polymer decrease regularly with increasing concentrations of allyl chloride. In this copolymerization reaction, allyl chloride monomer adds to styrene free radical or to allyl chloride free radical much more slowly than does styrene monomer.

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

Properties of the Electrical Double Layer at a Mercury Surface. II. The Effect of Frequency on the Capacity and Resistance of Ideal Polarized Electrodes[1]

BY DAVID C. GRAHAME

The nature of the interaction of ionized substances with metallic surfaces is most effectively studied by investigation of the interfacial tension and electrical capacity of such surfaces. In the first paper of this series,[2] hereafter called Paper I, a method was presented for the determination of the electrical capacity of mercury–solution interfaces with a precision not previously attained. In that method the capacity of the surface of an expanding mercury droplet in contact with an aqueous solution was measured by means of an impedance bridge operating with an alternating current having a frequency of 1000 cycles. It was found that the values obtained were in agreement with values calculated from the corresponding electrocapillary curves obtained by Gouy[3] in 1903.

Other investigators,[4–8] working with stationary polarized mercury surfaces, have reported that the capacity of such surfaces depends upon the frequency of the alternating potential used for the measurement, although no two workers have agreed concerning the magnitude of the effect. It is apparent that no reliable conclusions can be drawn from measurements of the capacity of the double layer so long as a fairly large unexplained frequency effect persists in the measurements. In the present paper we shall describe the results of measurements made in an effort to ascertain as certainly as possible the cause of the frequency dependence reported by other workers. In our own measurements the effect was finally eliminated by very careful design, but it was not very large even in the original relatively crude apparatus. This was due to the use of a dropping mercury electrode, which automatically overcomes most of the major difficulties associated with this work.

It is possible in principle to obtain all of the significant thermodynamic properties of mercury–solution interfaces by measurements of the interfacial tension,[9,10] but as a practical matter the precision required in such measurements for the calculation of the differential capacity is so great that direct measurement of this quantity is generally to be preferred. In addition, measurements of differential capacity and resistance under non-equilibrium conditions give information not derivable from the electrocapillary curves and reveal interesting and important properties of the surfaces studied. For example, it will be shown in a paper to follow that the slow step in the discharge of hydrogen ions on a mercury surface can be identified with the reaction

$$H_3O^+ + e^- \longrightarrow H + H_2O$$

Experimental

Many forms of apparatus were tried and used. One of the best is shown in Fig. 1. B is a fully shielded R.C.A. beat frequency oscillator with its neon indicator removed to eliminate a slight electrical disturbance. S and S′ are carbon resistors of approximately equal resistance, used to reduce the voltage input to the bridge to a suitable value. T is a General Radio shielded bridge transformer with the shield of the secondary not grounded, a vital point. This transformer has spacers between the primary and secondary which serve to isolate the source of alternating potential. R_s, R_2 and R_3 are Leeds and Northrup A-C resistance boxes, their types 4750, 4748 and 4631, respectively. C_s is a mica capacitor decade of total capacity 1.1 microfarads adjustable in steps of 0.0001 microfarads. A is a two-stage high-gain amplifier connected to an oscillo-

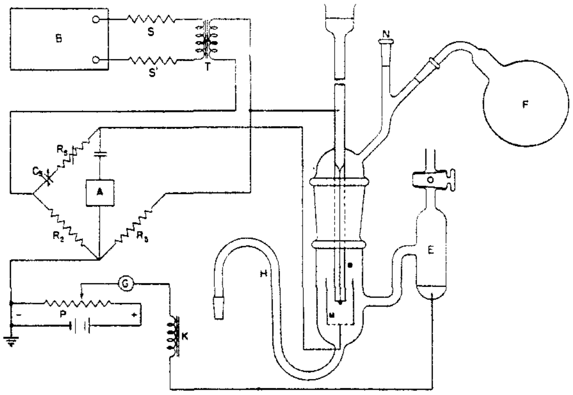

Fig. 1.—Experimental arrangement for the measurement of the capacity of the electrical double layer between mercury and conducting solutions.

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[1] Supported by a grant from the Penrose Fund of the American Philosophical Society.

[2] D. C. Grahame, THIS JOURNAL, **63**, 1207 (1941).

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

[4] M. Wien, *Ann. Phys.*, [2] **58**, 37 (1896); [4] **8**, 372 (1902).

[5] P. Schönherr, *ibid.*, [4] **6**, 116 (1901).

[6] F. Kruger, *Z. physik. Chem.*, **45**, 1 (1903).

[7] N. Thon, *Compt. rend.*, **198**, 1219 (1934); **200**, 54 (1935).

[8] T. Borissowa and M. Proskurnin, *Acta Physicochim. U. R. S. S.*, **12**, 371 (1940).

[9] F. O. Koenig, *J. Phys. Chem.*, **38**, 111, 339 (1934).

[10] D. C. Grahame and R. B. Whitney, THIS JOURNAL, **64**, 1548 (1942).

graph and headphones. P is a Leeds and Northrup student potentiometer. G is a lamp and scale D-C galvanometer with a maximum sensitivity of 0.025 microamperes per millimeter. K is a choke coil of high impedance (about 80 henries) which serves to block alternating currents from this part of the circuit. Tests on this bridge of mica condensers of good quality showed no systematic variation of capacity with frequency up to 15,000 cycles. In addition it was shown that the bridge readings were not affected by reversing the leads from the transformer T, and this test served as a useful criterion of reliability whenever circuit difficulties were encountered or suspected. D is a capillary of about 0.04 mm. bore. In some designs this capillary had an outside diameter of about 0.1 mm. or less. Capillaries constructed in this manner are hereafter called "fine." Tips of the type illustrated in Fig. 1 are called "blunt." For proper operation, the tips of these fine capillaries had to be broken off square. No suitable technique for producing these tips consistently could be found, but out of a great many, a few were always found to be satisfactory.

The construction of the cell is evident from the diagram. M is a platinized platinum electrode having a total apparent surface area of several sq. cm. The capacity of its series combination with the mercury surface under test is not perceptibly different from that of the mercury surface alone, as shown by the fact that increasing the area of the platinum electrode did not alter the measured capacity by a detectable amount. E is a reference electrode using the electrolyte under test. F is a flask connected as shown through an ungreased ground glass joint. The joint N was connected to a source of nitrogen purified as described in Paper I and passed through a column of Norit A (bone black). Tube H is a capillary of large bore through which mercury could be withdrawn from time to time to permit the rate of flow of mercury from the fine capillary to be ascertained.

In operation, the system was evacuated, the solution in F boiled to remove dissolved gases and then allowed to flow into the cell by rotation of the flask through 180°. Nitrogen was then admitted to the cell. Mercury flowed by gravity through the capillary D, and the size of the mercury droplet at any instant was found by timing methods, as described in Paper I. At low frequencies it was necessary to eliminate power line hum as completely as possible, and it was very advantageous to work at exact multiples or sub-multiples of the power line frequency to insure a stationary pattern on the screen of the oscilloscope even in the presence of power line hum.

Very similar types of apparatus have been built for the measurement of *stationary* mercury surfaces. For the most part these surfaces were formed within the cell by allowing mercury to overflow from a carefully formed tube or cup sealed into the cell. The area of these mercury surfaces varied from 1 to 10 sq. cm. An upper limit to the size of the mercury surface which could be used without error was set by the inductance of the low-impedance arms of the bridge circuit. This inductance must in any case be kept as low as possible.

In most of the experiments here described the solution was deaërated by bubbling purified nitrogen through the solution. The results obtained in this manner did not differ perceptibly from those obtained by the boiling-out technique described above and illustrated in the figure. Solutions used were made up in conductivity water from c. p. salts which had been recrystallized from water at least once. Pure dry mercury was triple-distilled in vacuum before use. Sodium chloride after recrystallization with hydrogen chloride was fused in platinum to remove traces of organic matter. The octyl alcohol was Eastman Kodak Co. methyl-*n*-hexylcarbinol, free of ketones. It was not further purified. Solutions were protected from contact with organic matter, and no rubber connections were used in the apparatus.

Summary of Results

Previous investigators have not always attempted to make a clear distinction between the properties of polarized and non-polarizable electrodes. Many of the electrodes actually studied appear to have been partially polarizable.[10a] An examination of the literature reveals that the largest effects of frequency on capacity have always been observed with non-polarizable electrodes and the smallest effects with ideal polarized electrodes.[4–8,11,12] The present study is concerned only with the latter.

Moving Mercury Surfaces.—Measurements made with the dropping electrode technique in solutions of inert salts and acids such as potassium nitrate, sodium chloride, hydrochloric acid and perchloric acid were satisfactorily reproducible for a given experimental set-up, but were somewhat dependent upon the shape and position

TABLE I

EFFECT OF FREQUENCY ON THE DIFFERENTIAL CAPACITY OF THE ELECTRICAL DOUBLE LAYER BETWEEN MERCURY AND AQUEOUS SOLUTIONS[a]

Solution	Capillary	E_{volts}	Percentage deviation 240~	Percentage deviation 5000~	C', μf/sq. cm.
1 N NaCl	Fine	+0.11	0.3	0.1	43.0
		− .24	.5	− .1	20.4
		− .64	.1	.2	16.2
	Blunt	+ .11	.2	−1.8	43.0
		− .04	.2	−1.2	35.0
		− .24	.2	−0.8	20.4
		− .64	.3	− .8	16.2
		−1.04	.0	− .4	18.5
1 N KNO_3	Blunt	+0.50	.6	− .6	25.7
		.00	.5	− .7	31.5
		− .20	.7	− .8	25.2
		− .50	1.1	− .8	16.8
0.1 N NaCl	Fine	+ .36	0.2	− .2	39.5
		+ .06	.5	− .3	35.1
		− .24	.4	− .4	18.6
		− .64	.4	− .2	15.6
	Blunt	+ .31	2.1	−6.4	37.7
		+ .11	2.4	−5.5	38.2
		+ .01	2.2	−6.1	30.2
		− .24	1.7	−4.8	18.6
		− .64	0.3	−5.3	15.6
		−1.24	0.4	−2.5	19.0
1 N KI	Blunt	−0.14	−1.0	−3.0	69.3
		− .44	0.5	−1.2	39.4
		− .84	− .2	0.0	18.3
1 N KNO_3	Fine stationary	+ .70	.3	.4	33.6
		+ .60	.6	− .4	28.4
		.00	.2	− .3	31.5
		− .50	.3	− .3	16.8

[a] Dropping mercury electrodes, except as noted.

(10a) A polarized electrode is one whose potential difference changes when current flows across it; a non-polarizable electrode is one whose potential does not change under these circumstances. An ideal polarized electrode is one for which no charge crosses the phase boundary when the potential is altered slightly. These definitions are amplified and discussed in ref. 10.

(11) E. Neumann, *Ann. Phys.*, [2] **67**, 500 (1899).

(12) G. Jones and S. M. Christian, THIS JOURNAL, **57**, 272 (1935).

of the tip on which the mercury droplets were formed. Some representative data are shown in Table I. Values of E are stated here and elsewhere in the paper relative to the potential of the electrocapillary maximum. The percentage deviations given show the amount by which the capacity changed when the frequency was changed from 1000 cycles per second to the values named. The right-hand column gives the capacity of the surface in microfarads per sq. cm. according to our best absolute determinations. The random experimental error in the columns marked "percentage deviation" was about 0.3% with blunt capillaries and 0.5% with fine-tipped capillaries. This does not mean that blunt capillaries are better than fine-tipped capillaries, however, since there are systematic errors associated with the use of the former as discussed below.

Below 240 cycles no measurements are reported since there were no detectable capacity changes below that frequency except in dilute solutions with blunt capillaries. Between 240 and 5000 cycles no anomalies were observed other than a continuous trend in the direction indicated by the figures given. Above 5000 cycles and below 60 cycles the accuracy of measurement fell off so rapidly that no reliable results could be obtained.

These data show that with fine-tipped capillaries no capacity changes large enough to be observed are found up to 5000 cycles in normal and tenth-normal solutions. It is concluded, therefore, that the circuit shown in Fig. 2a represents the electrical behavior of the double layer at any one potential at frequencies up to at least 5000 cycles per second. With blunt capillaries definite changes of capacity were generally observed, especially at the higher frequencies. The probable explanation of this result is given below, and does not contradict the conclusion here reached.

In order to ascertain whether the presence of surface-active anions would alter the character of the results, a few measurements were made with solutions of potassium iodide. Some typical results are shown in Table I. The frequency effect was no greater than that found for sodium chloride solutions under comparable conditions. The relatively large frequency effect found at $E = -0.14$ volt is related to the large value of C'. It will be noted, for example, that the frequency effect with blunt capillaries was generally greater when the capacity per sq. cm. was large. In more dilute solutions the frequency effects were also larger, for a reason to be explained later.

It has been demonstrated several times that there exists at the surface of some electrodes a resistance of uncertain origin called the polarization resistance.[4,12] All the evidence indicates that this polarization resistance varies with the frequency. The work of Jones and Christian[12] is particularly convincing in this respect. But in our experiments the series resistance R_s needed to balance the bridge for a given experimental set-up did not ordinarily vary with the frequency, or varied only a little, when fine-tipped capillaries were used. This leads to the conclusion that polarization resistance was practically absent in our measurements.

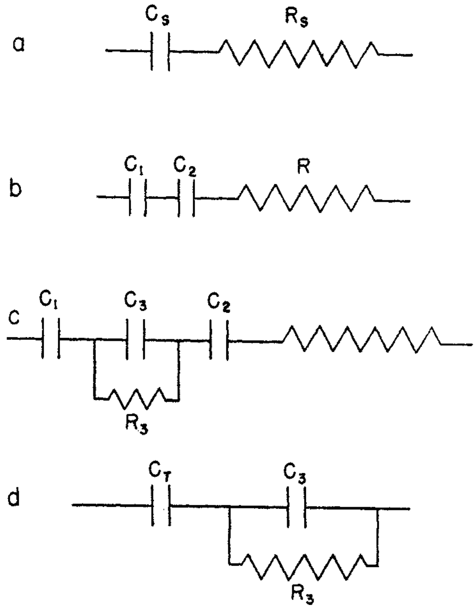

Fig. 2.—Equivalent circuits representing the electrical double layer.

Occasionally a small change of resistance, ΔR, would be necessary to preserve the balance of the bridge when the frequency was changed. The largest such change observed under supposedly good experimental conditions amounted to about 0.12 ohm-cm.^{2} from 240 to 5000 cycles. Using the empirical relation[12] $\Delta R\sqrt{\omega}$ = constant, where ΔR is the polarization resistance at the frequency $\omega/2\pi$, this gives for ΔR the value 0.075 ohm-cm.^{2} at 1000 cycles. For comparison we may cite the value 4.5 ohm-cm.^{2} obtained by Jones and Christian at 1000 cycles for silver in contact with tenth normal silver nitrate. Thus even our largest values are insignificant by comparison with values obtained for other types of electrodes.

A check for the possible presence of frequency-independent polarization resistance was made by comparing the observed resistance with that calculated for a similar geometrical disposition of the electrodes. A polarization resistance of about 0.02 ohm-cm.^{2} was indicated by these measurements, but the result is not to be regarded as evidence of a real effect since systematic errors of that order of magnitude could not be excluded with any certainty. In any event, no polarization resistance was ever observed comparable in magnitude to the values reported by Jones and Christian for other types of electrodes. Within present limits of error, therefore, the ideal polarized electrode shows no polarization resistance.

Measurements have been made with a fine-

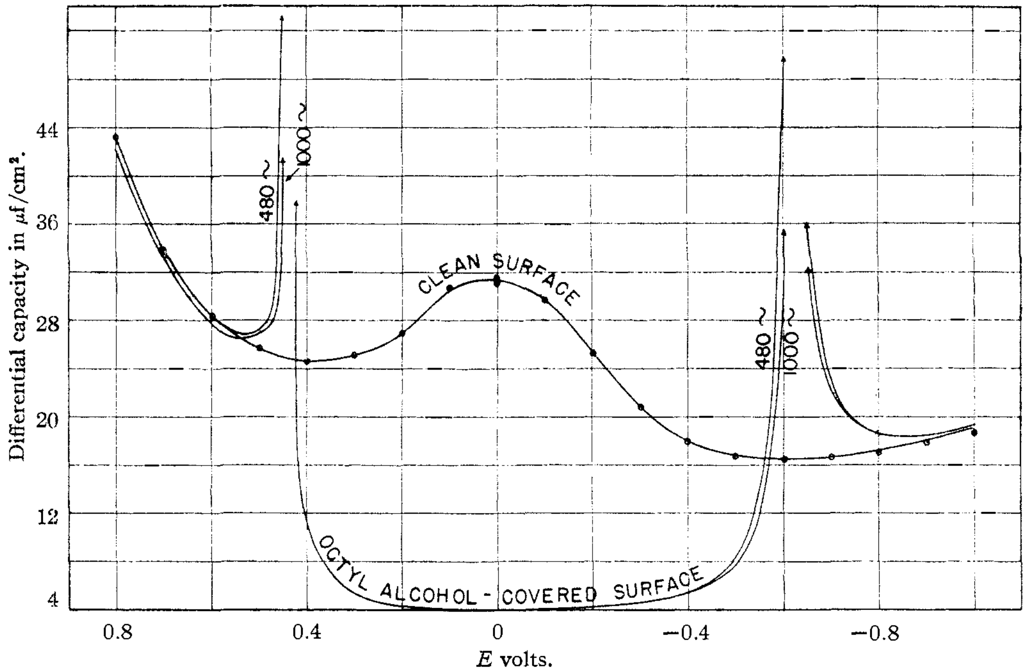

Fig. 3.—Differential capacity of the electrical double layer in normal potassium nitrate solutions with and without the addition of octyl alcohol.

tipped capillary on the capacity and resistance as a function of frequency and potential of mercury surfaces in contact with solutions of potassium nitrate, sodium chloride, and hydrochloric acid, all saturated with octyl alcohol. The results obtained with all three were similar and differed only in detail from those obtained by Proskurnin and Frumkin[13] at 50 cycles with octyl alcohol in sodium sulfate. Part of our results for octyl alcohol in normal potassium nitrate are shown in Fig. 3. More detailed data and some resistance values are given in Tables II and III. Two peaks are observed in the capacity *vs.* potential curves, corresponding to the abrupt formation or removal of a layer of the alcohol on the surface of the mercury. The capacity is nearly independent of the frequency, except in the neighborhood of the crests of the peaks. The resistance, on the other hand, shows a marked dependence upon the frequency, being higher the lower the frequency. Near the electrocapillary maximum, the resistance varied approximately inversely as the square of the frequency. In the neighborhood of the

TABLE II

CAPACITY OF THE ELECTRICAL DOUBLE LAYER BETWEEN MERCURY AND ONE NORMAL AQUEOUS POTASSIUM NITRATE SATURATED WITH OCTYL ALCOHOL,[a] $t = 25°$

	Capacity µf/cm.²				
E_{volts}	240~	480~	1000~	5000~	10,000~
+0.80	43.0	42.8	42.3	42.2	41.7
+ .50	27.2	27.2	27.0	26.8	26.5
+ .475	28.9	28.6	27.8	27.6	27.0
+ .45	56.5	45.5	41.5	31.8	29.3
+ .40	11.0	10.6	10.5	10.1	10.0
+ .30	5.21	5.21	5.20	5.15	5.14
.00	4.00	4.03	4.00	4.03	4.05
− .20	4.30	4.28	4.30	4.30	4.33
− .50	8.36	8.08	7.88	7.71	7.66
− .55	14.1	13.5	12.6	11.8	11.6
− .60	49.6	41.4	35.5	28.1	26.4
− .65	36.1	34.2	32.4	27.6	25.3
− .70	22.7	22.4	22.2	21.8	21.4
− .90	18.8	18.7	18.7	18.7	18.7

TABLE III

SERIES RESISTANCE OF THE ELECTRICAL DOUBLE LAYER BETWEEN MERCURY AND ONE NORMAL AQUEOUS POTASSIUM NITRATE SATURATED WITH OCTYL ALCOHOL,[a] $t = 25°$

	Resistance ohm-cm.²			
E_{volts}	240~	480~	1000~	5000~
+0.80	0.05	0.08	0.04	0.01
+ .50	.40	.10	.01	.00
+ .475	.42	.24	.09	.00
+ .45	3.90	1.38	.74	.11
+ .40	2.25	1.11	.35	.01
+ .30	5.71	1.53	.54	.03
.00	2.42	0.65	.14	.01
− .20	1.79	0.79	.13	.03
− .50	2.17	1.38	.66	.08
− .55	3.83	2.26	1.03	.12
− .60	4.60	2.47	1.22	.21
− .65	1.68	1.03	0.69	.19
− .70	0.14	0.15	.15	.04
− .90	0.72	0.22	.02	.01

[a] Potentials of mercury in solutions containing octyl alcohol are stated relative to the potential of the electrocapillary maximum in the *absence* of octyl alcohol.

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(13) M. A. Proskurnin and A. N. Frumkin, *Trans. Faraday Soc.*, **31**, 110 (1935).

peaks it varied more nearly inversely with the first power of the frequency. Beyond the peaks, where the surface was clean, the resistance was small and nearly independent of frequency. The explanation of this behavior is given below. It should be understood that the resistance values here given are very rough, since the resistance was reasonably large only at the lower frequencies, where resistance measurements were particularly difficult for other reasons. The values are in some cases not more accurate than ±20%.

Solutions containing very small amounts of octyl alcohol (~1% of saturation) gave results almost indistinguishable from pure solutions except in the neighborhood of the electrocapillary maximum, where the capacity was slightly depressed. Thus we conclude that capillary-active substances unavoidably present even in carefully purified solutions do not alter greatly the results obtained by the dropping mercury electrode technique. This is not true of measurements made with stationary mercury surfaces and constitutes one of the chief advantages of the dropping mercury electrode for capacity measurements.

Stationary Mercury Surfaces.—Two types of stationary mercury surfaces were employed. In one type the mercury surface was formed by causing mercury to overflow from a carefully shaped tube or cup mounted in the solution. The mercury was transferred to this cup in such a manner that impurities could not be carried to the surface. In one experiment, for instance, the mercury was distilled directly into the tube leading to the mercury surface.

In the second type of stationary mercury surface employed, a droplet of mercury was caused to hang suspended from the tip of a fine-tipped capillary such as that used previously with the dropping mercury electrodes. It was found possible to arrest the flow of mercury from such a tip by means of a greased stopcock in the mercury column.[14] The mercury droplet formed in this manner was never wholly stationary although a single droplet could sometimes be maintained for an hour or more.

So far as could be ascertained, results obtained with the hanging droplet were not significantly different from those obtained with the dropping mercury electrode (see Table I). The frequency effect on the capacity, in particular, was unchanged; that is, only a negligible effect was observed. The situation was quite otherwise when stationary surfaces of conventional types were employed. With such surfaces the frequency effect always exceeded that found with mercury droplets, and its magnitude depended critically upon the size and shape of the exposed mercury surface. Large surfaces in general gave better results (*i. e.*, smaller frequency effects) than small surfaces, but the usefulness of this fact was limited by the sensitivity of the bridge to error from inductance in the circuit when large surfaces were used. This sensitivity arises from the fact that the high capacity of the double layer entails so low an impedance that the residual inductance of the bridge circuit becomes significant.

When stationary mercury surfaces were employed, the capacity always changed somewhat with time. A detailed study of the rate of drift showed that this rate was greatest at the electrocapillary maximum and almost disappeared at potentials above or below those at which contamination from surface-active materials could occur. These results show that the change of capacity with time is to be ascribed to the presence of traces of surface-active substances from the solution or elsewhere which find their way to the mercury surface. The amounts of such substances needed to form a monomolecular layer on the mercury surface are so small that ordinary chemical methods of purification are inadequate for their removal. When a large platinum foil was repeatedly ignited and immersed in the solution, a considerable improvement in the rate of drift and in the shape of the capacity curves (capacity *versus* potential) was noted. Unfortunately, such a procedure causes a decomposition of some electrolytes, notably nitrates. Intensive efforts to eliminate this capacity drift with stationary electrodes have not yet been made by us, since the drift did not alter the frequency effect, which was our principal concern.

Effect of Changing the Magnitude of the Alternating Potential.—In balancing an impedance bridge where the magnitude of the capacity or resistance of one of the elements of the bridge depends upon the potential, as in the present case, it is desirable that the alternating potential impressed upon the impedance to be measured should be kept as small as possible. In Paper I this potential did not exceed one millivolt, but the use of so small a potential limits the accuracy with which a bridge can be balanced, especially at frequencies well removed from 1000 cycles. The use of a larger input potential results in the production of noticeable overtones, particularly the second harmonic. It can be shown that if the capacity is a linear function of the potential over the range of potentials involved in a single measurement,[15] the correct reading will be obtained by balancing the bridge at the frequency of the fundamental, ignoring the overtones. This expectation was checked experimentally and found to be correct within very small limits of error. Thus it was possible to use input potentials as large as 30 millivolts without serious error in regions where the capacity was nearly a linear function of the potential, and this fact was of great service in making measurements at frequencies far removed from 1000 cycles.

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(14) The mercury forming the droplet did not come into direct contact with the greased stopcock when the column was filled.

(15) The actual potential at any instant is the algebraic sum of the direct and alternating potentials, and therefore changes at the frequency of the alternating potential.

One would expect the amplitude of the second harmonic at a given potential to be independent of the frequency of the alternating potential. This fact has been roughly verified, showing that the electrical double layer is not anomalous in this respect.

Discussion and Interpretation of Results

Theory of the Variation with Frequency of the Capacity and Resistance of Clean Ideally Polarized Electrodes.—It has been stated that theoretical considerations lead one to expect that the capacity of an electrode should vary inversely as the square root of the frequency, or nearly so.[7,11,16,17] The methods used to derive this result, however, are not at all applicable to completely polarized electrodes, although this fact does not seem to have been very generally realized. The only theoretical treatment by which a variation of capacity with frequency in such an electrode might be accounted for would depend upon the assumption that there exists a slow step in the process of forming the double layer. If the activation energy were so low that the half-period of the reaction were comparable to the period of the alternating current, the limited speed of the reaction would cause the measured properties to vary greatly with the frequency. If the activation energy were so large that the extent of the process were nearly negligible in the period of the current, its existence would be revealed by an abnormally high resistance, or by a low capacity, or both.[18] In such a case, also, the properties (especially the resistance) would vary with the frequency. An example of these cases is found in octyl alcohol-covered surfaces, *q.v.* These effects are not observed with clean polarized surfaces, and there is no reason to believe on any grounds that any important slow step, other than the ohmic resistance of the solution, delays the formation of the double layer.

One special type of slow step is to be expected, however, in all cases as a result of the finite rates of diffusion of ions. Since the rate at which charges approach the double layer under the influence of an electrical field is not, in general, identical with the rate at which they are received into the double layer, a type of polarization resistance develops which is in some respects analogous to that which arises during the electrolysis, say, of silver nitrate solutions between silver electrodes. We have estimated the magnitude of this effect by an application of the methods of Rosebrugh and Lash Miller.[19] According to our calculations, the ratio of the real differential capacity, C', to the apparent differential capacity, C'_{app}, as measured on an impedance bridge, is given by the relation[20]

$$\frac{C'}{C'_{\text{app}}} = 1 - \frac{\Delta n}{zF}\sqrt{\frac{\omega}{2k}}\left(\frac{\partial q}{\partial \ln z}\right)$$

where z is the concentration of the electrolyte in equivalents per cubic centimeter, F is the magnitude of the faraday, Δn is the transference number of the cation in the double layer minus the transference number of the same ion in solution, ω is 2π times the frequency, k is the diffusion constant of the ion in question in the solution, and q is the charge per sq. cm. of surface. This equation is derived on the assumption that the thickness of the double layer is small compared to the distance traveled by an ion during the course of the charging and discharging processes which accompany the measurement of the differential capacity. The transference number of an ion in the double layer is taken to be the fraction of the current carried by that ion into or out of the double layer.

Let us estimate the magnitude of the ratio C'/C'_{app} for normal potassium chloride at a potential on the negative branch of the electrocapillary curve. Since the double layer will be composed principally of potassium ions, the transference number of that ion in the double layer will not differ greatly from unity. In the bulk of the solution this transference number is ~ 0.5. Therefore $\Delta n = 0.5$ *ca.* The coefficient $\partial q/\partial \ln z$ can be estimated from the change in the static capacity with concentration, and its value varies from zero at the electrocapillary maximum to about 6×10^{-7} coulomb per sq. cm. at the most negative potential for which measurements can be made. Taking for k[21] the value 2×10^{-5} cm.^{2}/sec. and for ω 3.14×10^4 (at 5000 cycles) one finds $C'/C'_{\text{app}} = 1\text{–}0.000087$. This result means that one anticipates an error of about 0.01% at 5000 cycles and even less at lower frequencies. Errors of this magnitude are much smaller than the experimental errors inherent in the measurements. In hundredth-normal solutions the error predicted by the above equation amounts to about 1% at 5000 cycles, but since at this concentration the experimental errors are much enhanced, owing to the high specific resistance of the solution, it remains true that the effects of concentration polarization on the capacity are inappreciable.

According to our calculations the spurious *resistance* caused by concentration polarization is given by the equation[20]

$$R = \frac{-\Delta n}{zFC'\sqrt{2k\,\omega}}\left(\frac{\partial q}{\partial \ln z}\right)$$

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[16] E. Warburg, *Ann. phys.*, [2] **67**, 493 (1899); [4] **6**, 125 (1901).

[17] A review of the subject is given by Jones and Christian, ref. 12.

[18] Any slow step acts to retard the formation of the double layer and thus simulates the behavior of a poorly conducting system. But if the step is so slow that the ions fail to take it at all, then the ions are prevented from reaching the surface and a low capacity results.

[19] T. R. Rosebrugh and W. Lash Miller, *J. Phys. Chem.*, **14**, 816 (1911).

[20] The derivation of this equation is given in an appendix to this paper reproduced by the American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C.; remit $0.50 for microfilm or $0.50 for 6" × 8" photocopies.

[21] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 45.

For normal potassium chloride the value of R calculated from this equation does not exceed -0.013 ohm-cm.^{2} at 60 cycles, a value so small that it could not be detected at this frequency. Thus we conclude that concentration polarization is also of negligible importance in measurements of the resistance associated with ideal polarized electrodes.

In confirmation of these conclusions it may be noted that the frequency effects predicted by the equations depend upon the potential and become zero at the electrocapillary maximum because of the presence of the factor $\partial q/\partial \ln z$. The observed frequency effects (with blunt tips or large surfaces, for instance) did not in any case show this behavior.

The explanation of the observed frequency effects which best fits the facts is as follows: Since the mercury surface must be supported in the solution, some part of that surface will be shaded by the supporting member, and the resistance to that part of the surface per unit of surface area will be greater than the resistance to other parts of the surface which are not shaded. Fine-tipped capillaries are the most nearly free from this difficulty. Even when the mercury rests as a nearly plane surface in a cup, the edges are unsymmetrically situated with reference to the large platinum electrode. If the resistance from every element of surface to the platinum electrode is not uniform, a frequency effect affecting both the capacity and resistance will result since the equivalent circuit is no longer the series combination of a single capacitor and resistor but rather the parallel combination of many such combinations with different impedance ratios. With increasing frequency the apparent capacity and resistance of such a combination will decrease,[21a] which is the observed result when the mercury surface is shaded. With increasing dilution the effect may be expected to be enhanced, since the resistance per unit of area will be larger and more nearly comparable to the impedance of the double layer at audio frequencies, and this enhancement of the effect is also very clearly observed. The correct experimental measurement of capacity would then be obtained at low frequencies or with fine-tipped capillaries. At frequencies so low that the resistance is negligible compared to the impedance of the double layer no further change of capacity with frequency is to be expected. Thus with one normal solutions we seldom if ever found a detectable frequency effect below 240 cycles, except when the mercury surface was very badly shaded. In more dilute solutions lower frequencies were required to reach this limit. When the capacity per sq. cm. is high, the frequency effect is enhanced for the reason stated above for dilute solutions.

In using a blunt capillary, gas bubbles sometimes collect on the tip close to the mercury surface. These bubbles shade the mercury surface and exaggerate very markedly the frequency effects ordinarily observed with blunt capillaries. This fact lends added support to our explanation of the frequency effect.

Theory of the Variation of Capacity with Concentration and Potential on Clean Ideal Polarized Electrodes.—It is desirable to present an outline of the theory of the electrical double layer upon which the discussions to follow are based. Although the theory is in many respects similar to that of Stern,[22] it differs from it in certain important particulars. In any discussion of the theory of the capacity of the electrical double layer it is necessary to take into account the fact that the finite radius of the ions in the solution prevents the electrical centers of these ions from coming within a certain minimum distance of the metallic surface. The locus of all points at this distance from the surface forms a surface which we shall call the Helmholtz plane. In the original Helmholtz theory the electrical centers of all the ions of the electrical double layer were thought of as situated in the Helmholtz plane. Because of thermal agitation the ions do not actually come to rest in the Helmholtz plane unless they are subject to specific adsorptive forces analogous to chemical binding and varying much more abruptly with distance than one expects for simple coulombic forces.[22a] In contrast to the assumptions of the Stern theory, we therefore assume no layer of ions in the Helmholtz plane except for such ions as may be held by specific adsorptive forces.

Although the ions of the double layer do not lie in the Helmholtz plane (always with the exception noted), they are to be found very close to this plane in all but the most dilute solutions, as Gouy[23] has shown. The equations derived by Gouy apply, however, only up to the Helmholtz plane and not up to the metallic surface, as has usually been assumed by subsequent writers. One can avoid this error and yet represent the physical situation in a very simple manner by supposing the existence at the Helmholtz plane of two imaginary layers of charge, one equal and opposite to the charge on the mercury surface, the other equal and opposite to the charge of the diffuse double layer.[24] The algebraic sum of these two hypothetical charges then equals the charge of the specifically adsorbed ions. In the absence of specific adsorption the hypothetical charges are equal and opposite. The system of charges, including the imaginary ones, is elec-

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[21a] This fact can be understood by noticing that as the frequency is lowered the impedance of a condenser rises until it exceeds that of any resistor with which it may be in series. Thus at zero frequency all the capacity and all the resistance is measured, whereas at high frequencies a condenser in series with a high resistance is effectively out of the circuit.

[22] O. Stern, *Z. Elektrochem.*, **30**, 508 (1924).

[22a] The ions do not in any case come to rest, of course, but they move relatively much less in the presence of the stronger field.

[23] G. Gouy, *J. phys.*, [4] **9**, 457 (1910). A useful review is given by W. Horwitz, *J. Chem. Ed.*, **16**, 519 (1939).

[24] In the diffuse double layer we include all ions except those specifically adsorbed.

trically equivalent to two condensers in series, as illustrated in Fig. 2b. Since the sum of the imaginary charges in the Helmholtz plane equals the real charge in the Helmholtz plane, Fig. 2b is also a correct representation of the real electrical double layer. (R is the resistance of the solution, however, not of the double layer.) The particular advantage of this representation is that it has the mathematical properties of the real double layer and permits one to visualize the electrical properties of the double layer in terms of the familiar properties of series condensers. In Fig. 2b, C_1 is the capacity of the condenser formed by the mercury surface and the Helmholtz plane, C_2 is the capacity of the condenser formed by the diffuse double layer and the Helmholtz plane, and R is the ordinary ohmic resistance of the solution.

The capacity C_2 for uni-univalent electrolytes is given by Gouy's theory as

$$C_2 = F\sqrt{\frac{Dc}{2000\pi RT}}$$

where D is the dielectric constant and c is the concentration in moles per liter. For aqueous solutions at 25° this becomes $C_2 = 234\sqrt{c}$ microfarads per sq. cm. These equations are valid only in the neighborhood of the electrocapillary maximum. At potentials remote from the electrocapillary maximum C_2 is increased, especially in very dilute solutions. It is assumed in the derivation of these equations that the dielectric constant D has a constant value throughout the double layer up to the Helmholtz layer, but not necessarily beyond it. Although it is probable that this assumption is not valid in relatively concentrated solutions, or in dilute solutions at potentials well removed from the electrocapillary maximum, these are the circumstances for which C_2 is considerably larger than C_1 so that the series capacity of C_1 and C_2, which is the only observable quantity, is not seriously affected by the assumption.

The value of C_1 cannot be calculated from more fundamental data at the present time. It depends upon the charge distribution and polarizability of the ions themselves and of the water molecules surrounding these ions. Except near the electrocapillary maximum of very dilute solutions, C_1 controls the over-all capacity because it is so much smaller than C_2. This accounts for the fact that the Gouy theory, which gives only C_2, was long regarded as erroneous because it gave capacity values so much larger than the observed values in all but very dilute solutions. In the absence of specific adsorption each ion appears to confer upon the double layer its own characteristic value of C_1, the actual value then being an average dependent upon the relative amounts of the several ions in the neighborhood of the Helmholtz plane.[25]

In fairly concentrated solutions (1 N) the variations of the static and differential capacities with potential in the neighborhood of the electrocapillary maximum are attributable to variations of C_1, *vide infra*, but the reasons for the kind of variation shown are not, in our opinion, known, although many explanations have been advanced. Fluorides, nitrates, chlorides and hydroxides show distinct and different types of behavior, and none of the theories would seem to account for the differences.

In the absence of specific adsorption C_1 varies from about 20 to 40 microfarads per sq. cm. All anions seem to show specific adsorption when the mercury surface is rendered sufficiently positive.[2] The effect of this adsorption is to increase C_1 very greatly. If this effect be represented by an adsorption potential, then it is necessary to express this potential as a function of the electrical potential, a point not anticipated in the Stern theory.

Effects of Octyl Alcohol.—Although at first sight the variations of capacitance and resistance with frequency and potential when octyl alcohol is present appear very complicated, the concept of imaginary equal (or almost equal) and opposite charges at certain defined planes again reduces the problem to one of a type familiar in alternating current theory. Between the potentials +0.45 and −0.65 volt, octyl alcohol in normal potassium nitrate covers a mercury surface with a film of the alcohol which is probably an uncompressed monomolecular layer. The specific resistance of this layer is greater than that of the solution, and the plane which separates these two phases may be called the delta plane to suggest the change of properties which there occurs. Imagine now two equal and opposite charges at the Helmholtz plane and another pair of equal and opposite charges at the delta plane. All of these charges are to be taken numerically equal to the charge q on the mercury surface and to the charge $-q$ of the diffuse double layer. If there is no specific adsorption of ions at the mercury surface, this system of charges represents the condition of the electrical double layer in the presence of an octyl alcohol layer or other surface-active layer.[26] The electrical analog of this system of charges is three series condensers, two of which are identical in significance with those shown in Fig. 2b for a clean surface and the third of which represents a virtual condenser of capacitance C_3 whose dielectric is the octyl alcohol layer. The resistance R_3 of the octyl alcohol layer may be represented by a resistor shunting this capacitance, while the resistance of the solution is in series with the network and leads finally to the equivalent circuit shown in Fig. 2c. Combining C_1 and C_2 into a single condenser C_T and omitting the resistor representing the resistance of the solution gives the simplest form of the equivalent circuit of the covered surface, shown in Fig. 2d.

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(25) M. A. Vorsina and A. N. Frumkin, *Compt. rend. acad. sci. U. R. S. S.*, **24**, 918 (1939).

(26) In the presence of specific adsorption the charges will not be equal, but the equivalent circuit will be the same.

The capacitance C_T is the coefficient dq/dE measured at equilibrium conditions, *i. e.*, at zero frequency. As a practical matter, measurements at low enough frequencies to permit the evaluation of C_T in this manner cannot be made with our present apparatus, so that we are obliged to estimate q (and C_T) by a method which uses the equations given below. This estimate is rough and is presented (in Fig. 4) primarily as an aid to the understanding of the discussion. The coefficient dq/dE is small for a covered surface because the space normally occupied by ions is now occupied by octyl alcohol. When the potential becomes large enough, either positively or negatively, to cause the ions to displace the alcohol, q changes rapidly to its characteristic value for clean surfaces. In the range of potentials over which this change occurs, dq/dE ($= C_\text{T}$) is very large. At the same time R_3, the resistance of the layer, falls from a maximum of about 500 ohm-cm.^{2} to about 5 ohm-cm.^{2} in the transition interval. For a clean surface R_3 is presumably zero. The capacity of the octyl alcohol layer, C_3, rises as the alcohol of low dielectric constant is replaced by water of high dielectric constant. The minimum value of C_3 observed with octyl alcohol is about 20μf/sq. cm. at the electrocapillary maximum, $E = 0$.

When the circuit shown in Fig. 2d is compared on an impedance bridge with a circuit containing a resistance R_s and capacitance C_s in series, the following relations hold

$$C_s = C_\text{T}(1 + R_3^2C_3^2\omega^2)/(1 + R^2C_3^2\omega^2 + R_3^2C_3C_\text{T}\omega^2)$$
$$R_s = R_3/(1 + R^2C_3^2\omega^2)$$

Near the electrocapillary maximum $R_3^2C_3^2\omega^2 >> 1$ so that

$$C_s = C_3C_\text{T}/(C_3 + C_\text{T})$$

and

$$R_s = 1/(R_3C_3^2\omega^2)$$

These [illegible]ions show that near the electrocapillar[illegible]imum the series capacity C_s is independent [illegible]equency while the series resistance varies inversely as the square of the frequency. Both of these effects are observed in Tables III and IV.

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED VALUES OF THE SERIES RESISTANCE AND CAPACITANCE OF MERCURY SURFACES IN CONTACT WITH AQUEOUS POTASSIUM NITRATE SATURATED WITH OCTYL ALCOHOL

			f	R_s Obs. ohm-cm.^{2}	R_s Calcd. ohm-cm.^{2}	C_s Obs. μf/cm.^{2}	C_s Calcd. μf/cm.^{2}
E	0.0	v.	240~	2.42	(2.42)	4.00	4.00
C_T	5.00	μf/cm.^{2}	480	0.65	0.60	4.03	4.00
C_3	20.0	μf/cm.^{2}	1000	0.14	0.14	4.00	(4.00)
R_3	455	ohm-cm.^{2}	5000	0.01	0.01	4.03	4.00
E	0.3	v.	240	5.71	(5.71)	5.21	5.24
C_T	7.00	μf/cm.^{2}	480	1.53	1.46	5.21	5.21
C_3	20.2	μf/cm.^{2}	1000	0.54	0.34	5.20	(5.20)
R_3	182	ohm-cm.^{2}	5000	0.03	0.01	5.15	5.20
E	−0.6	v.	240	4.60	(4.60)	49.6	(49.6)
C_T	59.0	μf/cm.^{2}	480	2.47	3.01	41.4	39.5
C_3	55.0	μf/cm.^{2}	1000	1.22	1.19	35.5	32.0
R_3	5.58	ohm-cm.^{2}	5000	0.21	0.06	28.1	28.6

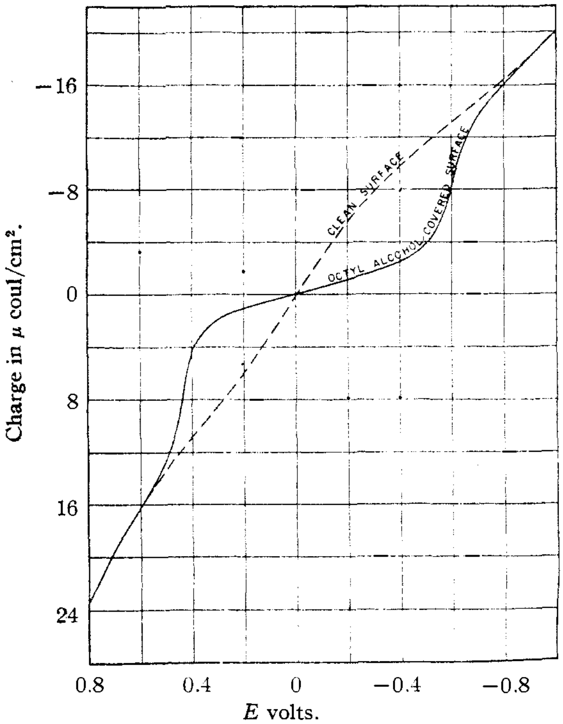

Fig. 4.—Charge–potential curves for mercury in contact with aqueous normal potassium nitrate.

In the transition intervals the quantity $R_3^2C_3^2\omega^2$ is comparable to unity and the complete equations must be used. Table IV shows the character of the agreement at three representative points. Values in parentheses were used to evaluate C_3 and R_3. C_T was chosen to represent the variation of the quantities with frequency as well as possible. It appears probable that the equations represent the facts within the limits of the experimental error, which was rather large, especially in the resistance measurements. In the neighborhood of the crests of the capacity peaks, no exact agreement is to be expected because the delta plane ceases to be well defined. The important point is not the numerical agreement but the qualitative and semi-quantitative agreement of the properties of the electrical double layer with those of its equivalent circuit.

The increase in the series resistance at $E = -0.90$ v. is occasioned by the reduction of nitrate ion, which becomes significant at this potential. The same phenomenon is observed in the reduction of hydrogen ion. Further investigations are in progress concerning this point.

It is noteworthy that the hump in the potassium nitrate curve disappears completely in the presence of octyl alcohol (Fig. 3). This fact seems to show that the hump is not caused by factors operating within the diffuse part of the double layer, which means that the hump is caused by variations in C_1 rather than in C_2, as mentioned above.

The series resistance of octyl alcohol-covered surfaces at no time varied inversely as the square root of the frequency. Since this was the behavior of the polarization resistance of non-polarizable or partially polarized electrodes observed by Jones and Christian, it may be assumed that their polarization resistances were not caused primarily by the presence of surface-active substances. Other less direct types of evidence might be cited to substantiate this conclusion. The most probable cause of true polarization resistance is therefore the concentration polarization first treated in this connection by Warburg.[16,27] Our results have shown that this effect is negligible in ideal polarized electrodes. The fact that the "polarization capacity" of non-polarizable electrodes fails to obey Warburg's equation with accuracy is undoubtedly to be ascribed, at least in part, to the additional presence of the ordinary double layer capacity, not caused by polarization. The term "polarization capacity" ought, therefore, to be limited to that part of the capacity of a non-polarizable electrode attributable to the concentration polarization which accompanies the flow of alternating current across its metal-solution phase boundary. This quantity appears not yet to have been measured, except in a few cases where the double layer capacity was relatively very small.[11]

Conclusion and Acknowledgment

The experiments described in this paper show that when suitable techniques are used the electrical characteristics of the double layer do not exhibit any anomalous behavior. This result makes it possible to interpret measurements on the capacity of the double layer in a satisfactory manner and to correlate these measurements with other types of electrocapillary measurements.

It is a pleasure to express my gratitude to the American Philosophical Society for financial support during the course of this work and to Ruth Levin Merblum for valuable technical assistance.

Summary

1. Theoretical considerations show that the effect of frequency on the capacity and resistance of a clean ideally polarized electrode should be negligible.

2. Experimental studies on mercury surfaces confirm this conclusion.

3. There is no slow step in the formation of the electrical double layer even when surface-active ions are present.

4. On octyl alcohol-covered mercury surfaces the capacity and resistance vary in a complex manner which can be understood by assuming the octyl alcohol layer to have an electrical resistance whose magnitude depends upon the potential.

5. Significant errors arise in the measurement of capacity and resistance when the electrical resistance from every element of the surface to the reference electrode is not the same.

6. On clean polarized mercury surfaces the polarization resistance of the double layer is zero within the probable experimental error.

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[27] Warburg's equation led to the variation of polarization resistance with frequency observed by Jones and Christian.

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Specific Heats at Low Temperatures of TiO, Ti_2O_3, Ti_3O_5, and TiN[1]

BY C. HOWARD SHOMATE[2]

The thermochemical properties of the titanium oxides and nitride are of interest in the production of ferrotitanium from titanium ores and in the refining of steels. The Pacific Experiment Station of the Bureau of Mines has undertaken a program to obtain certain thermodynamic data for these compounds and related substances. This paper presents low-temperature specific heat and entropy data for the monoxide, sesquioxide, tritapentoxide and mononitride of titanium. No such data have been reported previously for any of these substances; however, McDonald and Seltz[3] have made measurements on rutile, a form of titanium dioxide.

Experimental

Materials

Titanium monoxide was prepared by the reaction of equimolal quantities of titanium dioxide and titanium metal at 1,350° *in vacuo*. Analysis of the product showed it to be 99.2% titanium monoxide, 0.1% titanium carbide and 0.7% silicon. The sample used in the measurements weighed 223.24 g.

Titanium sesquioxide was prepared by the carbon reduction of the dioxide, according to the reaction: $2TiO_2 + C \rightarrow Ti_2O_3 + CO$. The finely ground reaction mixture was heated *in vacuo* to 1,400° for twenty hours. Analysis showed 99.4% Ti_2O_3, 0.3% TiC, and 0.3% SiO_2. A 175.87-g. sample was used in the measurements.

Titanium tritapentoxide was prepared also by the carbon reduction of titanium dioxide. The reaction, $3TiO_2 + C \rightarrow Ti_3O_5 + CO$, was carried out *in vacuo* at 1,350° for eight hours. Analysis of the product gave 99.1% Ti_3O_5, 0.2% TiC and 0.7% SiO_2. The measurements were made on a 137.32-g. sample.

Titanium nitride was prepared by passing a stream of

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Chemist, Pacific Experiment Station.

[3] McDonald and Seltz, THIS JOURNAL, **61**, 2405 (1939).