as here used. It also appears that the hot oxide when transferred in the air absorbs enough carbon dioxide to vitiate the results. From the experimental data obtained it seems quite evident that the oxide-chloride ratio cannot be applied to dysprosium by the methods thus far tried. The ratio is accordingly being abandoned in favor of the chloride-silver ratio which has given good results in this laboratory.

10. Summary.

1. Dysprosium material already in a high state of purity was further fractionated as the ethyl sulfates and the bromates. The ethyl sulfates were found to be more efficient for the separation of dysprosium from neodymium, praseodymium and terbium. Neither of the two methods was found efficient for the separation of dysprosium from holmium.
2. The hydrate $Dy_2(SO_4)_3.8H_2O$ was not found to be constant in composition when dried over sulfuric acid.
3. The ratio $Dy_2O_3 : DyCl_3$ was further studied. The value 163.83 as the atomic weight was obtained as the mean of 9 determinations. A study has been made to account for the difference of this value and that of a higher value (164.228) obtained in a previous investigation.
4. In studying the ratio $DyCl_3 : 3\ Ag$ the value 162.52 was obtained as the mean of 8 determinations. A comparative study of the two values has been made to account for the difference in the values obtained by the two methods.
5. The dysprosium oxide as prepared for the oxide-chloride ratio by ignition of the oxalate was found to contain some carbonate. Several different methods for preparing a pure oxide were tried but by no method could concordant results be obtained by the oxide-chloride ratio.
6. The results obtained by the oxide-chloride ratio are accordingly discarded in favor of the results (162.52) obtained by the chloride-silver ratio.

URBANA, ILL.

THE LEAD ELECTRODE.

[SECOND COMMUNICATION.]

BY FREDERICK H. GETMAN.

Received January 28, 1918.

Since the publication of a previous paper[1] on the lead electrode some doubt has arisen as to whether lead really exhibits the phenomenon of allotropy.[2] If the metal does exist in more than one form, each modification should possess its own specific potential, and a careful study of the electromotive behavior of lead electrodes prepared in various different ways should afford valuable evidence as to whether or not allotropes exist.

---

[1] Getman, THIS JOURNAL, 38, 792 (1916).

[2] Lewis and Brighton, *Ibid.*, 39, 1906 (1917).

With this end in view and also with a view to determining the normal potential of the lead electrode, the following investigation was undertaken:

Method of Investigation.

In studying the electromotive behavior of lead, the following system was employed:

$$\overset{-}{\mathrm{Pb}} \mid 0.1\,M\ \mathrm{KCl\ sat.\ with}\ \overset{\longleftarrow}{\mathrm{PbCl_2}} \parallel 0.1\,M\ \mathrm{KCl,\ Hg_2Cl_2} \mid \overset{+}{\mathrm{Hg}}$$

The direction of the current outside of the cell is indicated by the arrow. All measurements, except those involved in the determination of the temperature coefficient of the cell, were made at 25°.

Purification of Materials.

Potassium Chloride.—A high grade specimen of potassium chloride which had previously been twice recrystallized from conductance water, was subjected to three successive recrystallizations.

Lead Chloride.—A solution of recrystallized lead nitrate was precipitated with a solution of pure hydrochloric acid with constant stirring. After washing the precipitate nearly free from acid with cold water, it was dissolved in boiling distilled water and allowed to crystallize from solution. The crystals of lead chloride were thoroughly dried and preserved in a desiccator.

Mercury.—Redistilled mercury was washed by repeated spraying through a column of nitric acid (1 : 10) after which it was redistilled by Hulett's method.

Mercurous Chloride.—Pure mercury[1] was dissolved in a deficiency of freshly distilled nitric acid. The solution was poured into a dilute solution of nitric acid and the calomel precipitated by the addition of a solution of pure hydrochloric acid. The calomel was washed repeatedly by decantation with hot water for several hours and then transferred to a filter where the washing was continued until the wash water failed to give an acid reaction. After being dried at 110°, it was preserved in dark bottles.

Lead.—The specimens used were obtained from several different sources and were found to be of a very high degree of purity.

Water.—Ordinary distilled water was used in the early stages of the purification of the materials, while conductance water was employed in all of the final recrystallizations and also in the preparation of all solutions. This latter was prepared by the method of Kendall[2] and in no instance was the conductance found to exceed 3×10^{-6} reciprocal ohms at 25°.

Apparatus.

The measurements of electromotive force were made by means of a Leeds and Northrup potentiometer in conjunction with a sensitive galvanom-

---

[1] Loomis and Acree, *Am. Chem. J.*, **46**, 596 (1911).

[2] Kendall, THIS JOURNAL, **38**, 2463 (1916).

eter and a Weston cell recently certified by the Bureau of Standards. All temperatures were measured by means of a thermometer which had previously been carefully compared with a thermometer calibrated by the Physikalische Reichsanstalt.

Preparation of Cells.

Two different types of cell were employed: (*a*) an ordinary H cell, and (*b*) a cell in which diffusion between the calomel and lead electrode compartments could be prevented by means of a stopcock.

The H form of cell was used almost entirely for the study of lead amalgams. Before introducing the solutions, a loose plug of absorbent cotton was placed in the horizontal portion of the cell to minimize diffusion. Into one arm of the cell, mercury, calomel paste and 0.1 M potassium chloride saturated with calomel were introduced in the order mentioned, thus forming a 0.1 M calomel electrode. Into the other arm of the cell a weighed amount of mercury was introduced and then, after adding sufficient saturated solution of lead chloride in 0.1 M potassium chloride to fill the arm up to the horizontal connecting tube, a slow current of pure hydrogen was bubbled through the solution to displace dissolved air. After the gas had been passed through the solution for 10 minutes the requisite weight of pure lead to give an amalgam of the desired concentration was added and the passage of the gas was continued for another interval of 10 minutes. This procedure prevented any oxidation of the amalgam. Connection with the calomel electrode and the amalgam was established by means of platinum wires sealed into glass tubes in the usual manner.

The other type of cell, in addition to the stopcock already mentioned, was furnished with a side tube and stopcocks so that a fresh surface of contact between the solutions could easily be established when desired. The connecting tubes were of sufficiently large bore to eliminate the disturbing capillary effects pointed out by Cumming.[1]

Two calomel electrodes made up from carefully purified materials obtained from different sources, were connected in succession with the half-element containing the Pb electrode.

The saturated solution of lead chloride in 0.1 M potassium chloride was obtained by agitating an excess of finely crystallized lead chloride with 0.1 M potassium chloride at 25° for 48 hours. Two portions of the solution were then removed and the content of lead chloride determined with the following results: 16.98 and 16.91 millimols per liter. These values are in good agreement with those previously found by Noyes[2] and Von Ende,[3] *viz.*, 16.97 and 16.90 millimols per liter.

---

[1] Cumming, *Trans. Faraday Soc.*, **8**, 86 (1913).

[2] Noyes, *Z. phys. Chem.*, **9**, 623 (1892).

[3] Von Ende, *Z. anorg. Chem.*, **26**, 151 (1901).

Experimental Data.

The results obtained with fifteen different lead electrodes are given in the following tables:

TABLE I.

$$\text{E. M. F.}\quad \text{Pb} \left| \begin{matrix} 0.1\,M & \text{KCl.} \\ \text{Sat.} & \text{PbCl}_2. \end{matrix} \right\| \begin{matrix} 0.1\,M & \text{KCl} \\ \text{Sat} & \text{Hg}_2\text{Cl}_2 \end{matrix} \left| \ \text{Hg.} \right.$$

No. of electrode.	Untreated electrodes. E. M. F.
1	0.5383
2	0.5402
3	0.5383
4	0.5394
5	0.5396
6	0.5395
7	0.5394
8	0.5403
9	0.5388
10	0.5392
11	0.5391
Mean,	0.5393
	Treated electrodes.
12	0.5443
13	0.5472
14	0.5513
15	0.5489
Mean,	0.5479

Electrodes 1, 3, 4 and 5 were cast from the same sample of pure lead, while electrode 2 was cast from an exceptionally pure specimen of lead prepared especially for this investigation. All of the cast electrodes were scraped with a glass plate to remove any film of oxide before placing them in the cells. Electrodes 6, 7 and 8 were prepared by depositing lead electrolytically upon platinum spirals from a solution of recrystallized lead acetate acidified with acetic acid. The weight of the deposits varied from 0.0039 g. to 0.0078 g.

Electrodes 9, 10 and 11 consisted of lead amalgams containing approximately 0.75% of lead. The potentials of these amalgams against a stick of pure lead are given in Table II.

TABLE II.

$$\text{E. M. F.}\quad \text{Pb amalg.} \left| \begin{matrix} 0.1\,M & \text{KCl.} \\ \text{Sat.} & \text{PbCl}_2. \end{matrix} \right| \ \text{Pb.}$$

No. of electrode.	Untreated electrodes. E. M. F.
9	0.0111
10	0.0104
11	0.0132

The values of the e. m. f. given in Table II were added to the corresponding values of the e. m. f. of the amalgam cells to obtain the data recorded in Table I for electrodes 9, 10 and 11. Electrodes 12, 13, 14 and 15 were cast from pure lead and were then immersed in Heller's solution for different periods of time. This solution, consisting of 400 g. of lead acetate in 1000 cc. of water to which has been added 100 cc. of nitric acid (sp. gr. 1.16), has been shown by Heller[1] and Cohen[2] to promote the transformation of lead into the modification which is stable at room temperature. The times of immersion of the electrodes were as follows: No. 12, 21 days; No. 13, 14 days; Nos. 14 and 15, 25 days. Before introducing these electrodes into the cell, they were washed in dilute nitric acid, then in conductance water and finally in 0.1 *M* potassium chloride.

The variations of the values of the e. m. f. given in Table I for untreated electrodes are so small that we may conclude that the potential of the electrode is independent of its form, *i. e.,* that whether the metal is cast, deposited electrolytically or dissolved in mercury the value of the e. m. f. will remain the same. On the other hand, the values recorded for treated electrodes not only show a greater variation among themselves, but for each electrode, the corresponding value of the e. m. f. is appreciably higher than any of the values given for untreated electrodes. The mean value of the e. m. f. for cells in which the lead electrode had been treated with Heller's solution was over 8 millivolts higher than the mean e. m. f. of cells in which the lead electrode had not been so treated.

Lewis and Brighton[3] point out that notwithstanding the fact that some of the lead sticks which they used were at least 6 years old they failed to show any difference of potential when measured against a freshly deposited lead tree. This observation is confirmed by the present series of experiments: electrodes 1, 3, 4 and 5 were about 4 years old and yet the value obtained with these are in close agreement with the values obtained with the electrolytically deposited electrodes 6, 7 and 8. As Cohen has frequently pointed out, a metal may remain in a metastable condition for years without undergoing any perceptible transformation, but when placed in a sufficiently concentrated solution of one of its salts the transformation takes place in a relatively short time.

It will be observed that the e. m. f. of cells containing lead electrodes which have been immersed in Heller's solution increases with the time of immersion of the electrode. Not only does the potential of the metal increase with the time of immersion but there is a gradual loss of pliability until at the end of 3 weeks the lead has become decidedly brittle.

Calculation of the Normal Electrode Potential of Lead.

The normal electrode potential of lead may be calculated by the familiar formula

---

[1] Heller, *Z. phys. Chem.*, 89, 761 (1915).

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

[3] *Loc. cit.*

$$\mathbf{E}^\circ = (\mathbf{E} - 0.0529) + \frac{RT}{nF} ln\, c$$

where **E** denotes the observed e. m. f. of the cell, c the concentration of Pb^{++} in the solution of lead chloride and where 0.0529 is the difference of potential between the tenth normal and the normal electrode.[1] The remaining symbols in the equation have their usual significance.

The solubility of lead chloride at 25° is 0.0388,[2] and the corresponding degree of ionization is 0.58.[3]

Hence the solubility product of lead chloride $= 0.022504 \times (2 \times 0.022504)^2 = 0.0000456$.

The degree of ionization, $\alpha_{25}{}^\circ$, for 0.1 M potassium chloride is 0.78,[3] hence

$$c = \frac{0.0000456}{(2 \times 0.0225 + 0.078)} = 0.003013.$$

Substituting this value of c in the formula for the normal electrode potential, we have

$$\begin{aligned}\mathbf{E}^\circ &= (0.5393 - 0.0529) - 0.0295 - \log \frac{1}{0.003013} \\ &= \mathit{0.4121} \text{ volt.}\end{aligned}$$

This result is in close agreement with that of Lewis and Brighton who found the normal electrode potential of lead to be 0.4125 volt. If we take the potential of the normal calomel electrode to be —0.2828 volt against the normal hydrogen electrode as zero,[4] then the normal potential of the lead electrode referred to the hydrogen electrode will be *0.1293* volt.

The normal potential of the lead electrode as recently determined by Henderson and Stegeman[5] is 0.4696 volt against the tenth-normal calomel electrode. Recalculating this result in terms of the normal calomel electrode we obtain 0.4168 volt, a value appreciably higher than that obtained by Lewis or than that obtained in the present investigation.

Temperature Coefficient and Thermal Data.

By determining the temperature coefficient of the cell

$$Pb \mid PbCl_2,\ 0.1\ M\ KCl \parallel 0.1\ M\ KCl,\ Hg_2Cl_2 \mid Hg$$

and substituting the value of dE/dT thus found in the Gibbs-Helmholtz equation

$$\mathbf{E} = \frac{Q}{nF} + T\frac{dE}{dT}$$

---

[1] Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2255 (1917).

[2] Von Ende, *Loc. cit.*

[3] Lewis and Brighton, *Ibid.*

[4] Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2259 (1917).

[5] Henderson and Stegeman, *Ibid.*, 40, 89 (1918).

the heat of the reaction $Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$ can be readily calculated.

The mean e. m. f. of the cell at 20° was found to be 0.5382 volt and hence the value of dE/dT is 0.00022. Substituting in the Gibbs-Helmholtz equation and solving for Q, we have

$$\begin{aligned} Q &= 2 \times 96500 \times 0.2389(0.5393 - 298 \times 0.00022) \\ &= 21840 \text{ cal.} \end{aligned}$$

This result is in close agreement with the value recently found by Günther,[1] namely 21800 cal.

The heat of formation of mercurous chloride has been determined calorimetrically by both Nernst[2] and Varet[3] who obtained identical results, namely 62600 cal. By combining the preceding thermochemical data, the heat of formation of lead chloride can be calculated in the following manner:

$$\begin{array}{l} Pb + Hg_2Cl_2 = PbCl_2 + 2Hg + 21840 \text{ cal.} \\ \underline{2Hg + Cl_2 = Hg_2Cl_2 + 62600 \text{ cal.}} \\ Pb + Cl_2 = PbCl_2 + 84440 \text{ cal.} \end{array}$$

This result agrees well with the following values obtained by direct calorimetric measurement: 83900 cal. (Berthelot), 82800 cal. (Thomsen), and 85570 cal. (Braune and Koref).[4]

Günther[5] from a study of the cell $Pb \mid PbCl_2$ sat. $\| Hg_2Cl_2 \mid Hg$ obtained 85380 cal. for the heat of formation of $PbCl_2$, while Lewis and Brighton obtained 84000 cal. On the other hand, W. C. Lewis[6] employing Haber's equation[7]

$$Q = Nh\,(\Sigma\nu_{\text{resultants}} - \Sigma\nu_{\text{reactants}}),$$

where N is the number of molecules in 1 gram molecule, h the familiar Planck constant, and ν the critical frequency of any given molecular species entering into the reaction, finds the heat of formation of one-gram molecule of lead chloride to be 77660 cal.

The equation of Nernst and Lindemann[8] may be employed to calculate the heat of reaction, U_0, and from this the maximum work A at any desired temperature may be derived. Thus, on integrating the Nernst-Lindemann equation

$$\Sigma nC_p = \frac{dU}{dT} = {}^3/_2 R\Sigma n \left[\frac{(\beta\nu/T)^2 e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} + \frac{(\beta\nu/2T)^2 e^{\beta\nu/2T}}{(e^{\beta\nu/2T} - 1)^2}\right] + \Sigma nkT^{3/2}, \quad (1)$$

---

[1] Günther, *Z. Elektrochem.*, **23**, 197 (1917).

[2] Nernst, *Z. phys. Chem.*, **2**, 23 (1888).

[3] Varet, *Ann. chim. phys.*, 8, 102 (1896).

[4] Braune and Koref, *Z. Elektrochem.*, **18**, 818 (1912).

[5] *Loc. cit.*

[6] W. C. Lewis, *J. Chem. Soc.*, **112**, 1086 (1917).

[7] Haber, *Ber. Deutsch. physik. Ges.*, **13**, 1117 (1911).

[8] Nernst and Lindemann, *Sitz. Preuss. Akad. Berlin*, 1160 (1912).

we have

$$U = U_\circ + {}^3/_2 R\Sigma n \left[\frac{\beta\nu}{(e^{\beta\nu/T} - 1)} + {}^1/_2 \frac{\beta\nu}{(e^{\beta\nu/2T} - 1)}\right] + {}^2/_5 \Sigma nkT^{5/2}, \quad (2)$$

whence we obtain

$$A = U_\circ + {}^3/_2 R\Sigma n\, [ln(e^{\beta\nu/T} - 1) - ln(e^{\beta\nu/2T} - 1)] - {}^9/_4 R\Sigma n - {}^4/_{15}\Sigma nkT^{5/2}. \quad (3)$$

At 234° A. mercury solidifies so that not only must its heat of fusion, L, be taken into account in our calculations but also the mean specific heat c of liquid mercury from 298° A. to its freezing point. Introducing these additional terms, Equation 2 becomes

$$U_{298^\circ} = U_\circ + {}^3/_2 R\Sigma n \left[\frac{\beta\nu}{(e^{\beta\nu/T} - 1)} + {}^1/_2 \frac{\beta\nu}{(e^{\beta\nu/2T} - 1)}\right] + {}^2/_5 \Sigma nkT^{5/2} - nL - nc\,(298\text{–}234). \quad (4)$$

The necessary data for the application of the Nernst-Lindemann equation to the reaction

$$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$$

is given by Pollitzer[1] and is here reproduced in Table III.

TABLE III.

Substance.	n_1.	$\beta\nu_1$.	n_2.	$\beta\nu_2$.	$k \times 10^5$.
Pb............	1	92	..	...	7.8
Hg (solid)......	1	97	..	...	21.0
HgCl..........	1	93	1	324	12.0
$PbCl_2$..........	1	85	2	270	18.0

The values of the heat of fusion and of the specific heat of mercury are taken to be 555 and 6.68, respectively. Substituting the above data in Equation 4 and making use of Pollitzer's tables[2] we find $U_\circ = 24035$ cal. Introducing this value of $U_\circ$ in Equation 3 together with the appropriate data from Table III we find 24041 cal. on solving the equation for A_{234°. Having computed the maximum work at 234° A., the e. m. f. of the cell involving this reaction may be calculated as follows:

$$\mathbf{E} = \frac{24041}{0.2389 \times 2 \times 96500} = 0.521 \text{ volt.}$$

This result is in close agreement with the value obtained experimentally by Pollitzer, *viz.*, 0.525 volt.

Summary of Results.

(1) The e. m. f. of the cell

$$\overset{-}{Pb} \mid 0.1\,M \text{ KCl sat. w. } PbCl_2 \parallel 0.1\,M \text{ KCl, } Hg_2Cl_2 \mid \overset{+}{Hg}$$

has been measured at 25° using different lead electrodes; the values of the

---

[1] Pollitzer, *Z. Elektrochem.*, **19**, 523 (1913).

[2] Pollitzer, *Ahren's Samm ung chemischer Vorträge*, **17**, 498 (1912).

e. m. f. obtained with different specimens of lead cast in sticks, with electrolytically deposited lead and with amalgams, were practically identical.

(2) The normal electrode potential of lead was calculated to be *0.4121* volt referred to the normal calomel electrode and *0.1293* against the normal hydrogen electrode.

(3) The values of the e. m. f. of cells containing electrodes which had been immersed for varying periods of time in Heller's solution were found to be uniformly higher than the values obtained with cells containing electrodes which had not been subjected to this treatment.

(4) The heat of the reaction

$$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg,$$

was calculated and found to be 21840 cal., whence the heat of formation of lead chloride was computed to be 84440 cal.

(5) The heat of reaction U_o, and the maximum work $A_{234°}$ were calculated by means of the Nernst-Lindemann equation and the computed value of the e. m. f. at 234° A. was found to be in close agreement with the observed value.

STAMFORD, CONN.

NOTES.

The Oxidation of Sulfides with Potassium Iodate.—In a previous article[1] it was shown that in the oxidation of sulfides with potassium iodate, the amount of sulfur oxidized to sulfuric acid depended on the concentration of hydrochloric acid, and that with an amount of iodate nearly equivalent to the sulfide, the greatest amount of oxidation obtainable with any strength of acid was represented by the equation

$$3MS + 3KIO_3 + 12HCl \rightleftarrows 3MCl_2 + 2S + 3ICl + 5H_2O.$$

We find that if a *large excess* of iodate be used the sulfur may be completely oxidized, whatever the strength of hydrochloric acid provided it be strong enough to prevent the hydrolysis of ICl. This is evidenced by the following analyses:

Freshly prepared hydrogen sulfide water was measured with a 25 cc. pipet into flasks kept at 0°. Some of the samples were titrated with $N/10$ iodine solution and found to contain 0.00154 g. hydrogen sulfide per cc. 100 cc. of 0.05 molar potassium iodate and the desired amount of hydrochloric acid were added to the other flasks and the excess of iodate was titrated with an equivalent iodide solution. The results were as follows

Normality hydrochloric acid......	6.40		4.00		3.00	
Iodate used......................	45.32	45.30	45.31	45.28	45.30	45.32

Theory for complete oxidation according to the equation

$$H_2S + 2KIO_3 + 4HCl \rightleftarrows 2ICl + H_2SO_4 + 2H_2O + 2KCl$$

is 45.30 cc.

---

[1] THIS JOURNAL, **37**, 1134 (1915).