

We hope to be able to evaluate the moments of some O^+-M^- bonds after further investigations in this series.

The arsenic and antimony valence angles in the trihalides are approximately 100° . The halogen atoms are thus very nearly in contact with one another, leaving a portion of the central atom exposed. Coördination with dioxane probably occurs in such a manner as to form trigonal bipyramids or octahedra (depending on whether one or two dioxane molecules coördinate with one halide molecule) in which the unshared electrons occupy one of the corners and the three chlorines are adjacent to one another. These configurations would have maximum moments, and the $SbCl_3 \cdot 2C_4H_8O_2$ complex should have a larger moment than the $SbCl_3 \cdot C_4H_8O_2$ molecule. The moments of the arsenic and antimony trihalides should, therefore, increase with increasing degree of solvation. The freezing points obtained for dioxane solutions of arsenic and antimony trichloride indicate that the solutes are monomolecularly dispersed, ruling out the presence of complexes in which one molecule of dioxane coördinates with two molecules of solute.

The O^+-As^- moment should be slightly greater than the O^+-Sb^- moment because of the greater electron attraction of the arsenic atom. Solvation with dioxane should bring about a greater increase in moments for the arsenic trihalides

than for the corresponding antimony compounds. The data of Table III reveal that this increase is actually smaller for the arsenic halides, indicating that dioxane coördinates less completely with the arsenic halides than with the antimony halides. This is probably due to the smaller size of the arsenic atom.

It may be objected that the moments calculated for these halides in dioxane are of questionable accuracy, as these molecules are solvated. It can be demonstrated that the difference in moment calculated for the solute as MX_3 and as $MX_3 \cdot C_4H_8O_2$ is small. The moment of antimony chloride listed in Table II is 5.16. The value calculated for the solute as $SbCl_3 \cdot C_4H_8O_2$ is 5.15.

Summary

1. Dielectric constants and densities are reported for dioxane solutions of phosphorus trichloride, phosphorus tribromide, arsenic trichloride, arsenic tribromide, arsenic triiodide, antimony trichloride, and antimony tribromide.

2. The $\Delta\epsilon/C_2$ ratios for the dioxane solutions of the phosphorus trihalides decrease with increasing solute concentration.

3. The electric moments determined for the arsenic and antimony trihalides indicate that coördination in dioxane solution occurs to a greater extent with antimony than with arsenic.

NOTRE DAME, INDIANA RECEIVED NOVEMBER 24, 1941

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Heat Capacities of Red and Yellow Lead Monoxides at High Temperatures

BY HUGH M. SPENCER AND W. MONROE SPICER¹

The individuality and allotropy of the red tetragonal and yellow orthorhombic forms of lead monoxide have been the subject of numerous papers in recent years. References to most of these are given in a paper by one of the authors² in which the free energies of formation of the red and yellow forms are shown to be $-45,101$ and $-44,956$ cal., respectively, at 25° .

In order to round out our knowledge of the thermodynamic properties of the two oxides, their ΔH 's of formation and their heat capacities

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(2) Hugh M. Spencer and John H. Mote, *THIS JOURNAL*, **54**, 4618 (1932).

TABLE I
HEAT CAPACITY OF LEAD MONOXIDE

Form	Temp., °C.	Mean sp. ht. cal. deg. ⁻¹ g. ⁻¹	Investigator
"Crystalline" ^a	22-98	0.05118	Regnault ³
Fused oxide ^a	22-98	.05089	Regnault ³
Crystalline powder ^b	19-50	.0553	Kopp ⁴
Commercial product ^c	17-99	.05078	Magnus ⁵
Commercial product ^c	19-268	.0523	Magnus ⁵

^a The fused oxide was prepared from red lead and was probably the yellow form, but no reference as to the color of the crystalline sample was made. ^b Larger particles of litharge freed from finer ones by sieving. ^c No reference to color or crystalline form.

(3) H. V. Regnault, *Ann. chim. phys.*, [3] **1**, 129 (1841).

(4) H. Kopp, *Liebig's Ann. Suppl.*, **3**, 1, 289 (1865).

(5) A. Magnus, *Physik. Z.*, **14**, 5 (1913).

are necessary. The first of these topics is the subject of a forthcoming paper.

Existing data on the heat capacity of lead monoxide above room temperature are very meagre. They are summarized in Table I.

In the present investigation the heat capacities of carefully prepared samples of the red and yellow forms have been measured over more extended ranges of temperature.

Apparatus and Materials

The hydrous lead monoxide, from which the red tetragonal oxide was produced, was prepared by a modification of the method of Pleissner⁶ from carbon dioxide-free solutions of thrice recrystallized barium hydroxide and lead acetate. The barium hydroxide solution was siphoned under an atmosphere of nitrogen into a flask equipped with a stirrer, and the lead acetate solution was siphoned into this drop by drop. After a number of washings with conductivity water the hydrous oxide was transferred to a flask with a sealed-on air condenser and soda-lime trap.

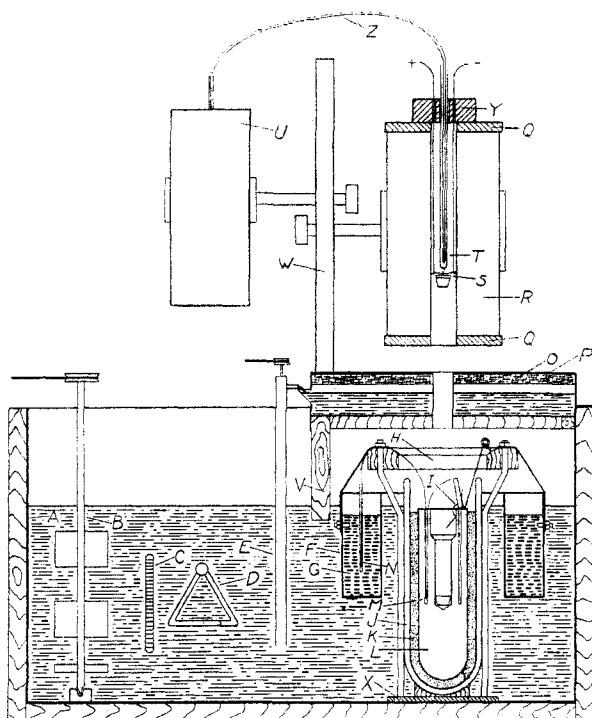


Fig. 1.—Diagrammatic sketch of apparatus.

Sodium hydroxide solution (about 13.5 M) was siphoned in and the mixture was heated to the boiling point. Transformation to the red form occurred rapidly. After the mixture had cooled, the excess sodium hydroxide was removed by washings with cold, and finally hot, conductivity water conducted in an atmosphere of nitrogen. The oxide was dried in a vacuum desiccator, first with potassium hydrox-

(6) M. Pleissner, *Arch. kaiserl. Gesundh.*, **26**, 384 (1907); see also note 9 of ref. 2.

ide, and later for two weeks with anhydrous magnesium perchlorate. The oxide lost no weight when heated in an oven to 140° and later in a furnace to 400° and above. This latter fact also proved the absence of lead carbonate, which according to Brill⁷ is completely decomposed in the atmosphere at 337°.

A modification of the aneroid calorimeter developed by Magnus⁸ and by Jaeger and Rosenbohm and others⁸ was used. The successful application of the method required (1) the maintenance of constant temperature environment of the calorimeter, (2) the accurate measurement of the change in temperature of the calorimeter and (3) accurate knowledge of the original high temperature of the sample.

Calorimeter and Environment.—A general idea of the apparatus can be obtained from the simplified cross section, Fig. 1. The air space above the calorimeter was completely confined and transformer oil at $25 \pm 0.001^\circ$ was pumped (E) through a series of baffles in the jacket before being returned to the thermostat. A thick board of insulating material (O) and a woolen blanket (P) shielded the calorimeter environment from the furnace while the furnace was in place. During the progress of a run the temperature of the room was kept at $25 \pm 0.5^\circ$ in so far as possible.

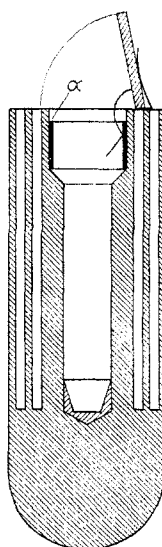
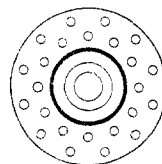


Fig. 2.—Calorimeter.

The calorimeter block (L) of Duralumin was suspended from (H) by three cords. The space between the block and the Dewar flask was packed with 30-mesh granular zinc (K). The lower part of the central bore of the block was shaped to afford good thermal contact with the crucible (S). The trigger top (I) closed very quickly when tripped by the falling crucible. The variable thermel junctions (M) were placed in the twenty-four small holes arranged in two concentric circles (see Fig. 2). The constant temperature junctions were imbedded in paraffin in the copper trough (F).

Calorimeter Thermel.—The change in temperature of the calorimeter was followed by means of a 24-junction copper-constantan thermel constructed in two equal sections and used in accordance with the suggestions of White.⁹

The fixed points used in the calibration were $32.383 \pm 0.001^\circ$ ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s)$, $\text{Na}_2\text{SO}_4(s)$ and solution) as reported by Dickinson and Mueller,¹⁰ $13.154 \pm 0.0011^\circ$ ($\text{NaNO}_3(s)$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s)$,

(7) O. Brill, *Z. physik. Chem.*, **57**, 736 (1907).

(8) (a) F. M. Jaeger and E. Rosenbohm, *Rec. trav. chim.*, **47**, 513 (1928); (b) F. M. Jaeger, E. Rosenbohm and J. A. Bottema, *ibid.*, **62**, 61 (1932).

(9) W. P. White, *THIS JOURNAL*, **36**, 2292, 2011 (1914); *Rev. Sci. Instr.*, **4**, 142 (1933).

(10) H. C. Dickinson and E. F. Mueller, *Bur. Standards Bull.*, **3**, 641 (1907).

NaNO₃·Na₂SO₄·H₂O(s), and solution) and 17.878 ± 0.0022° (NaCl(s), Na₂SO₄(s), Na₂SO₄·10H₂O(s) and solution) as reported by Redlich and Löffler.¹¹ The salts used were of reagent quality and were recrystallized twice from distilled water and once from conductivity water. The ice for the cold junction was obtained by freezing conductivity water. The sensitivity of measurement of temperature change corresponded to 0.0001°.

Furnace and Furnace Thermel.—The ratio of the height to the diameter of the bore of the furnace (R) was 11 to 1. Isothermal conditions were found to persist in a region of length 3.5 cm. The crucible and thermel were placed in this region.

The furnace was held in a vertical position by means of the support (W) which consisted of a rod securely fixed to the thermostat. On this same support was a Dewar flask (U) in which was placed the cold junction of the furnace thermel (Z). While the furnace was being heated it was swung into a position away from the thermostat and its lower end closed with a soapstone plug (not shown in Fig. 1). The furnace was moved into the position in which it is shown only when the hot crucible was ready to be dropped into the calorimeter. The Dewar flask moved in conjunction with the furnace so that bending of the thermel wires was prevented.

The platinum -10% rhodium thermel (Z) was constructed according to the method of Jaeger.¹² The melting points of the following salts were used in the calibration: K₂Cr₂O₇ (397.5 ± 0.5°), 45% KCl-55% Na₂SO₄ (517.1 ± 1.0°), 30.5% NaCl-69.5% Na₂SO₄ (627.0 ± 0.5°), KCl (770.3 ± 0.5°) Na₂SO₄ (884.7 ± 0.5°).¹³ They were of reagent quality and were further recrystallized twice from distilled water and once from conductivity water.

The hot junction of (T) the thermel encased in a silica tube was held in position by a soapstone block (Y). A small loop of fine platinum wire carrying the crucible was connected to two nickel wires fixed in the soapstone block. Current through these wires melted the platinum wire instantaneously and the crucible dropped into the calorimeter through a glass tube lined with asbestos. The glass tube was then removed, the opening through the copper cover closed with a cork stopper, and the blanket replaced over that part of the cover. According to Jaeger and Rosenbohm^{3a} the heat loss in falling so short a distance is negligible, especially since the first, and therefore the slowest, part of the descent, takes place in the furnace.

Treatment of Data

The temperature rise of the calorimeter was determined by analytical extrapolation according to Newton's law of cooling.

The water equivalent of the calorimeter was determined from measurements on platinum. For this purpose pure platinum scrap was added to the crucible, which was of pure platinum except for a mere trace of gold used in attaching the ring

(11) O. Redlich and G. Löffler, *Z. Elektrochem.*, **36**, 716 (1930).

(12) F. M. Jaeger, "Eine Anleitung zur Ausführung exakter physiko-chemischer Messungen bei höheren Temperaturen," J. B. Wolters, Groningen (1913), p. 7.

(13) H. S. Roberts, *Phys. Rev.*, [2] **23**, 386 (1924).

to the top. The heat content of platinum has been most carefully investigated. The present data have been recalculated on the basis of recent results by Jaeger and co-workers,^{14,15} which are expressed: (a) between 0 and 500°

$$Q_{t-0} = 0.031357t + 4.507 \times 10^{-6}t^2 - 1.61 \times 10^{-9}t^3 \text{ cal. g.}^{-1} \quad (1)$$

and (b) between 400 and 1600°

$$Q'_{t-0} = 0.031622t' + 3.172 \times 10^{-6}t'^2 \text{ cal. g.}^{-1} \quad (2)$$

From three determinations with $t' = 601.5^\circ$ and four with $t' = 662.25^\circ$ the average value of the water equivalent of the calorimeter was found to be 709.7 ± 0.64 cal. deg.⁻¹.

The final temperature varied from run to run (25.7 to 26.5°), therefore h , the heat given up per gram of oxide in falling from t' to 25° was calculated from h' , that given up in falling from t' to t^0 and an approximate value of the specific heat, 0.0526 cal. deg.⁻¹ g.⁻¹, derived from the equation of Randall and Spencer¹⁶ for yellow lead monoxide

$$C_p = 11.25 + 0.0016T \text{ cal. deg.}^{-1} \text{ mol.}^{-1}$$

No similar data were available for the red oxide, and since the heat capacities of the two forms differ by only about 2% (shown by present investigation) this value of specific heat was used without significant error in effecting the small adjustment of h' to h for the red lead monoxide.

Results

Table II presents a summary of the values of h for red lead monoxide between the various t'' 's and 25°.

TABLE II
HEAT CONTENTS OF RED LEAD MONOXIDE BETWEEN 25 AND t''°

t'	h , cal. g. ⁻¹					Average h	Probable error
400	21.020	21.012	21.086	21.171	20.989	21.056	±0.022
450	24.123	24.140	23.797	23.905		23.991	.057
500	27.517	27.236	26.680	27.068		27.170	.094
550	30.329	30.444	30.658	29.943		30.344	.101

Some slight changes in the state of oxidation occurred. In ten successive heatings at 400° (due to poor fit of crucible in the block six of them were not complete runs) one sample increased in weight from 16.1747 to 16.1927 g., corresponding to a change from PbO to PbO_{1.0069}. The maximum oxidation encountered occurred in runs at 500° where the ratio of oxygen to lead atoms reached

(14) Private communication from F. M. Jaeger;

(15) F. M. Jaeger and E. Rosenbohm, *Physica*, **6**, 1123 (1939).

(16) "International Critical Tables," McGraw-Hill Book Company, New York, N. Y., 1930, Vol. VII, p. 248.

1.0246. In all the samples therefore the oxides were well within the range in which the original lattice of lead monoxide is maintained.¹⁷ Two periods of heating this sample to 550° reduced the weight to the original value. This evolution of oxygen is in qualitative agreement with the studies of Clark and Rowan,¹⁸ showing absorption of oxygen by lead monoxide at 500° and atmospheric pressure and complete dissociation of higher oxides *in vacuo* at the same temperature, and data for the dissociation of red lead.^{17,19}

Yellow Lead Monoxide.—Yellow lead monoxide was prepared by heating the red monoxide at 600°, *i. e.*, above the transition point, for approximately three hours. Microscopic examination, as well as results after later heating to 650°, proved that this was sufficient. The data on yellow lead monoxide are summarized in Table III.

TABLE III
HEAT CONTENTS OF YELLOW LEAD MONOXIDE BETWEEN
25 AND t°

t°	h , cal. g. ⁻¹				Average h	Prob- able error
400	20.537	20.584	20.442	20.316	20.283	±0.040
500	26.582	26.600	26.648	26.884	26.598	.038
600	32.691	33.241	33.236	33.111	33.070	.088
650	35.992	36.430	35.918	36.140	36.120	.076

No oxidation of the yellow monoxide was observed even at 500° where that of the red was considerable. This result contradicts the statement of Le Blanc and Eberius,¹⁷ but agrees with those of Brown and Nees²⁰ and of Clark and Rowan¹⁸ to the effect that the red monoxide absorbs oxygen faster than the yellow.

Though various choices of form of equation and weights will yield satisfactory expressions for h as a function of t° (hereafter written t^0), the choice seriously affects the relation between specific heat and t^0 . It has seemed best to weight the results at the various temperatures proportionally to the reciprocals of the probable errors of the average h 's and find the least square solution of the form

$$h_{t-25} = a(t - 25) + b(t - 25)^2 + c(t - 25)^3$$

For red lead monoxide (weights 6, 3, 2, and 2 at 400, 450, 500 and 550°) the constants are $a = 5.82893 \times 10^{-2}$, $b = -1.79343 \times 10^{-5}$ and $c = 3.24788 \times 10^{-8}$. The calculated values of h at the four temperatures are 21.049, 24.027, 27.122

(17) M. Le Blanc and E. Eberius, *Z. physik. Chem.*, **A160**, 69 (1932).

(18) G. L. Clark and R. Rowan, *THIS JOURNAL*, **63**, 1305 (1941).

(19) W. Reinders and L. Hamburger, *Z. anorg. Chem.*, **89**, 71 (1914).

(20) O. W. Brown and A. R. Nees, *Ind. Eng. Chem.*, **4**, 867 (1912).

and 30.339 cal. g.⁻¹, and the deviations (*cf.* Table II) are well within the probable errors. This equation leads (0°C. = 273.16°K.) to

$$\text{Sp. ht.} = 0.05925 - 4.074 \times 10^{-5}t + 9.744 \times 10^{-9}t^2 \text{ cal. deg.}^{-1} \text{ g.}^{-1} \quad (3)$$

$$C_p = 17.331 - 0.02098T + 2.175 \times 10^{-5}T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (4)$$

Since many heat capacity data at high temperatures have been expressed in the form recommended by Maier and Kelley²¹ the following least square solutions (same weights as above) are given

$$H_{T-298.1} = 0.551T + 7.828 \times 10^{-3}T^2 - (8.780 \times 10^6)/T + 2085 \text{ cal. mole}^{-1} \quad (5)$$

$$C_p = 0.551 + 1.566 \times 10^{-2}T + 8.780 \times 10^6/T \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (6)$$

In Eqs. 5, 6, 9 and 10, 0°C. = 273.1°K.

Similar treatment of the heat contents of yellow lead monoxides (weights 3, 4, 2 and 3 at 400, 500, 600 and 650°) yields $a = 4.34134 \times 10^{-2}$, $b = 3.90003 \times 10^{-5}$ and $c = -2.55081 \times 10^{-8}$. The calculated values of h at the four temperatures are 20.419, 26.687, 33.008 and 36.140 cal. g.⁻¹, again well within the probable errors (*cf.* Table III). Hence

$$\text{Sp. ht.} = 0.041456 + 8.183 \times 10^{-5}t - 7.652 \times 10^{-9}t^2 \text{ cal. deg.}^{-1} \text{ g.}^{-1} \quad (7)$$

$$C_p = 2.981 + 0.02760T - 1.708 \times 10^{-5}T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (8)$$

Equation 8 indicates a maximum in the heat capacity of yellow lead monoxide at 525°.

The yellow lead monoxide data may also be expressed (weights 3, 4, 2, 3):

$$H_{T-298.1} = 16.754T - 9.583 \times 10^{-4}T^2 + (7.352 \times 10^6)/T - 7376 \text{ cal. mole}^{-1} \quad (9)$$

$$C_p = 16.754 - 1.917 \times 10^{-3}T - (7.352 \times 10^6)/T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (10)$$

Whereas for the red lead monoxide Eq. 5 yields slightly smaller deviations from the experimental points than Eq. 3, for the yellow monoxide Eq. 9 yields slightly large deviations than Eq. 7. Equation 10 indicates a maximum in the heat capacity at 642°.

Greater accuracy in fixing the heat contents at higher temperatures is obviously desirable, and it is the hope of the authors that circumstances may permit further attention to this subject. It is pertinent to note that for both forms of the oxide errors of opposite sense less than the probable errors in the values of h at the two higher tempera-

(21) C. G. Maier and K. K. Kelley, *THIS JOURNAL*, **54**, 3243 (1932).

tures would lead to equations for the specific heat which do not exhibit maxima and do not have positive second differences.²²

(22) On first consideration it might be thought that a sufficiently good fit might be made with two constants. For the red lead monoxide similar weighting yields

$$h_{t-25} = 0.051895(t-25) + 1.1143 \times 10^{-5}(t-25)^2 \quad (11)$$

$$C_p = 10.100 + 4.9743 \times 10^{-3}T \quad (12)$$

Two of the deviations of Eq. 11 are within the probable errors and the sum of the squares of the deviations is about twice as large as that derived from the cubic equation. For the yellow lead monoxide all the deviations from an equation similar to Eq. 11 are larger than the probable errors and the sum of the squares of the deviation is seven times as large as that from the cubic equation.

Summary

1. The construction of an aneroid calorimeter of the type used by Jaeger and co-workers has been described.

2. The heat contents of yellow and red lead monoxides have been measured between 25° and 400 to 650° and 400 to 550°, respectively.

3. Equations expressing the heat capacities of the yellow and red lead monoxides have been derived.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Conductances of Aqueous Solutions of the Hydroxides of Lithium, Sodium and Potassium at 25°

BY LAWRENCE S. DARKEN¹ AND HARRY F. MEIER²

Previous work done in this Laboratory on the conductance of acids and salts led to the belief that the application of this same conductance method to the hydroxides of lithium, sodium, and potassium would give information as to whether these bases behaved as typical strong electrolytes or whether they exhibited evidence of incomplete ionization.

The conductances were measured using the same apparatus and technique described in previous publications.^{3,4,5} The values of Jones and Bradshaw⁶ for the specific conductivities of potassium chloride solutions were used to determine the cell constants.

The hydroxide solutions were prepared by dilution of saturated solutions. In the case of the saturated solution of potassium hydroxide, a small amount of saturated barium hydroxide solution was added to precipitate the carbonate completely. This was unnecessary in the cases of the saturated solutions of the other two hydroxides. Preliminary tests showed that the conductances of lithium hydroxide solutions were the same whether the saturated solutions from which they were prepared had been treated with barium hydroxide or not. The saturated solutions were

prepared in all cases from the highest grade hydroxides. The standardization of the bases was accomplished indirectly as follows: the stock solution was titrated, using phenolphthalein indicator, against benzoic acid and also against potassium acid phthalate, both certified by the Bureau of Standards. A hydrochloric acid solution was then titrated against the stock solution, using phenolphthalein indicator, thus establishing the titer of the acid solution. The accepted titer of the stock solution of base was obtained by titration against this acid solution using sodium alizarine sulfonate indicator; this value thus included both the base and the carbonate content of the solution. It differed from the direct standardization (using phenolphthalein indicator) by about 0.1% for the 0.2 demal stock solution, while for the more concentrated solution the difference was negligible. The titrations were performed with weight burets and were completed with a solution one-tenth the concentration of the main solution; the reproducibility was about one part in ten thousand. Care was exercised to exclude carbon dioxide at all times. All stock solutions were prepared from water having a measured specific conductance less than 10^{-6} reciprocal ohms.

Λ_0' was plotted against C , as shown in Fig. 1, in an attempt to express the measured equivalent conductances in the dilute region by means of Shedlovsky's extension of Onsager's equation.^{7,8,9}

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(2) Present address: The Upjohn Company, Kalamazoo, Michigan.

(3) Saxton and Langer, *THIS JOURNAL*, **55**, 3638 (1933).

(4) Saxton and Meier, *ibid.*, **56**, 1918 (1934).

(5) Saxton and Darken, *ibid.*, **62**, 846 (1940).

(6) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(7) Onsager, *Physik. Z.*, **27**, 388 (1926), **28**, 277 (1927).

(8) Onsager, *Trans. Faraday Soc.*, **23**, 341 (1927).

(9) Shedlovsky, *THIS JOURNAL*, **54**, 1405 (1932).