be so in small amounts. The value of K_6 was obtained by the use of the a_{H^+} measured by the glass electrode

$$\mathrm{Ni(OH)_2(s)} + 2\mathrm{H^+} \rightleftarrows \mathrm{Ni^{++}} + 2\mathrm{H_2O} \qquad (6)$$

$$K_6 = \frac{m_{\mathrm{Ni^{++}}}\gamma_{\mathrm{Ni^{++}}}}{m^2_{\mathrm{H^+}}\gamma^2_{\mathrm{H^+}}} = 6.5 \times 10^{10}$$

$$\Delta F^\circ = -15{,}000 \text{ cal.}$$

the values of $m_{\mathrm{Ni^{++}}}$ are given in column 3 of Table II, and the values of $\gamma_{\mathrm{Ni^{++}}}$ were obtained from a table of activity coefficients for divalent ions compiled by Harned and Owen.[6] Further evidence that the reaction indicated by equation 5 has little or no effect on the value of K_6 is the constancy of K_6 over the concentration range of $m_{\mathrm{HCl}} = 0$ to 0.1. The error in K_6 is in the order of $\pm 0.5 \times 10^{10}$.

The high solubility of nickel hydroxide in acid solution and its low solubility in alkaline solution indicate qualitatively that nickel hydroxide is a relatively strong base. Finally, the calculated values of the acid and base constants of nickel hydroxide fully verify the strong basic character.

The Value of the Water Solubility at 25°.—The value of the water solubility of nickel hydroxide, 1.0×10^{-4}, was determined by extrapolating the solubility of nickel hydroxide in dilute acid solution of $m_{\mathrm{HCl}} = 0$ (see Figs. 2 and 3). The extrapolation was made graphically (large scale) by the aid of the value of the slope of the line obtained in 0.006 to 0.05 molal acid solutions. This procedure was necessary because the solubility of nickel hydroxide in water is below that which can be determined accurately by any classical chemical method. Furthermore, this is probably a more accurate value than could be obtained by direct measurement, were a satisfactory method of analysis available, because of the error involved in a direct measurement due to (1) any adsorbed hydroxyl ions on the nickel hydroxide and (2) the colloidal nature of highly purified samples of nickel hydroxide. The value of the water solubility is probably good to $\pm 0.5 \times 10^{-4}$.

The Solubility Product Constant.—From the value of the ion product K_w of water and $K_6 = 6.5 \times 10^{+10}$ obtained from the solubility of nickel hydroxide in acid, the solubility product constant K_1 was calculated for the equation

$$\mathrm{Ni(OH)_2(s)} \rightleftarrows \mathrm{Ni^{++}} + 2\mathrm{OH^-} \qquad (1)$$

$$K_1 = \frac{K_6 K^2_w}{a^2_{\mathrm{H_2O}}} = m_{\mathrm{Ni^{++}}}\gamma_{\mathrm{Ni^{++}}}m^2_{\mathrm{OH^-}}\gamma^2_{\mathrm{OH^-}}$$

$$K_1 = 6.5 \times 10^{-18}$$

$$\Delta F^0 = 23{,}000 \text{ cal.}$$

Summary

The solubility of nickel hydroxide has been determined in dilute acid and base at 25 ± 0.02°. The data show nickel hydroxide to be a relatively strong base. The reactions occurring in basic and acid solution are shown by equations

$$\mathrm{Ni(OH)_2(s)} + \mathrm{OH^-} \rightleftarrows \mathrm{HNiO_2^-} + \mathrm{H_2O} \qquad (3)$$

$$\mathrm{Ni(OH)_2} + 2\mathrm{H^+} \rightleftarrows \mathrm{Ni^{++}} + 2\mathrm{H_2O} \qquad (6)$$

The value for the solubility product of nickel hydroxide, is 6.5×10^{-18}. The value for the water solubility of nickel hydroxide is 1.0×10^{-4}. The acid dissociation constant of nickel hydroxide is 6×10^{-19}.

COLUMBUS, OHIO RECEIVED APRIL 14, 1949

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Measurement of the Capacity of the Electrical Double Layer at a Mercury Electrode

BY DAVID C. GRAHAME

It has long been known that the slope of the electrocapillary curve of a liquid metal in a salt solution gives the surface charge density of electricity at the interface.[1-5] In a like manner the second derivative of the electrocapillary curve gives the differential capacity,[3,4] a quantity which can also be measured directly with fair precision. It is less well known that from the interfacial tension or from the differential capacity one can obtain a considerable amount of further information about the electrical double layer. For example, it is possible to calculate the charge contributed by each ion separately,[4] the entropy and enthalpy changes associated with the electrochemical process which accompanies an infinitesimal transfer of charge through the cell,[6] and other less easily described properties.[6] In addition there are certain non-thermodynamic properties which are obtained by combining the thermodynamic properties with quantities calculated from the kinetic theory of the electrical double layer.[4] All this has been discussed elsewhere.

It is a matter of great difficulty to make interfacial tension measurements with sufficient precision to serve for these calculations, and we have accordingly attempted to develop apparatus for the precise measurement of the differential capacity of the double layer at a mercury surface. Two models of this apparatus have already been described.[3,7] Considerable changes have now

(1) Lippmann, *Ann. Physik Chem.* (*Wied. Ann.*), **11**, 316 (1880).

(2) Koenig, *J. Phys. Chem.*, **38**, 111, 339 (1934).

(3) Grahame, THIS JOURNAL, **63**, 1207 (1941).

(4) Grahame, *Chem. Revs.*, **41**, 441 (1947).

(5) Grahame and Whitney, THIS JOURNAL, **64**, 1548 (1942).

(6) Grahame, *J. Chem. Phys.*, **16**, 1117 (1948).

(7) Grahame, THIS JOURNAL, **68**, 301 (1946).

been made, and it is the principal function of the present paper to describe these changes, which are of importance to anyone planning a duplication or extension of the work. Some results obtained with the new form of the apparatus are also described.

Experimental Method

In principle the method remains unchanged. A droplet of mercury forms at the tip of a fine capillary (o. d. *ca.* 0.10 mm., i. d. *ca.* 0.04 mm.), Fig. **1**, under the deaerated solution to be investigated. A second electrode, for which we use a platinized platinum gauze sphere Pt, with openings at the poles, surrounds the mercury droplet symmetrically. The system mercury–solution–platinum now forms a cell somewhat like a conductivity cell except that we are primarily interested in its capacity rather than its resistance. This cell is made the fourth arm of a bridge which differs from conventional conductance bridges primarily in that it measures the *series capacitance* of the cell. Stray capacitance and inductance must be severely limited, the effects being minimized by the use of a low frequency; 1000 cycles is convenient and sufficiently low, with good technique, for tenth-normal and possibly hundredth-normal salt solutions, but below this concentration the unavoidable bridge errors become large and a lower frequency must be used. The results obtained are believed to be independent of frequency within the experimental error.[7]

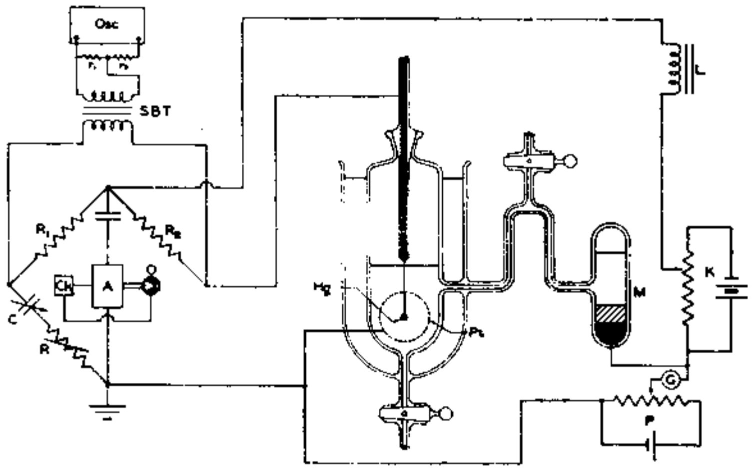

Fig. 1.—Schematic representation of the apparatus used for the determination of the capacity of the electrical double layer at a mercury–solution interface. The cell shown schematically here is depicted in more detail in Fig. 3 of the following paper.

The capacity of the double layer in contact with the platinum is enormous because of its relatively large surface area. Thus the observed capacity is sensibly the capacity of the double layer in contact with the mercury, the two capacitances being in series.

Because the capacity of the electrical double layer depends upon the d. c. potential, an additional electrode is required. Usually a calomel electrode is employed, especially when chlorides are to be investigated. A type K potentiometer, K, is used to impose a potential upon the double layer, as shown in Fig. 1. In order to keep the d. c. resistance from the mercury to the potential-fixing electrode as low as possible, the platinum gauze electrode in the solution is employed as the potential-fixing electrode. Since its potential wanders in an unpredictable manner relative to that of the calomel electrode M, the potential difference between the two is measured with a conventional potentiometer–galvanometer system P–G, and the difference applied as a correction to the potential imposed by the other potentiometer. In the circuit shown, the potentiometer P not only measures the correction but also applies it simultaneously, so that no actual reading of the magnitude of the correction is required.

An important new feature of the circuits was the inclusion of wholly different timing methods from those previously described. Since the mercury droplet is constantly growing in size until it falls, it is necessary to measure the time interval from the moment of its "birth" to the moment at which the bridge is balanced. Knowing the rate of flow of the mercury, which is also measured, it is then a simple calculation to find the area of the droplet at the moment of bridge balance. It may be mentioned in passing that the measured capacity is proportional to this area, other things being equal, as accurately as can be measured from 0.2 sec. after the "birth" of the droplet until just before the moment of fall, perhaps five seconds later.

The new method of timing is as follows: When a droplet falls, it produces a very abrupt change in the amplitude of the signal representing the degree of unbalance of the bridge. This signal is rectified or "detected" and applied to the grid of a thyratron which actuates a relay which starts a high-speed (2 r. p. s.) interval timer, Ck, Fig. **1**. The interval timer is arranged so that with every revolution of the hand it produces a pulse which starts the sweep of the oscilloscope on which the bridge unbalance is presented. The sweep presents an expanded view of the manner in which the state of the bridge balance varies with time. A long-persistence screen is necessary, since successive sweeps do not present the same pattern. When R and C are adjusted to values such that a moment of perfect balance occurs during the lifetime of a droplet, one sees on the oscilloscope screen a pattern like that depicted in Fig. 2. The moment at which this state of perfect balance occurs is ascertained by means of auxiliary markers obtained from the clock and presented on the screen.

The instrumental accuracy is estimated at 0.1% or better in tenth-normal solutions under not-too-unfavorable conditions. Systematic errors not associated with the electrical circuits as such probably produce somewhat greater errors, perhaps up to 1% in unfavorable cases.

The rate of flow of the mercury is ascertained by weighing the mercury delivered from the capillary over an interval of about 500–1000 seconds. The rate of flow was usually of the order of 0.8 mg./sec., although capillaries with rates ranging from 0.5 to 1.5 mg./sec. have been used satisfactorily.

The solutions were deaerated with nitrogen. It was not found necessary to remove the last traces of oxygen.

Experimental Results

In the development of the above technique, a tenth-normal solution of twice recrystallized potassium chloride in conductivity water was most often used for test purposes. Most of the measurements at this concentration were taken at 1000 cycles and at 25°. The results obtained are given in Table I, together with values of the first and second integrals with respect to potential. The integration was done by numerical summation, using segments 10 mv. wide in the potential interval 0.14–1.90 volt, and one mv. wide in the potential interval 0–0.14 volt. The adequacy of this procedure was checked by checking certain "critical" regions over still smaller intervals.

TABLE I

SOME ELECTROCAPILLARY PROPERTIES OF 0.1 N KCl AT 25°

E, volts	C, $\mu f/\text{cm.}^2$	$\int C\text{d}E$ μcoul./cm.^{2}	$\int\int C\text{d}^2E$ ergs/cm.^{2}
0	123	22.19	49.03
0.005	109	21.61	47.93
.01	97.4	21.09	46.86
.02	81.4	20.20	44.80
.03	71.2	19.44	42.82
.04	63.9	18.77	40.91
.05	58.5	18.16	39.06
.07	51.9	17.05	35.54
.10	45.80	15.60	30.65
.15	40.48	13.46	23.40
.20	38.30	11.50	17.16
.23	38.00	10.36	13.89
.25	38.16	9.59	11.89
.30	38.94	7.669	7.574
.35	39.86	5.695	4.231
.40	39.01	3.715	1.880
.45	35.62	1.838	0.4992
.50	30.50	0.1825	.00555
.506	29.91	0.0000	.0000
.55	25.91	−1.223	.2758
.60	23.00	−2.440	1.198
.65	21.23	−3.542	2.698
.70	20.04	−4.572	4.729
.80	18.40	−6.491	10.27
.90	17.15	−8.264	17.66
1.00	16.40	−9.94	26.77
1.10	16.06	−11.56	37.52
1.15	16.04	−12.36	43.50
1.20	16.08	−13.16	49.88
1.30	16.38	−14.79	63.85
1.40	17.00	−16.45	79.46
1.50	17.80	−18.19	96.8
1.60	18.83	−20.03	115.9
1.70	20.05	−21.97	136.9
1.80	21.77	−24.05	159.9
1.90	24.46	−26.36	185.0

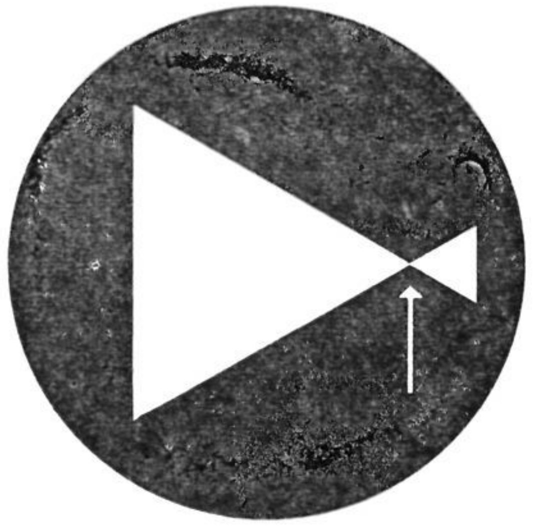

Fig. 2.—Appearance (except for the arrow) of the oscilloscope screen during a measurement. The pattern is a sine wave of variable amplitude, but because of the relatively slow sweep speed (~10 in./sec.) the sine waves are not resolved. At the point marked by the arrow the bridge is in a state of balance. A mark is made on the screen indicating the position of the sweep at a known time after the birth of the mercury droplet, and the bridge is adjusted to make its moment of balance coincident with this mark.

The results are mostly given to one more place (in small figures) than the absolute accuracy of the data warrants because the differences are known more accurately than the absolute values. The first column in Table I gives the potential relative to a normal calomel electrode. The liquid junction between normal and tenth-normal potassium chloride is not, of course, a source of any uncertainty. The second column gives the differential capacity C in microfarads per sq. cm. A plot of these data is not noticeably different from a plot already published[4] for tenth-normal sodium chloride. Minima occur at $E = 0.23$ and 1.15 volts. The intervening maximum occurs at $E = 0.35$ volt. The third column gives the value of $\int C\text{d}E$ starting from the potential of the electrocapillary maximum which we take at $E = 0.506$ volt as found in the following paper. The values of $\int C\text{d}E$ given in column 3 represent the surface charge density of electricity, as one can readily deduce from our two opening remarks.

Column 4 gives values of $\int\int C\text{d}^2E$ where the second constant of integration has been arbitrarily set at zero at the potential of the e. c. max. At 18° its true value would be 426.7 ergs/cm.^{2} according to Gouy,[8] and it is usually considered that this changes very little with temperature, although there seem to be no published data on the matter. Fortunately, it is of minor consequence. Except for this slight uncertainty as to the magnitude of the additive constant, this

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(8) Gouy, *Compt. rend.*, **146**, 1374 (1908); *Ann. phys.*, [9] **6**, 25 (1916).

column then gives the electrocapillary curve of tenth-normal potassium chloride. There are no published data of high precision with which to compare these results.

Discussion of Results

A rather full treatment of the significance of electrocapillary data has been published in another place.[4] The data here presented differ from those already published for *sodium* chloride[4] by only a small amount, the differential capacities of the two chlorides being within 2% of one another at comparable potentials over the range of potentials $E = 0.01$ to 1.2 volts. This great similarity indicates that sodium and potassium ions are hydrated in the double layer, since otherwise their different radii would necessarily be reflected in their capacities. Investigations with other cations now under way also point to this conclusion.

A further interpretation of the data (beyond that given in reference 4) has been attempted, but since it is not the purpose of this paper to present an extensive theoretical treatment of the electrical double layer, this interpretation will be postponed. For the present we shall be content to show, in the following paper, how the differential capacity may be used in conjunction with other data to give a fairly precise value of the potential of the e. c. max.

Acknowledgment.—The author is grateful to the Research Corporation for a Frederick Gardner Cottrell grant of funds in support of this work.

Summary

1. Recent modifications in the author's apparatus for measurement of the capacity of the electrical double layer at a mercury surface in contact with aqueous salt solutions are described.

2. The differential capacity of the electrical double layer, the surface charge density, and the electrocapillary curve of mercury in tenth-normal potassium chloride are presented in tabular form.

AMHERST, MASS. RECEIVED FEBRUARY 23, 1949

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Potential of the Electrocapillary Maximum of Mercury

BY DAVID C. GRAHAME, ROBERT P. LARSEN[1] AND MARILYN A. POTH

The potential of the electrocapillary maximum (e. c. max.) of mercury in contact with aqueous solutions is of the first importance in any theoretical or experimental study of the electrical double layer at such an interface. In addition to its direct thermodynamic significance, it has interest in connection with the kinetic theory of the electrical double layer, and a knowledge of its value is indispensable if one wishes to make full use of the very extensive information provided by studies of the differential capacity of the electrical double layer. In particular, integration of the last-named quantity with respect to potential gives the magnitude of the surface electronic charge except for a constant of integration, which is *zero* if the integration is begun at the potential of the electrocapillary maximum.

To the authors' knowledge there are only four papers on this subject, plus a few incidental measurements of the potential of the e. c. max. to be mentioned later. The first paper of importance in this connection, by Paschen,[2] uses a technique which has not been successful in the hands of later workers (who have found it necessary to remove dissolved oxygen), and it therefore comes as a surprise to find, as a result of the present work, that Paschen's values are very nearly correct. The second paper is by Gouy,[3] whose values of the e. c. max. potential are often quoted, but which the authors now believe to be somewhat in error for reasons explained below. A third paper by Winkel and Siebert,[4] gives value which sometimes agree and sometimes disagree with those of Gouy. The fourth paper, by Erdey-Gruz and Szarvas,[5] is difficult to compare with the others because these authors employed a saturated potassium chloride salt bridge, unlike the rest, and so measured a somewhat different quantity. We have attempted to make the conversion in a few simple cases and find satisfactory agreement with our own results when this is done.

The present authors have measured the potential of the electrocapillary maximum of mercury in tenth-normal potassium chloride and sodium chloride by five more or less independent methods. It is the principal function of this paper to describe these methods and their results.

Principle of Experimental Methods I, II and III

It is desirable to describe first the main principle upon which the first three methods depends. These three methods are really only variants of a single method, but since the least certain measurement is carried out differently in the three variants, we regard them as essentially independent.

Suppose that one knows the differential capacity of the electrical double layer in the solution in

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(1) Present address: Department of Chemistry, Ohio Wesleyan University.

(2) Paschen, *Ann. Physik*, **43**, 568 (1891).

(3) Gouy, *Ann. chim. phys.*, [7] **29**, 145 (1903).

(4) Winkel and Siebert, *Z. Elektrochem.*, **44**, 127 (1938).

(5) Erdey-Gruz and Szarvas, *Z. physik. Chem.*, **A177**, 277 (1936).