In the system tin tetrachloride-sulfur dioxide we have a rather unusual case. A curve for the two-liquid phase system was obtained, and over the same composition range a curve for the solubility of the solid tin tetrachloride in sulfur dioxide was obtained, the first curve lying completely below the latter. However, the fact that such curves exist need not be unexpected, and several such systems are known.

It is interesting to note that in determining the solubility of the solid in liquid at concentrations where the two curves ran close together, opalescence was observed after the solid had completely dissolved. This would seem to indicate that opalescence may occur at times other than those at which the mixtures are caused to transform from the binary-liquid state to the homogeneous state.

Summary

1. Sulfur dioxide in contact with the liquid tetrahalide compounds forms mixtures which are but partially miscible at lower temperatures.

2. The relative positions of the critical mixing temperatures are such as might have been predicted from the polarities, internal pressures and the melting points of the compounds involved.

3. In the case of the system sulfur dioxide-tin tetrachloride a metastable binary-liquid system was found.

4. Compound formation was not apparent at temperatures above the melting point of sulfur dioxide.

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[Contribution from the Bureau of Mines, United States Department of Commerce]

ADJUSTED VAPOR PRESSURES OF ZINC AND CADMIUM[1]

By Charles G. Maier

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During recent experimental determinations of certain reduction equilibria of zinc oxide, carried out at the Berkeley station of the Bureau of Mines, need arose for data on the free energy and heat of vaporization of zinc and cadmium, from both the solid and liquid state. For both of these metals experimental vapor-pressure determinations of solid and liquid metal, as well as values for the heat of fusion, are available. It was found, however, that direct calculation of the heat and free energy from these values does not lead to entirely consistent results unless some adjustment of the data is made. This is especially true when one attempts to extrapolate to ordinary temperature, in order to calculate the standard free-energy change.

[1] Published by permission of the Director of the Bureau of Mines, Department of Commerce.

In order to obtain sets of consistent values for both solid and liquid metal, a recalculation of the best of the original vapor-pressure data has been made. Since such values are of fundamental use in discussion of any chemical reaction involving elementary zinc or cadmium, a brief résumé of the results of these recalculations may be of interest.

Basis of Adjustment

Using the notation of Lewis and Randall, the standard free energy equation of the form

$$\Delta F^\circ_T = -RT\ ln\ K = \Delta H_0 - \Delta\Gamma_0 T\ ln\ T - {}^1/_2\Delta\Gamma_1 T^2 - {}^1/_6\Delta\Gamma_2 T^3 \ldots + IT \quad (1)$$

has been applied to the data for fusion, sublimation and vaporization, according to the method devised and used by Dr. Randall. Considering the original measurements, for each temperature at which a datum exists the value of

$$\Sigma = -R\ ln\ K + \Delta\Gamma_0\ ln\ T + {}^1/_2\Delta\Gamma_1 T + {}^1/_6\Delta\Gamma_2 T^2 \ldots \quad (2)$$

has been calculated, using representative specific-heat values. A plot of Σ *vs.* $1/T$ must, if the data are accurate, result in a straight line whose slope is ΔH_0. I was then calculated for each point as the difference between Σ and computed values of $\Delta H_0/T$.

Since in the cases of zinc and cadmium data exist for fusion, sublimation and vaporization, consistent data will fulfil the conditions of: (a) constancy of I in any set of values; (b) additivity of ΔH_0 between sets; and (c) additivity of I between sets. Further, since values for the entropy of the solid metals, as calculated from low-temperature specific-heat data, are available with probable errors of less than 0.1 entropy unit, a final check may be made by comparison of the entropy of the vapor as calculated from vapor-pressure measurements, with that calculated for a monatomic gas from the theoretical equations of Sackur or Tetrode.

The last mentioned method will seem to be a reversal of the usual treatment, in that experimental values of vapor pressure have commonly been used to test the validity of the theoretical equations. For example, Fogler and Rodebush[2] have compared the entropy of cadmium vapor as determined from their vapor-pressure data with that calculated from the Sackur equation, using the value derived by Lewis[3] for the constant of that equation. In a later paper, Rodebush and Dixon[4] have compared the entropy of zinc vapor with a value calculated from the Tetrode equation.

Upon treating the experimental data in the manner of recalculation indicated above, it soon becomes evident that the close concordance between the entropy of zinc and cadmium vapors as calculated from vapor-pressure data and that calculated from either the Sackur or Tetrode equation depends very considerably upon the choice of values taken for

[2] Fogler and Rodebush, This Journal, **45,** 2080 (1923).

[3] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923,** p. 458.

[4] Rodebush and Dixon, This Journal, **47,** 1042 (1925).

specific heats and entropy change of fusion. In some cases the choice seems to have been more largely determined by the desire to secure concordance than by judicious selection of the most representative data.

If the statement of Lewis and Randall,[3] "the accuracy of the physical constants used in obtaining Equation 4 (Sackur equation) permits the calculation of the constant of that equation to about 0.01 entropy unit, which is far more accurate than any present experimental value," be accepted, it would seem entirely justifiable to correct obviously imperfect data by the use of the constant.

Vapor-Pressure Data of Zinc

In setting up the standard free-energy equations for zinc, the values of specific heats chosen for solid zinc are those of Eastman, Williams and Young,[5] leading to the expression $C_p = 5.10 + 0.003\ T$.

In accordance with Lewis and Randall, the specific heat of zinc vapor (monatomic gas) is taken as 5.0 whereas for liquid zinc, the value of Braune[6]

$$Cp_{\mathrm{Zn(l)}} = 7.24$$

has been chosen. Rodebush and Dixon[4] chose Wüst's[7] values for liquid zinc, despite the fact that this "leads to results in error at the boiling point by several degrees." The value of Braune for liquid zinc leads to a free-energy equation which represents very well the vapor-pressure data for liquid zinc, not only for the results of Braune[6] but also those of Rodebush and Dixon[4] and Greenwood,[8] as well as the boiling points both of Berthelot and of Heycock and Lamplough.[9]

Since the data on the vapor pressure of liquid zinc are not only extensive, but also of high relative accuracy compared to the sublimation and fusion data, these will be considered first, especially since they are to be the basis of further adjustment of the less certain data. Braune[6] shows five points of vapor pressure, ranging from 1 to 81 mm. of mercury, obtained by an inert gas-saturation method, and seven points from 356 mm. to 1521 mm. obtained by a boiling-point method. Rodebush and Dixon[4] show 30 points, from 8 to 49mm. vapor pressure, also by the boiling-point method.

Fig. 1 shows the plot of the function Σ *vs.* $1/T$, for these data. In the calculation appropriate correction has been made for the activity of the liquid in all cases where the correction would be appreciable. When separately plotted on a larger scale than is shown in Fig. 1, Braune's inert-gas method data lead to a value of ΔH_0 (slope of Σ *vs.* $1/T$ plot) of 30,585 cal., whereas his boiling-point data would indicate $\Delta H_0 = 30{,}495$. The large

[5] Eastman, Williams and Young, This Journal, **46,** 1184 (1924).

[6] Braune, *Z. anorg. Chem.*, 111, 109 (1920).

[7] Wüst, *Verh. deut. Ing. Forsch-arb.*, No. 204 (1918).

[8] Greenwood, *Proc. Roy. Soc.* (London), **83A,** 483 (1910).

[9] Heycock and Lamplough, *ibid.*, **28,** 3 (1912).

scale plot of the data of Rodebush and Dixon shows 30,540, which is exactly the mean of Braune's values. This seems definitely to fix the heat of vaporization of zinc as $\Delta H_0 = 30{,}540 \pm 30$ cal. This is the value which has been used in computing $\Delta H_0/T$ for the calculation of I for each set of data on liquid zinc, leading to the results given in Table I.

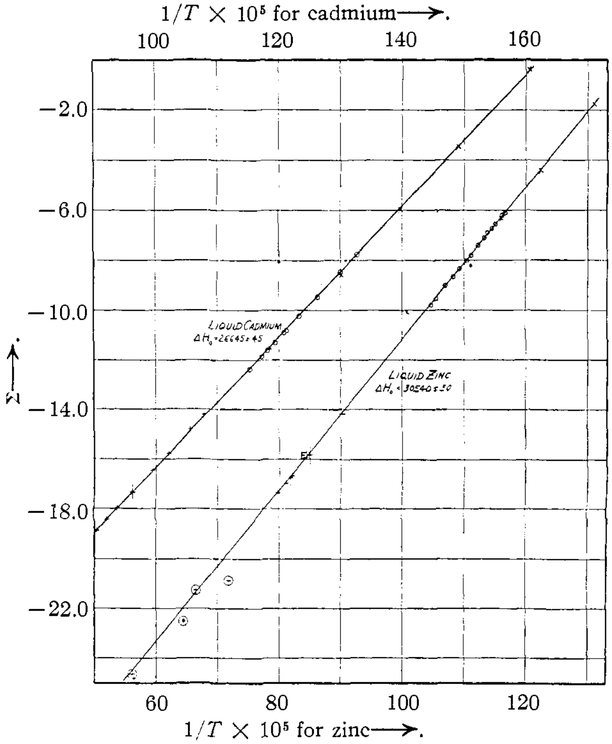

Fig. 1.—Sigma function plot. $Zn_{(l)} = Zn_{(g)}$. $Cd_{(l)} = Cd_{(g)}$. ×—Braune, inert gas method. +—Braune, boiling points. ○—Rodebush and Dixon—Zinc. ○—Fogler and Rodebush—Cadmium. ⊕—Greenwood. †—Heycock and Lamplough. ⊞—Berthelot.

TABLE I

COMPARISON OF INTEGRATION CONSTANTS (I) OF FREE ENERGY EQUATION FOR VAPORIZATION OF LIQUID ZINC

Data of	Method	No. of points	Weighted mean value of I	A. d. of m.
Braune	Inert gas	5	−41.766	±0.022
Braune	B. p.	7	−41.733	± .006
Rod. and Dix.	B. p.	30	−41.761	± .012
Greenwood Berthelot Heycock and Lamplough	B. p.	6	−41.780	± .106
All data		48	−41.760	± .014

For the reaction $Zn_{(l)} = Zn_{(g)}$ we have then, $\Delta F°_T = 30{,}540 + 2.24\, T \ln T - 41.760\, T$; $\Delta F°_{298.1} = 21{,}887$.

The remarkable concordance obtained in the value of I in the various sets of data above, over a wide range of vapor pressures and temperatures, justifies confidence in the essential correctness of the data on liquid zinc. This is not true, however, of the experimental data on the vapor pressure of solid zinc, consisting only of the values of Egerton.[10] Egerton's data show 11 points on the vapor-pressure curve of solid zinc, over a temperature range of about 100°. Upon calculating the Σ function and plotting against $1/T$, as is done in Fig. 2, it is immediately evident that the data might fairly well be represented by a number of lines with markedly different slopes.

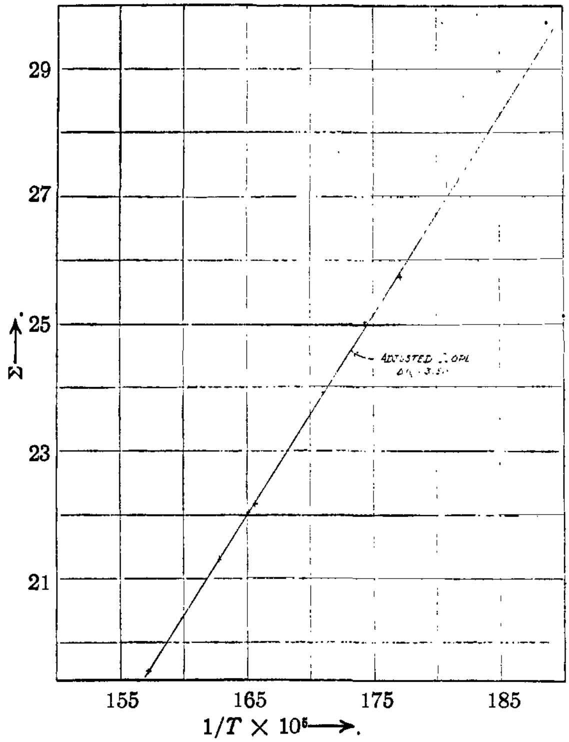

Fig. 2.—Sigma function plot. $Zn_{(s)} = Zn_{(g)}$. Data of Egerton.

Although the desired slope should be obtainable as the sum of the heats of fusion and vaporization, an examination of the existing thermal data on the heat of fusion of zinc does not offer great assistance in this case. The data on the heat of fusion of zinc fall into two groups, the values

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[10] Egerton, *Phil. Mag.*, [6] **33,** 33 (1917).

of each consistent in themselves. Mazzotto,[11] Person[12] and Heycock and Neville[13] obtained 28, —28.13 and 28.33 calories per gram, respectively, whereas Wüst[7] and Iitaka[14] had 23.0 and 23.2. Other determinations are those of Glaser[15] (29.9) and Greenwood (26.0). If the mean of the first three values be chosen, the free-energy equation for the reaction $Zn_{(s)} = Zn_{(l)}$ becomes $\Delta F^\circ_T = 1077 - 2.14\ T\,ln\,T + 0.0015\ T^2 + 11.402\ T$; $\Delta F^\circ_{298.1} = +975$, whereas the values of Wüst and Iitaka lead to the expression $\Delta F^\circ_T = 747 - 2.14\ T\,ln\,T + .0015\ T^2 + 11.879\ T$; $\Delta F^\circ_{298.1} = +787$.

By combining the value of ΔH_0 in these fusion equations with the accurate value 30.540 for volatilization, the slope of the plot of Egerton's data (Σ *vs.* $1/T$) should be either 31,617 or 31,287 cal. If now I be calculated as before from these values of $\Delta H_0/T$ and the respective values of Σ, for the first case I of the reaction $Zn_{(s)} = Zn_{(g)}$ is by experimental data —30.107, but by the addition of the value for fusion to that of vaporization —30.358, and in the second case —29.541 from the vapor-pressure data compared with —29.881 by addition. But the value of I is related to the entropy change by the expression[16]

$$\Delta S = \Delta\Gamma_0\ (ln\ T + 1) + \Delta\Gamma_1\ T + \tfrac{1}{2}\ \Delta\Gamma_2\ T^2 \ldots\ -I \qquad (3)$$

According to Lewis and Randall, $S^\circ_{298(Zn_s)} = 9.83$. And $S^\circ_{298(Zn_g)} = 38.1$ as calculated from the Sackur equation with Lewis' constant, ΔS becoming the difference, 28.34. Substituting in Equation 3, including the appropriate specific-heat terms, and solving for I, the value —29.932 is obtained, a value intermediate between those obtained by the application of the two sets of heat of fusion data. Choice of a suitable value for ΔH_0 of the sublimation may now be made; the value $\Delta H_0 = 31,515$ gives a mean value of I of —29.931 ± 0.107 calculated from the vapor-pressure data. On this basis, for the reaction $Zn_{(s)} = Zn_{(g)}$ the acceptable free-energy equation is $\Delta F^\circ_T = 31,515 + 0.10\ T\,ln\,T + 0.0015\ T^2 - 29.932\ T$; $\Delta F^\circ_{298.1} = 22,885$.

By subtraction, the free-energy equation for fusion becomes $Zn_{(s)} = Zn_{(l)}$, $\Delta F^\circ_T = 975 - 2.14\ T\,ln\,T + 0.0015\ T^2 + 11.828\ T$; $\Delta F^\circ_{298.1} = 998$.

The value of $\Delta H_0 = 975$ for fusion, derived in this manner, corresponds to a heat of fusion of 1737 cal. per mole, or 26.6 cal. per gram at the melting point, somewhat nearer to the older values of Mazzotto, Person, Heycock and Neville, than the more recent ones of Wüst or Iitaka used by Rodebush and Dixon. It is felt that the equations derived for the reaction $Zn_{(s)} = Zn_{(g)}$ offer a more satisfactory expression for Egerton's actual experimental data than could be derived from the experimental values alone.

[11] Mazzotto, *Atti. accad. sci. Torino*, **17**, 132 (1881–1882).

[12] Person, *Ann. chim. phys.*, [3] **21**, 333 (1847).

[13] Heycock and Neville, *J. Chem. Soc.*, **71**, 383 (1897).

[14] Iitaka, *Science Repts. Tôhoku Imp. Univ.*, **8**, 99 (1919).

[15] Glaser, *Metall.*, **1**, 121 (1904).

[16] Tolman, THIS JOURNAL, **42**, 1185 (1920).

Vapor-Pressure Data of Cadmium

The same general method was used in treating the data for cadmium as in the case of zinc and minor details will be omitted.

By replotting the data of Griffiths[17] and Naccari[18] the specific heat of solid cadmium was obtained as

$$Cp_{Cd(s)} = 5.46 + 0.0026\ T$$

The value for liquid cadmium used is that of Braune[6] = 7.50.

For the vapor pressure of liquid cadmium Fogler and Rodebush[2] show 11 points with vapor pressures of 9 to 78 mm. of mercury, the plot of Σ *vs.* $1/T$ on a large scale giving $\Delta H_0 = 26{,}660$. Braune had 5 points for cadmium by the inert-gas method, from 0.2 to 52mm. pressure, $\Delta H_0 = 26{,}695$, and by the boiling-point method 9 points from 182 to 1506mm. pressure, $\Delta H_0 = 26{,}580$. Fig. 1 shows the plot of all the data. The mean value is 26,646 ± 43 cal. In the calculation of I the value was rounded off to 26,645 cal., with the results given in Table II.

Table II

Comparison of Integration Constants (I) of Free Energy Equation for Vaporization of Liquid Cadmium

Data of	Method	No. of points	Weighted mean value of I	A. d. of m.
Braune	B. p.	9	−42.980	±0.009
Braune	Inert gas	5	−43.176	± .051
F. and R.	B. p.	11	−43.105	± .011
H. and L.	B. p.	1	−43.010	.....
All data		26	−43.068	± .079

For the reaction $Cd_{(l)} = Cd_{(g)}$ the free energy equation becomes $\Delta F^\circ_T = 26{,}645 + 2.50\ T \ln T - 43.068\ T;\ \Delta F^\circ_{298.1} = 18{,}053$.

Egerton's[10] data on the vapor pressure of solid cadmium, although more extensive than for zinc, suffer from the same uncertainty as to the slope when Σ *vs.* $1/T$ is plotted. The individual points are shown in Fig. 3.

Lewis, Latimer and Gibson[19] have calculated the entropy of solid cadmium at 298.1 from the specific-heat data of Griffiths[17] to be 11.80, but later determinations of Rodebush[20] lead to a value[2] of 11.97. For this work a mean value, 11.885, is chosen. From the Sackur equation with the Lewis constant $S_{298.1(gas)} = 39.79$, then $\Delta\ S$ for sublimation is 27.905, and from Equation 3, I is calculated as —31.301. If ΔH_0 for sublimation be chosen as 27,050, the value of I calculated from the 36 points given by Egerton, omitting 11 obviously discordant values, is —31.302 ± 0.103. For the reaction $Cd_{(s)} = Cd_{(g)}$, $\Delta F^\circ_T = 27{,}050 + 0.46\ T \ln T + 0.0013\ T^2 - 31.301\ T;\ \Delta F^\circ_{298.1} = 18{,}616$.

[17] E. H. and E. Griffiths, *Proc. Roy. Soc.*, **88A,** 549 (1913).

[18] Naccari, *Atti. Tor.*, **23,** 107 (1887–1888).

[19] Lewis, Latimer and Gibson, This Journal, **44,** 1008 (1922).

[20] Rodebush, *ibid.*, **45,** 1413 (1923).

By subtraction, the free-energy equation of fusion is $\Delta F^\circ_T = 405 - 2.04\ T\ ln\ T + 0.0013\ T^2 + 11.767\ T$; $\Delta F^\circ_{298.1} = 563$.

The calculated value of heat of fusion equivalent to the above expression at the melting point is 1155 cal. per mole. The older values of Person[12] and Roos[21] are 1540 cal., but Wüst determined this as 1220 cal.

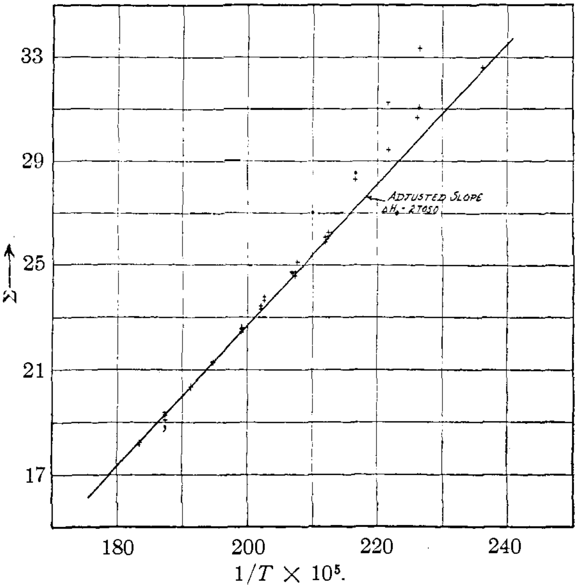

Fig. 3.—Sigma function plot $Cd_{(s)} = Cd_{(g)}$. Data of Egerton.

Derived Vapor-Pressure Expressions

The free-energy expressions derived for solid and liquid metal may be transformed to vapor-pressure expressions by means of the relationship

$$\Delta F^\circ_T = -RT\ ln\ K = -R\ ln\ p + R\ ln\ a$$

where p is the vapor pressure and a the activity of the condensed phase. For pressures near atmospheric, $ln\ a$ is negligible compared to $ln\ p$. Making this assumption, the adjusted vapor-pressure expressions for solid and liquid metal are

$$Zn_{(l)}\quad \log p_{mm.} = 12.0013 - (6670.0/T) - 1.1265 \log T$$
$$Zn_{(s)}\quad \log p_{mm.} = 9.4181 - (6883.0/T) - 0.05029 \log T - 3.277.10^{-4}\ T$$
$$Cd_{(l)}\quad \log p_{mm.} = 12.2870 - (5819.4/T) - 1.2572 \log T$$
$$Cd_{(s)}\quad \log p_{mm.} = 9.7170 - (5907.8/T) - 0.4323 \log T - 2.840.10^{-4}\ T$$

Summary

The best of the vapor-pressure data in the literature referring to zinc and cadmium have been critically recalculated in order to express the experimental values consistently for thermodynamic calculations.

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[21] Roos, *Z. anorg. Chem.*, **94**, 329 (1916).

Assuming that zinc and cadmium vapors are perfect monatomic gases, standard free-energy equations have been derived for volatilization, sublimation and fusion.

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[Contribution from the Bureau of Mines, United States Department of Commerce]

REDUCTION EQUILIBRIA OF ZINC OXIDE AND CARBON MONOXIDE[1]

By Charles G. Maier and Oliver C. Ralston

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For several years past, the Bureau of Mines at its Berkeley Station intermittently has studied metallic oxides. The great importance of the reduction equilibria of metallic oxides, especially in metallurgical operations, makes it highly desirable that these materials be studied systematically. Satisfactory determinations of free energy of formation of the heavy metal oxides are especially to be sought; for if these be known, the data treated thermodynamically should suffice for many utilitarian needs.

Zinc oxide is among the most interesting and important from this point of view. Not only are accurate equilibria measurements highly desirable because in this case theoretical results may be directly applied to metallurgical practice, but also the new use of zinc oxide as catalyst for methanol formation, etc., gives the problem of its reduction equilibria considerable general chemical interest.

Experimental Difficulties

In the temperature range through which zinc oxide is appreciably reduced by gases such as carbon monoxide or hydrogen, that is, above about 400°, the rate of reduction is moderately fast. This fact, combined with the relatively high vapor pressure of zinc in the temperature range of reduction, makes adequate sampling of gas, without change of composition from those concentrations in equilibrium with solid oxide and metal vapor, an extraordinarily difficult experimental problem.

The most ambitious past attempt to measure actual reduction equilibria of zinc oxide is undoubtedly to be found in the experiments of Bodenstein.[2] His experiments fall into two groups, in the first of which he attempted to measure the temperature of reduction of zinc oxide by carbon at various pressures by means of thermal and weight variations of mixtures of zinc oxide and charcoal during heating. In later experiments zinc oxide and graphite were heated in a silica chamber sealed by a lead trap. This

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[1] Published by permission of the Director of the Bureau of Mines.

[2] Bodenstein, *Z. Elektrochem.*, **23**, 105 (1917).