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:

$$\overset{-}{\text{Pb}} \text{ — sat. sol. Pb(NO}_3)_2 \ \| \ 0.10\ N \text{ KCl, HgCl — } \overset{+}{\text{Hg}}$$

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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THE DISSOCIATION PRESSURES OF MERCUROUS CHLORIDE.

BY ALEXANDER SMITH AND ROBERT PEYTON CALVERT.

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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).

Smith and Menzies.[1] The pressures of vapor in equilibrium with the solid calomel were determined by the former for temperatures below 180° and by the latter for temperatures above 361°. In the one series, the highest pressure obtained was 0.5 mm.; in the other, the lowest pressure was more than 450 mm. For some work now nearing completion in this laboratory it is necessary to have data for certain points in the wide temperature interval not previously investigated. In this paper, that information is supplied. Since the entropy of vaporization is a more significant relation than is Trouton's rule, or any of the modifications of that rule which have been so extensively applied to vapor and dissociation pressures, the values of this constant for several dissociating substances have been calculated. We have included, also, a discussion of the various confining fluids which may be used in the static isoteniscope.

The Apparatus.—The measurements were made by use of the static isoteniscope and the apparatus previously described by the authors.[2] The isoteniscope was heated in a vigorously stirred bath of the molten nitrates of sodium and potassium. The temperature scale is that based on the ice point, steam point, and sulfur boiling point (taken as 444.7°); it could be reproduced, in successive calibrations of the platinum thermometer, to within ±0.03°. The pressure readings are corrected to 0° and sea-level at latitude 45°.

Confining Fluids.—In any measurement with the static isoteniscope, the choice of a suitable material to confine the vapors is extremely important. In many cases alloys, or a pure metal, like bismuth, may be used, but they are of such high density that errors due to leveling may correspond to several tenths of a millimeter of mercury. The equimolar mixture of sodium and potassium nitrates is available at temperatures above its melting point, 222.4,[3] and below 450° at which the liberation of oxygen becomes appreciable. The mixture gives a light, mobile, perfectly transparent liquid which can be leveled with precision. But, unfortunately, the hot nitrates act chemically on many vapors and thereby disturb the vapor pressure equilibrium. The eutectic of lithium and potassium chlorides[4] gives, at high temperatures, a liquid having no appreciable vapor pressure and one which would seem admirably suited for confining the vapor of any chloride. But our experience has convinced us of the practical impossibility of using this mixture because, first, of its strongly hygroscopic nature and, secondly, of its attacking the glass, thus rendering the isoteniscope opaque.

The ideal material for confining a vapor is the liquid form of the sub-

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[1] This Journal, **32,** 1541 (1910).

[2] Smith and Calvert, *Ibid.*, **36,** 1363 (1914).

[3] Harkins and Clark, *Ibid.*, **37,** 1819 (1915).

[4] Zemczuzng and Rambach, *Z. anorg. Chem.*, **65,** 405 (1910).

stance whose vapor pressure is being determined. When the substance sublimes without melting, the temperature of melting can often be lowered below the boiling point, even for low pressures, by the addition of another salt. Thus, for confining the vapors of the chloride, the bromide and the iodide of ammonium, we have used the eutectic of the ammonium salt and the corresponding silver halide.[1] Also the eutectic of potassium chloride and the vaporizing substance has proved satisfactory in at least two vapor pressure measurements, the results of which are yet to be published.

In the work of Smith and Menzies on calomel,[2] the eutectic mixture of potassium and sodium nitrates was employed as confining liquid. Some interaction of the vapor with the nitrates occurred, causing a slow rise in pressure due to the accumulation of an excess of mercury vapor. The vapor was expelled and replaced by a fresh supply immediately before each reading. In the present work two different confining liquids were used in two series of measurements, namely, in the first, molten nitrates of sodium and potassium and, in the second, the eutectic of potassium chloride and silver chloride containing three mols of the former to seven of the latter and melting at 306°.[3] With the mixture of chlorides, the rise in pressure, caused by the dissolving of the mercuric chloride in the confining liquid and the accumulation of an excess of mercury vapor, was very much slower than when nitrates were employed. By distilling the vapor through the confining liquid and practically saturating the latter with mercuric chloride before making an observation, the increase for a five-minute interval was reduced to less than one-tenth of that observed with the nitrates as confining liquid.

During this boiling-out process a very large deposit of mercury formed as a mirror in the upper cool part of the isoteniscope, thus affording another proof that calomel vapor dissociates giving free mercury.

TABLE I.—VAPOR PRESSURES OF CALOMEL—OBSERVATIONS.

Temp. ° C.	$P_{obs.}$	ΔP.	P_0.
309.52*	105.1	+ 2.1	103.0
328.28	180.2	0.0	180.2
340.32*	259.1	+ 5.4	253.7
341.56	262.0	+ 0.6	261.4
354.57	372.3	+ 0.3	372.0
356.34*	399.1	+ 8.9	390.2
366.58	507.7	+ 0.1	507.6
367.72*	535.5	+13.0	522.5
375.10	621.3	+ 2.9	618.4
383.95*	781.4	+16.7	764.7

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[1] Smith and Calvert, *Loc. cit.*

[2] *Loc. cit.*

[3] Zemczuzng, *Z. anorg. Chem.*, 57, 275 (1908).

The Observations.—The pressures were read five minutes after the boiling out had been stopped ($P_{obs.}$) and again five minutes later. The difference (ΔP), when subtracted from $P_{obs.}$, gives the pressure (P_0) corrected to the time zero at which the boiling out ceased. The results are also shown graphically in Fig. 1.

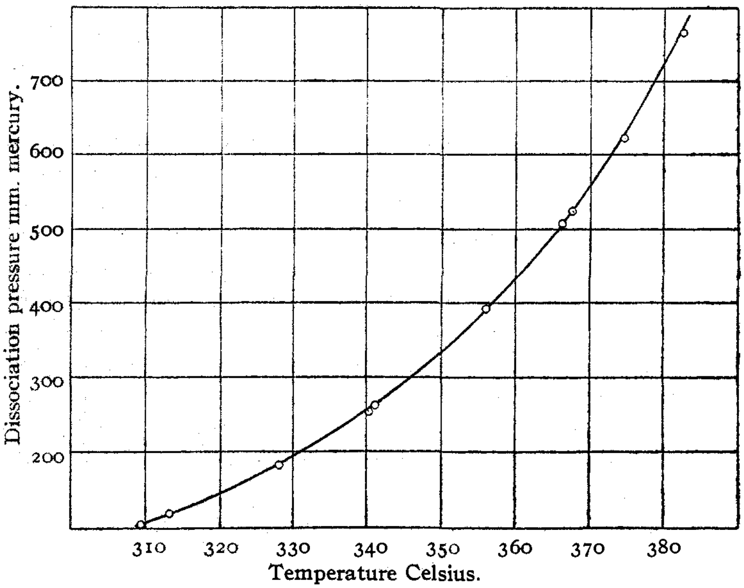

Fig. 1.

An asterisk indicates that the observation was made with the molten nitrates as confining fluid in the bend of the isoteniscope. Much more weight is to be given to the results obtained by the use of the chlorides

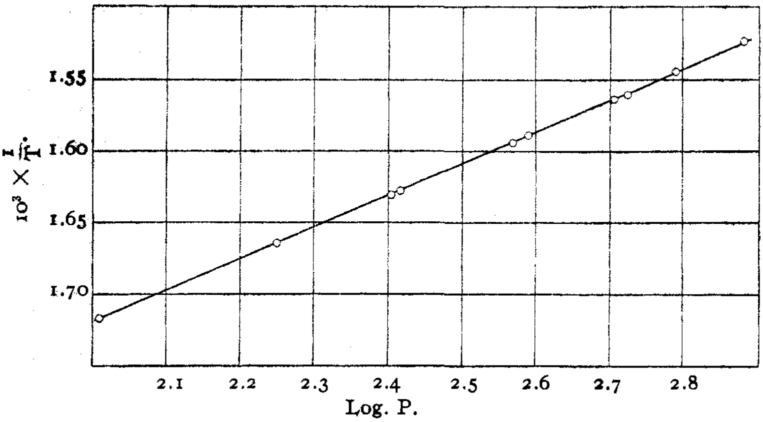

Fig. 2.

for the confining liquid; yet it will be observed that Fig. 2, in which log P is plotted against 1/T, that the final data for both series gives points lying closely along the same straight line. This has especial interest in view of the fact that the correction applied for the increase in pressure with time was very large in the one series and almost negligible in the other.

Kirchoff-Rankin-Dupre Equation.—For the purpose of interpolation and for testing the accuracy of our readings, we have derived an equation of the Kirchoff-Rankin-Dupré type.

$$\log p = -\frac{7792.10}{T} - 12.2309 \log T + 49.2048.$$

From this we have calculated the following dissociation pressures of calomel, in mm. of mercury, for even temperatures:

TABLE II.—DISSOCIATION PRESSURES OF CALOMEL AT EVEN TEMPERATURES.

Degree.	Mm.	Degree.	Mm.	Degree.	Mm.
300	74.4	340	251.4	380	696.8
310	103.0	350	329.9	383.7	760.0
320	140.5	360	428.0	...	...
330	189.2	370	548.9	...	...

The "boiling point," at 760 mm., is 383.7°. Harris and Meyer found 357°;[1] Jonker, 373°;[2] and Smith and Menzies, 382.5°.[3]

Although the solution of the above equation for the vapor pressure at any given temperature is quite easy, the calculation of the temperature corresponding to a given pressure is more troublesome. Now, in these measurements the chief errors lay in the temperature control and measurement and not in the reading of the pressure. Consequently, in testing the consistency of the result, it is preferable to express the deviations of the individual observations from the mathematical curves, represented by the Kirchoff-Rankin-Dupré equation, in degrees rather than in mm. Table III gives, for each pressure, the temperature observed

TABLE III.—DISSOCIATION PRESSURES OF CALOMEL.

Pressure.	Temp. (obs.).	Temp. (calc.).	Δ.
103.0	309.52*	309.98	+0.46°
180.2	328.28	328.34	+0.06°
253.7	340.32*	340.33	+0.01°
261.4	341.56	341.38	—0.18
372.0	354.57	354.56	—0.01
390.2	356.34*	356.40	+0.06
507.6	366.58	366.84	+0.26
522.5	367.72*	367.98	+0.26
618.4	375.10	374.94	—0.16
764.7	383.95	383.98	+0.05

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[1] *Ber.*, 27, 1484 (1894).

[2] *Chem. Weekblad*, 6, 1035 (1909).

[3] *Loc. cit.*

and the temperature calculated by means of the formula and the difference (Δ) between the two values. The arithmetical mean of these deviations is 0.15° which, divided by the square root of the number of observations, *i. e.*, by 3, gives ±0.05° as indicative of the precision of the measurements.

The Entropy of Vaporization.—Hildebrand[1] has pointed out that Trouton's rule, namely, that the ratio of the heat of vaporization to the boiling point of the absolute scale is a constant, or, as he states it, that the entropy of vaporization to one atmosphere pressure, is constant, does not hold even for normal substances, especially at extreme temperatures. The constants increase as the boiling points are higher. He points out that for normal liquids entropy of vaporization to a fixed molecular concentration of each vapor is more nearly constant.

For any vapor, at pressures so low that the laws of gases are applicable, $p = \mathrm{R}Tc$, where c is the molecular concentration. Hence, $\log p = \log \mathrm{T} + \log \mathrm{R}c$. When c is 0.00507 mol per liter, $\log \mathrm{R}c = -0.5$. Now, $d \log p/d \log \mathrm{T} = \mathrm{L}/\mathrm{RT}$. For the purpose of comparison with Hildebrand's results, we have calculated the value of the entropy of vaporization L/RT_c when $\log p = \log \mathrm{T} - 0.5$. Following him, we have also calculated the value of $\mathrm{L}/\mathrm{RT}_{p=100}$ where the vapor pressure is 100 mm., since at this lower pressure Trouton's rule should give more constant values than at 760 mm. The values at 760 mm. are given as well.

TABLE IV.—ENTROPY OF VAPORIZATION TO FIXED MOLAR CONCN. (c = 0.00507).

Substance.	L/RT_c where $\log p = \log \mathrm{T} - 0.5$.	$\mathrm{L}/\mathrm{RT}_{p=100}$ where $\log p = 2.00$.	$\mathrm{L}/\mathrm{RT}_{p=760}$ where p = 760 mm.	T_c. $c = 0.00507$.	T_p. p = 100 mm.	T_p. p = 760 mm.
PH_4I	20.7	20.5	17.6	301.5°	302.2°	335.6°
PCl_5	19.8	20.7	16.8	395	390	435.8
$N(CH_3)_4Cl$	17.5	16.4	25.4	469	450	506.3
$N(CH_3)_4I$	18.7	18.7	18.7	534	519	378.5
NH_4Cl	17.5	17.9	16.9	562	544	610.8
Hg_2Cl_2	17.7	18.7	14.9	604	582	656.7
NH_4Br	17.2	18.0	16.3	616	593	667.6
NH_4I	18.2	20.1	15.9	627	605	677.9
Normal liqs.	13.1–13.9	11–15.1	..	..	..	..
Assoc. liqs.	16.0–16.7	..	..	..	..	..

For the purpose of comparison, the corresponding values, as given by Hildebrand for normal and for associated liquids, are indicated. In the case of dissociating substances, such as our table contains, it was to be expected that the heats of vaporization (including heats of dissociation) would be higher. It should be noted that our values refer to a constant

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[1] THIS JOURNAL, 37, 970 (1915).

total molecular concentration both of the undissociated molecules and of the molecules of the products of the dissociation.

Summary.

The dissociation pressures of calomel for temperatures between 309° and 384° are given. The pressure, 760 mm., is reached at 383.7°.

The Kirchoff-Rankin-Dupré equation represents the results satisfactorily.

The entropies of vaporization to constant molecular concentration for eight dissociating substances are recorded.

Confining liquids are discussed.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION, WASHINGTON, D. C.]

THE OXIDES OF IRON. I. SOLID SOLUTION IN THE SYSTEM FE_2O_3–FE_3O_4[1].

BY R. B. SOSMAN AND J. C. HOSTETTER.

Received February 4, 1916.

CONTENTS.—Introduction. State of Knowledge of the Oxides of Iron. Apparatus Employed. Materials: Ferric Oxide; Merck's "Reagent Iron Oxide;" Oxide from Electrolytic Iron; Sibley Ore; Magnetite; Oxygen. Special Problems: Optical Properties of the Oxides of Iron; Reduction of Iron Oxides by Platinum; Disappearance of Oxygen in Furnace; Adsorption of Gases. Questions of Equilibrium: Reproducibility of Dissociation Pressures; Accuracy of Temperature and Pressure; Pressures from Ferric Oxide from Different Sources; Effect of Temperature Gradient in Furnace; Comparison of Rising and Falling Temperatures; Pressures Obtained by Oxidation of Magnetite. The System Fe_2O_3–Fe_3O_4: Experimental Results: General Plan; Methods of Analysis; Total Iron; Pressure-composition Isotherm at 1200°; Pressure-composition Isotherm at 1100°; Form of Dissociation-pressure Curve near Fe_2O_3; Optical Properties. Comparison with Previous Investigations. Summary.

Introduction.

The silicate systems which have hitherto been the subjects of study in this laboratory have all been made up of oxides which are apparently unaffected by atmospheric oxygen at temperatures below 1600°. They could therefore be melted in platinum-wound furnaces in the open air. The oxides which can be so treated include silica, alumina, magnesia, lime, and the alkalies. But iron, which is one of the most important constituents of natural silicates, changes its form of combination and the properties of its compounds according to the amount of oxygen which is combined with it, and, furthermore, the amount of oxygen so combined is constantly changing, especially at high temperatures. It becomes necessary, then, to take account of oxygen as one of the components in any silicate system containing iron.

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[1] Presented in abstract at the Seattle Meeting of the American Chemical Society, Sept. 1, 1915.