1024, and sometimes at 2048 and 4096 liters. These "percentage ionizations" obviously have no significance since the values of μ_∞ (reduced to mhos) are in no case as large as Λ_0 obtained by any method of extrapolation. The divergence is greatest in the case of polyionic salts. Moreover, conductivity measurements are in most cases unreliable at these extreme dilutions. In the papers cited the equivalent conductance at 2048 liters is often less than at 1024 liters. The method outlined in the present paper will enable one rapidly to extrapolate conductance values and in the case of inconsistent and incomplete data to obtain approximately correct percentage ionization values.

BERKELEY, CAL.

A STUDY OF THE LEAD ELECTRODE.

BY FREDERICK H. GETMAN.

Received February 1, 1916.

The present paper contains a brief summary of the results of a series of experiments carried out with a view to determining the constancy and reproducibility of the lead electrode. The methods employed are essentially those described in previous papers dealing with the reproducibility of the copper electrode[1] and the reproducibility of the cadmium electrode.[2] In both of these papers it was pointed out that the variations observed in the potential of electrodes cast or drawn from the metals under investigation were most satisfactorily explained on the ground of allotropism. The recent studies of Cohen and his co-workers[3] on the metastability of the metals, has established the existence of metallic allotropes beyond any question.

Evidence of the allotropism of lead has been adduced by Heller[4] who observed that when a piece of freshly cast, pure lead was immersed in a solution of lead acetate, acidified with nitric acid, it gradually underwent transformation into a gray modification, the change being complete in about three weeks. This gray modification was found to be brittle

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much confusion. Electrical measuring instruments as now manufactured are calibrated in international ohms and not in Siemen's ohms. In the paper of Watkins and Jones references are given to numerous other papers from the Johns Hopkins Laboratory in which Siemen's units are used. In the most recent article (Lloyd, Wiesel and Jones, THIS JOURNAL, 38, 121 (1916)) the conductances are presumably in Siemen's units although it is not so stated by the authors. In general, investigators both here and abroad use international ohms.

[1] Getman, *Trans. Am. Electrochem. Soc.*, 26, 67 (1914).

[2] Getman and Gibbons, THIS JOURNAL, 37, 953 (1915).

[3] Cohen, *Verslag Akad. Wetenschappen*, 16, 485, 565, 628, 632, 807 (1913–14); 17, 54, 59, 60, 122, 200 (1914); 23, 754, 896 (1914); 23, 1220 (1915); 18, 91 (1915); *Z. physik. Chem.*, 85, 419 (1913); 87, 409, 419, 426, 431 (1914); 89, 493, 728, 733, 742, 748, 757 (1915); *Trans. Faraday Soc.*, 10, 216 (1915).

[4] *Z. physik. Chem.*, 89, 761 (1915).

and easily reduced to a powder by pressure between the fingers. He also pointed out that the change takes place in solutions of lead nitrate and lead chloride, and that the transformation is accelerated by the addition of a small amount of nitric acid.

Furthermore, there is no change if lead is immersed in solutions of nitric acid, acetic acid or sodium acetate alone, thus proving that the transformation into the gray modification is due to the lead ions furnished by the lead salt. In a private communication to Prof. Cohen, Heller described an experiment in which a solution of lead acetate, acidified with nitric acid, was electrolyzed between lead electrodes in order to obtain a lead tree. After standing for three weeks, the electrodes were found to have crumbled to a grayish powder.

Upon inoculating a piece of freshly cast pure lead with some of the powder obtained in this experiment and immersing it in an acidified solution of lead acetate, Heller observed that the plate underwent rapid disintegration.

These results have since been confirmed by Cohen and Helderman[1] and also by the author.

Cohen and Helderman also noted that it is possible to produce a lead tree by immersing pure metallic lead in an acidified solution of lead acetate or in a 30% solution of lead nitrate, the rapidity of growth being increased by rise of temperature.

Similar results have recently been obtained by Creighton[2] by electrolyzing a solution of nitric acid (sp. gr. 1.42) between lead electrodes, employing a current of N. D_{100} = 12.5 amperes at 6 volts. At the end of eight hours, when the current was stopped, an examination of the cathode showed that it had lost the characteristic properties of lead and had become transformed into a gray mass which could be easily powdered between the fingers. This modification of lead appears to be identical with that obtained by Heller and Cohen.

The investigations of Cohen and Helderman[3] with the pycnometer and the dilatometer make it appear highly probable that more than two allotropic modifications of lead are present in freshly cast specimens of the metal. This is shown by the following data taken from Cohen's papers: The density of a freshly cast specimen of lead was found to be $d_{4^\circ}^{25^\circ} = 11.324$. The metal was then immersed in Heller's solution (400 g. lead acetate in 1000 cc. of water to which is added 100 cc. of nitric acid (sp. gr. 1.16)) and allowed to stand for three weeks at a temperature of 15°. The density was now found to have *increased* to 11.341. On repeating the experiment at 50° and allowing the metal to remain immersed

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[1] *Verslag Akad. Wetenschappen,* 17, 822 (1915).

[2] Creighton, THIS JOURNAL, 37, 2064 (1915).

[3] *Loc. cit.*

in the solution for five days, the density *decreased* to 11.313. Further immersion in the solution for six days at 25° caused the density to *increase* to 11.328. The following results were obtained by Cohen with the dilatometer: At 50.8° there was a *fall* of 700 mm. in 34 hours, whereas at 74.4° there was a *rise* of 275 mm. in $2^3/_4$ hours. In view of these results it seemed highly probable that electrodes of freshly cast lead would be more or less unstable and that, as in our previous work on copper and cadmium, a constant and reproducible lead electrode must be sought in a form of the metal which is stable under ordinary laboratory conditions.

Outline of Method.

Numerous galvanic combinations have been employed in studying the electromotive behavior of lead, but the one which seemed to be best adapted to the present problem is the following:

$$\overset{-}{\text{Pb}} - \text{sat. sol. PbCl}_2 \parallel 0.1\ N\ \text{KCl, HgCl} - \overset{+}{\text{Hg}}$$

A cell very similar to this was used by Abegg and Labendzinski[1] in an investigation of the constitution of salts, the lead electrode consisting of an electrolytic deposit of lead on a platinum wire and the calomel electrode being made up with N KCl. The electromotive force of the cell at room temperature was found to be 0.456 volt.

In the present investigation the lead electrode was prepared in a variety of different ways, with a view to determining the most constant and reproducible form. The study of the electrochemical behavior of the different lead electrodes was supplemented by microscopical examination as in our previous work on cadmium electrodes.

Preparation of Materials.

The lead used in this investigation was obtained from two different but equally reliable firms. It was purified with great care and its purity was tested by spectroscopic examination with a Hilger spectrograph. The only foreign metal which could be detected was a trace of molybdenum. The saturated solution of lead chloride was prepared by precipitating a solution of pure lead nitrate with hydrochloric acid, washing by decantation with cold distilled water until nearly free from acid and then finally washing on the filter with 95% alcohol. The lead chloride so obtained was transferred to a bottle and shaken with distilled water at 25°, thus insuring a saturated solution at the temperature at which the electromotive measurements were to be carried out. The calomel electrode was prepared in the usual manner, care being taken to use only the purest materials and to secure a 0.1 N KCl solution completely saturated with calomel.

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[1] *Z. Elektrochem.*, **10**, 77 (1904).

Apparatus.

The measurements of electromotive force were made by the familiar compensation method, using a Wheatstone bridge and enclosed type of capillary electrometer sensitive to 0.0001 volt as a null instrument.

The standard cell used was of the Weston type and was frequently compared with a cell recently standardized by the Bureau of Standards. All comparisons of the Weston cell with the laboratory standard cell were made by means of a potentiometer reading to 0.00001 volt.

The experimental cell was similar to that used by Gibbons and Getman[1] in their study of nonaqueous solutions of silver nitrate.

The lead electrodes were prepared in five different ways, as follows: (1) Casting the purified lead in sticks 3 mm. in diameter and 7 cm. long; (2) amalgamating cast stick electrodes; (3) depositing lead electrolytically on spirals of platinum wire; (4) depositing lead electrolytically on cast stick electrodes; and (5) immersing stick electrodes in an acidified solution of lead acetate (Heller's solution).

The amalgamated electrodes were obtained by rubbing mercury over the lead sticks with a piece of filter paper.

Considerable difficulty was experienced in securing an adhesive deposit of lead on the platinum spirals. After trying various methods, very satisfactory results were obtained by using, as an electrolytic bath, a 10% solution of lead nitrate containing 5% glacial acetic acid and 1% of Barbadoes aloes, as recommended by Mathers and McKinney.[2] The platinum spirals were made by coiling 3 cm. of No. 28 wire (B. and S. gauge) around the apex of a filter cone and then flattening the resulting conical spiral on a plane surface. Each of these spirals was made, in turn, the cathode of an electrolytic cell, in which a piece of pure lead served as the anode. A current of 20 milliamperes at 2 volts was passed for 30 minutes, at the end of which time a gray adherent deposit of lead was obtained. The same procedure was followed in depositing lead electrolytically upon the lead sticks.

All of the volumetric apparatus employed was carefully calibrated. The temperature of the cells was maintained constant to within 0.01° by means of an electrically heated thermostat having a capacity of 55 liters.

Experimental Results.

Two entirely independent series of experiments were carried out in the investigation of the electromotive behavior of lead. The materials used in making up the cells for the two series were derived from different sources and were subjected to separate processes of purification. In

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[1] THIS JOURNAL, **36**, 1645 (1914).

[2] *Trans. Am. Electrochem. Soc.*, **27**, 131 (1915).

Tables I, II, III, IV and V are given the results obtained with cells made up according to the following scheme:

$$\overset{-}{\text{Pb}} - \text{sat. sol. PbCl}_2 \,\|\, 0.1\ N\ \text{KCl, HgCl} - \overset{+}{\text{Hg}}$$

TABLE I.—FRESHLY CAST ELECTRODE.

T. (hrs.).	E. M. F. volt.
..	0.5206
2.5	0.5203
3.5	0.5201
4.0	0.5194
23.5	0.5198
24.0	0.5204
27.0	0.5210
28.0	0.5203
46.0	0.5196
Mean,	0.5202

TABLE II.—AMALGAMATED ELECTRODE.

T. (hrs.).	E. M. F. volt.
...	0.5178
0.75	0.5191
3.0	0.5196
4.0	0.5177
5.0	0.5188
24.5	0.5186
27.25	0.5134
72.0	0.5183
Mean,	0.5186

TABLE V.—ELECTROLYTIC LEAD ON PLATINUM.

T. (hrs.).	E. M. F. volt.
...	0.5221
0.5	0.5216
1.0	0.5228
2.25	0.5236
19.0	0.5219
20.25	0.5214
21.25	0.5223
24.0	0.5216
25.5	0.5221
41.5	0.5204
45.75	0.5214
50.0	0.5201
65.5	0.5225
Mean,	0.5218

TABLE III.—ELECTROLYTIC LEAD ON LEAD

T. (hrs.).	E. M. F. volt.
..	0.5231
0.5	0.5222
1.0	0.5226
3.0	0.5227
4.5	0.5224
23.0	0.5226
Mean,	0.5226

TABLE IV.—STICK ELECTRODE IMMERSED FOR 17 DAYS IN HELLER'S SOLUTION.

T. (hrs.).	E. M. F. volt.
...	0.5327
0.25	0.5302
1.00	0.5301
17.75	0.5306
20.0	0.5301
22.5	0.5327
Mean,	0.5310

TABLE VI (FIRST SERIES).

Freshly cast electrodes.

Observations.	Time (hrs.).	E. M. F. volt.
10	46.0	0.5202
7	24.0	0.5194
7	24.5	0.5190
	Mean,	0.5195

Lead on lead electrodes.

Observations.	Time (hrs.).	E. M. F. volt.
6	23.5	0.5217
6	23.0	0.5226
	Mean,	0.5221

Amalgamated electrodes.

Observations.	Time (hrs.).	E. M. F. volt.
8	28.5	0.5204
10	29.7	0.5170
8	72.0	0.5186
	Mean,	0.5187

Lead on platinum.

Observations.	Time (hrs.).	E. M. F. volt.
6	48.0	0.5212
5	23.5	0.5218
	Mean,	0.5215

Stick electrodes treated with Heller's soln.

Observations.	Time (hrs.).	E. M. F. volt.
12	95.5	0.5252[1]
9	52.75	0.5283[1]
11	114.4	0.5277[1]
9	71.0	0.5267[2]
10	96.0	0.5271[3]
6	335.5	0.5239[4]
	Mean,	0.5265

[1] 3 weeks' immersion in Heller's solution.

[2] 6 days' immersion in Heller's solution.

[3] 8 days' immersion in Heller's solution.

[4] Electrode cast from lead disintegrated by Heller's solution.

The character of the lead electrode was varied as indicated in each table. The temperature at which all of the cells were maintained was 25° ± 0.01°. In the first column of the tables is given the interval of time, T, which elapsed since the initial measurement at the moment when the cell was immersed in the bath, and in the second column is given the electromotive force. The probable error of these measurements is about 0.1%.

A summary of the results of the two series of experiments is given in Tables VI and VII.

TABLE VII (SECOND SERIES).

Freshly cast electrodes.			Lead on platinum.			Electrodes treated with Heller's soln.		
Observations.	T. (hrs.).	E. M. F. volt.	Observations.	T. (hrs.).	E. M. F. volt.	Observations.	T. (hrs.).	E. M. F. volt.
8	69.25	0.5183	9	27.75	0.5221	10	51.0	0.5200[1]
10	42.25	0.5200	10	74.5	0.5218	7	43.5	0.5274[1]
			13	65.5	0.5218	6	21.0	0.5193[2]
	Mean,	0.5192		5.9	0.5218	6	22.0	0.5310[3]
						8	20.1	0.5304[4]
				Mean,	0.5219			
							Mean,	0.5256

Discussion of Results.

An examination of the foregoing tables brings out the fact that while there is very little difference between the potentials of the five types of lead electrode studied, yet the most constant and reproducible is the electrode formed by deposition of lead on platinum. Contrary to our expectation the widest variation occurred with the lead sticks which had been immersed for different periods of time in Heller's solution. The experiments would seem to indicate that immersion in Heller's solution tends to make the lead electrode more negative. The change in potential, however, is not proportional to the time of immersion, as is shown by the experiment of Series II where an electromotive force of 0.5304 volt was obtained after eleven days' immersion in Heller's solution, whereas an immersion of three weeks in Series I developed an electromotive force of only 0.5283 volt.

The electromotive force of cells in which the lead electrode had been immersed in Heller's solution almost invariably diminished rapidly and came to constancy at about 0.5220 volt. The subjoined table gives a series of typical results.

TABLE VIII.

T. (minutes)	0	10	20	40	50	60
E. M. F. volt................	0.5304	0.5252	0.5232	0.5224	0.5220	0.5220

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[1] 1 week's immersion in Heller's solution.

[2] 3 days' immersion in Heller's solution.

[3] 17 days' immersion in Heller's solution.

[4] 11 days' immersion in Heller's solution.

On representing the data of this table graphically, plotting time on the axis of abscissae and logarithms of electromotive force on the axis of ordinates, it was found that the relationship between these two variables was not rectilinear, as should be the case if the change in electromotive force were due to the transition of one modification of lead into the other.

Furthermore, if the gray modification of lead is stable at ordinary temperatures, there should be no change in the electromotive force of a cell of which it forms a part.

In his recent lecture before the Faraday Society, Cohen[1] says:

> "It is generally known that when a bar of any metal which is more electronegative than lead is suspended in a solution of a lead salt, the lead is thrown out of solution and a lead tree is formed."

He then states that the same phenomenon occurred when a stick of pure lead was placed in Heller's solution or in a neutral solution of lead nitrate, the tree being formed within a few days at room temperature or more rapidly at higher temperatures. If the gray form of lead which separates on the surface of a stick of pure lead when immersed in Heller's solution, is identical with Cohen's lead tree, and hence is more positive than the freshly cast metal, then the electromotive force of a cell in which the gray modification forms the negative electrode should be less than the electromotive force of a cell in which the negative electrode consists of freshly cast lead. The results given in Tables VI and VII fail to confirm this prediction based on Cohen's statement, and furthermore, all of the attempts made with the lead used in these experiments to develop a tree in Heller's solution or in a solution of lead nitrate have failed. Additional experiments on cells involving the gray modification of lead were made with the following combination:

$$\text{Pb (freshly cast)} — 0.2\ N\ \text{Pb(NO}_3)_2 — \text{Pb (gray)}$$

The gray electrode was formed by immersing a freshly cast stick of lead in Heller's solution for two weeks. According to the data of Tables VI and VII, the electromotive force of such a cell at 25° should be about 7 millivolts, the current flowing outside of the cell from the freshly cast to the gray electrode. In Table IX is given the results of one of several experiments made with the above cell, a sensitive potentiometer having been employed to measure the minute electromotive forces developed.

TABLE IX.

Temp. 25°.

T. (hrs.)..........	0	0.5	1	2	3	4	5	6	7.5	9.5	21.5
E. M. F. millivolts	5.065	1.775	1.415	1.170	1.090	1.003	0.760	0.555	0.292	—0.068	—0.125

The initial value of the electromotive force is about 2 millivolts less than the predicted value, but this discrepancy may be ascribed to the rapidity with which the electromotive force is falling. It will be noticed that

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[1] *Loc. cit.*

after nine hours the polarity of the cell underwent a reversal, which suggests that a transition may have taken place in one of the electrodes. Unfortunately, attempts to duplicate these results proved quite fruitless and experiments of a similar nature carried out at the temperature of melting ice failed to reveal any change in the relative stability of the two forms of lead. In some cases rapid reversals of the polarity of the cell occurred, but this phenomenon is probably connected with surface strains in the freshly cast electrode.

On repeating the experiments with electrolytic lead electrodes the results were quite as unsatisfactory as when freshly cast sticks were employed. Thus, it is evident that. until some definite knowledge is obtained as to the limits of stability of the allotropic forms of lead and methods are developed for their isolation in a pure form, the exact value of the potential of a lead electrode, reproducible and constant at ordinary temperatures, cannot be obtained. The foregoing experiments indicate, nevertheless, that when lead is deposited electrolytically on platinum a *practically* reproducible and constant electrode is secured.

From the data of Tables VI and VII it is possible to compute the normal potential of the lead electrode. According to Nernst, the relationship between the potential of a single electrode and the concentration of the electrolyte is given by the equation

$$E_p = E - \frac{RT}{nF} \log_e C\alpha,$$

where E_p is the difference of potential between the electrode and a normal solution of ions furnished by the electrode, E the potential of the electrode in the given cell, C the concentration of the electrolyte, α the degree of ionization of the electrolyte, R the gas constant, T the absolute temperature, n the valence of the ion furnished by the electrode and F the faraday equivalent = 96,540 coulombs.

From the data compiled by Boettger[1] for difficultly soluble salts we obtain the following values for the normal concentration of a saturated solution of lead chloride and its degree of ionization: $C = 0.0692$ and $\alpha = 0.956$. Although these values were obtained at 18° it may be assumed that the corresponding data for 25° will not differ enough to prohibit their use in calculating the normal electrode potential of lead.

Since the potential of the calomel electrode with 0.1 *N* KCl at 25° is 0.6186 volt, the potential of the lead electrode is 0.6186 — 0.5217 = 0.0969 volt. Substituting in the above equation, we have

$$\begin{aligned} E_p &= 0.0969 - \frac{0.0591}{2} \log_{10} (0.0692 \times 0.956) \\ &= \mathit{0.1318} \text{ volt at } 25^\circ. \end{aligned}$$

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[1] *Z. physik. Chem.*, **46**, 521 (1903).

The value of the normal electrode potential of lead as given by the Deutsche Bunsen Gesellschaft is *0.129* volt at 18°.

The electrodes used in the preceding experiments were examined microscopically and numerous photomicrographs were made to facilitate further study of surface characteristics, particular attention being given to lead immersed in Heller's solution. The rapidity with which a piece of freshly cast lead undergoes transformation into the gray modification is well illustrated by the accompanying photomicrographs. Owing to the difficulty of securing a polished lead surface, the molten metal was cast in a mold, the bottom of which consisted of a piece of steel polished to a plane surface. In this way it was possible to secure a satisfactory mirror-like surface of lead. In Fig. 1 is shown such a surface under a magnification of 190 diameters. This piece of lead was then immersed in Heller's solution and allowed to stand at room temperature for twenty-four hours. It was then removed, washed in distilled water, dried with alcohol and ether, and reëxamined under the microscope. The change in its appearance is well shown by Fig. 2. The piece of lead was then replaced in the solution and, at frequent intervals, was removed in order that the change in the character of its surface might be observed under the microscope. The appearance of the same surface after an immersion of thirty-four days is shown in Fig. 3. The lack of

Fig. 1.—Mag. 190.

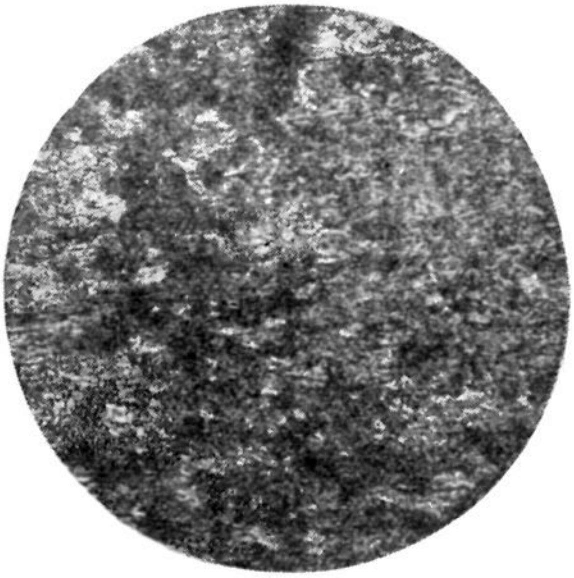

Fig. 2.—Mag. 190.

Fig. 3.—Mag. 190.

sharpness of definition in this photomicrograph is due to the fact that the surface was no longer plane, the solution having affected a greater transformation at some points of the surface than at others. These photomicrographs are of interest in connection with the photographs taken by Cohen[1] of the same phenomenon. While Cohen's photographs are natural size and hence do not reveal the rapidity with which the transformation into the gray modification of lead occurs, yet they bring out more satisfactorily than photomicrographs the extent of the disintegration.

Summary of Results.

(1) Five different types of lead electrode have been studied in a cell made up in the following manner:

$$\overset{-}{\mathrm{Pb}} \text{ — sat. sol. } \mathrm{Pb(NO_3)_2} \; || \; 0.10\ N\ \mathrm{KCl,\ HgCl} \text{ — } \overset{+}{\mathrm{Hg}}$$

Of these five electrodes the only one which proved to be constant and reproducible to within 0.3 millivolt was that in which the lead was deposited electrolytically on platinum.

(2) Freshly cast sticks of lead, after immersion for varying periods of time in an acidified solution of lead nitrate, lost their ductility and other properties commonly associated with lead. The gray mass thus obtained undoubtedly is an allotropic modification of the metal.

(3) Measurements of the electromotive force developed at 0° and 25° by cells in which freshly cast lead and the gray modification formed the electrodes and 0.2 N $Pb(NO_3)_2$ served as the electrolyte, failed to give any positive indication of a transition temperature.

(4) A calculation of the normal electrode potential of lead was made from the mean value of the electromotive force of cells involving a constant and reproducible lead electrode. The value of this potential was found to be *0.1318* volt at 25°.

(5) The electrodes were examined under the microscope and photomicrographs were made to show the rapidity with which freshly cast lead undergoes transformation when immersed in a solution of acidified lead nitrate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, NO. 262.]

THE DISSOCIATION PRESSURES OF MERCUROUS CHLORIDE.

BY ALEXANDER SMITH AND ROBERT PEYTON CALVERT.

Received February 14, 1916.

The vapor pressures of calomel, over limited ranges of temperature, have been studied by Wiedemann, Stelzner, and Niederschulte[2] and by

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[1] *Trans. Faraday Soc.*, 10, 228 (1915).

[2] *Ber. deut. physik. Ges.*, 3, 159 (1905).