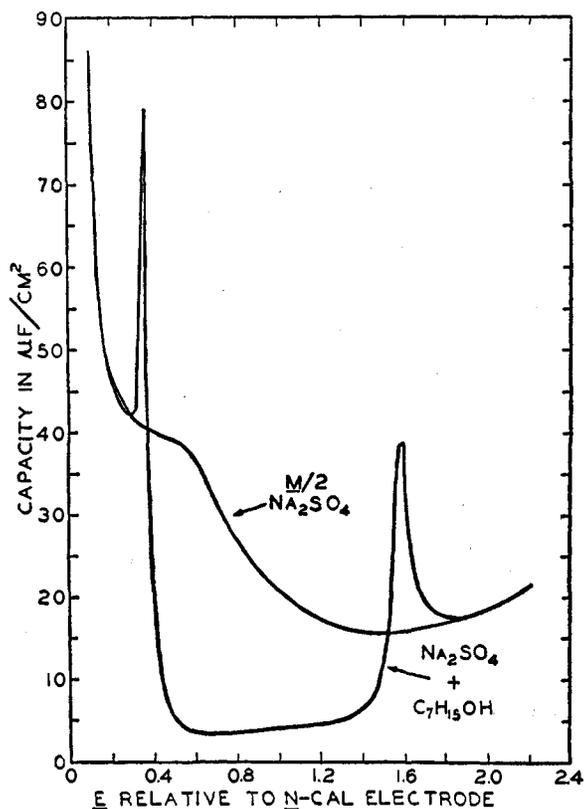

Fig. 21. Differential capacity of double layer between mercury and aqueous sodium sulfate solution with and without the addition of n-heptyl alcohol. The peaks do not occur exactly at the potentials of the breaks in the electrocapillary curve (figure 20), presumably because the temperature (and therefore the solubility of heptyl alcohol) was different in the two experiments.

chloride exhibits an apparent resistance, commonly termed a polarization resistance, not in excess of 0.02 ohm and possibly considerably less. The capacity of the interface under the conditions of this experiment was about 18 $\mu f/cm.^2$ The polarization resistance is in series with the capacity. The time constant of such a combination is RC or 3.6×10^{-7} sec. Thus the time required for virtually complete establishment of ionic equilibrium within the double layer is a microsecond or less. In practice the attainment of equilibrium will be delayed by the

finite resistance of the solution, of course, but that is a separate matter. The time constant of such delay is again given by RC, where R is now the total resistance between the electrodes and C is the series capacity of the electrodes.

The polarization resistance exhibited by other types of electrodes is associated with the occurrence of chemical reactions at the electrodes (43, 56, 90, 91). These reactions cause changes of concentration of the reactants at the interface, and because of the diffusion of these reactants or because the reactions are not rapidly reversible, the back E.M.F. does not remain in quadrature with the imposed alternating potential (82). A back E.M.F. not in quadrature with the imposed E.M.F. manifests itself as an electrical resistance in series (or in parallel) with the electrode. It has been shown both practically and theoretically (43, 44) that the changes of concentration which occur at an ideal polarized electrode give rise to diffusion effects too small to result in measurable polarization resistance. The electrical double layer therefore behaves very nearly like a pure capacitance.

X. CONCLUSION

A complete discussion of the applications of the theory of the electrical double layer would involve a discussion of electrokinetic phenomena, of the stability of colloids, of the conductance and chemical potentials of electrolytic solutions, of the behavior of clays and carbon black in suspension, of membrane equilibria, of hydrogen overvoltage, of the theory of corrosion phenomena, and of other phenomena not usually thought of as related to the double layer. Since the author has not had first-hand experience with most of these subjects, and since in any case excellent reviews of most of them are already available, they are omitted from this review. There are a few points upon which additional comments by the author may not be out of place, however.

At the surface of a non-metallic particle in a salt solution there exists an electrical double layer no different in principle from those which we have discussed above. It is convenient to regard the *neutral* surface of the particle as the counterpart of the metallic surface. Adsorbed ions then produce a charge on the particle, but since this is not an electronic charge, the particle is analogous to the metallic surface *at its electrocapillary maximum*. Beyond this layer of adsorbed ions lies the diffuse double layer, whose maximum potential ψ° is presumably to be regarded as the ζ-potential. At the isoelectric point this ζ-potential is zero, corresponding to a state in which the concentrations of the ions in the solution are so adjusted that positive and negative ions are equally adsorbed or unadsorbed (see Verwey (86a)).

Many attempts have been made to elucidate the structure of the double layer from studies of hydrogen overvoltage phenomena. In the opinion of the author, these phenomena are complicated by factors not yet well understood, with the result that reliable information about the double layer is not obtained in this way. There can be little doubt, however, that the high overvoltage of hydrogen on mercury is occasioned by the large activation energy associated with the reaction

$$H_3O^+ + e^- \rightarrow H + H_2O$$
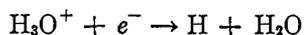
since this reaction is highly endoenergetic (65). The fact that mercury is a
poor catalyst for the *gas* reaction

$$H + H \rightarrow H_2$$

indicates that hydrogen atoms are not strongly bound to mercury, but does not
indicate that this latter reaction is slow when the necessary third body (which
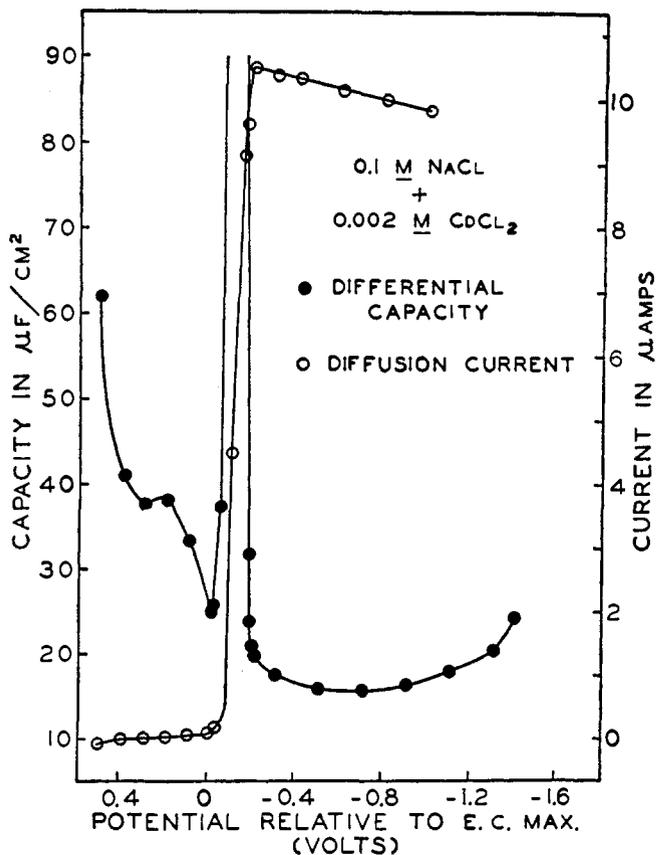

FIG. 22. Differential capacity observed in the presence of traces of reversibly reducible
substance (Cd^{++}). Open circles show polarographic diffusion current for same solution.

may be mercury) is present, as it is during the reduction of hydronium ions. A
critical discussion of the theories and experimental data pertaining to hydrogen
overvoltage on mercury is given by Frumkin (28).

When the reduction of an ion can occur reversibly, the apparent capacity of
an electrode is enormously increased (42). An example of this effect is given
in figure 22. The capacity is increased in this manner because the reduced

form of the ion acts as a reservoir of charge. The concentration of the reduced form of the ion is fixed either by the potential or by the rate of diffusion of the ions to the surface, depending upon whether one is below or above the "half-wave potential." When the potential of the metallic electrode is made so strongly negative that the concentration of the reduced form of the ion is limited by diffusion, changes of potential cause no further change in the concentration of the reduced form of the ion, and the differential capacity becomes normal. This is a particularly good illustration of an electrode which is not ideally polarized acting like one which is.

The enhanced capacity caused by the reversible reduction of ions has been called by the author (42) a "pseudo-capacity," since it does not correspond to any bound charge except in the sense that neutral metallic atoms represent bound charge. This pseudo-capacity is observed on extreme cathodic polarization of sodium, potassium, rubidium, ammonium, and tetramethylammonium salts and presumably would be found with practically all cations. Hydronium ions do not give this effect, however, which can only mean that hydronium ions are not reduced reversibly at a mercury cathode, a result in harmony with the supposition that the reduction of hydronium ions on mercury is a process requiring activation energy. This must be regarded as strong support for the slow-discharge theory of hydrogen overvoltage mentioned above.

The reduction of oxygen on mercury does not give rise to any pseudo-capacity (42). This observation indicates that the first step in the reduction of oxygen

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$
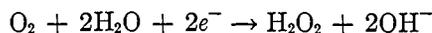
is a slow step, a fact which was known independently from the fact that it exhibits overvoltage. The absence of pseudo-capacity from the reduction of oxygen is fortunate for the making of differential capacity measurements, since the last traces of oxygen are difficult to remove from aqueous solutions at room temperature.

The reduction of nitrate ion is irreversible by the criterion of the absence of pseudo-capacity, a result which will occasion no surprise.

As an analytical tool the measurement of the pseudo-capacity at a dropping-mercury electrode might be found to possess the advantage of high sensitivity in the presence of small amounts of substances which are reducible but not reversibly reducible. The technique would be a modified form of polarography, but its greater complication would limit its usefulness to cases where ordinary polarographic methods fail. As a tool for investigating chemical reactions at an electrode, however, it can hardly be excelled.

References mentioned in the text and listed below are not comprehensive but include only those best suited to illustrate the points under discussion. In nearly every case the references cited give all of the essential information and provide a key to the earlier literature. Two other recent and fairly extensive reviews of electrocapillarity are those of Butler (10) and of Adam (3), to which the reader is referred for information about topics not here discussed.

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