# Electrical Conductance, Surface Tension, and Density in the Molten System $PbMoO_4$–$Bi_2(MoO_4)_3$

KELSO B. MORRIS,[1] NIMROD McNAIR,[2] and GORDON KOOPS[2]
Chemistry Section, Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio

BLOOM AND HEYMAN (*2*) in 1946 published an article which appears to have initiated much of the interest of present-day chemists in the measurement of properties of fused salt systems. A recent review by Janz and his collaborators (*6*) and the writings of others (*4*) give an idea of the unusually large amount of interest today in high-temperature research. This interest is obviously related to the quest for deeper theoretical knowledge about the liquid state and to the demands of modern technology for information on the properties of materials at greatly elevated temperatures.

It is logical that much of the research thus far has been centered around the properties of simple fused salt systems such as those involving the alkali metal halides and, to a lesser extent, 1-2 and 2-1 electrolytes. It was an interest of the senior author to continue an investigation of fused molybdate systems with scientific equipment superior to that employed in previous work with a molybdate system (*8*). No data have been published on the electrical conductance for the system lead molybdate–bismuth molybdate. The phase diagram of Zambonini (*13*) indicates a simple eutectic system. Therefore, the system should be a good one for study in an effort to ascertain whether any correlation exists between the phase diagram and electrical properties of the system. Another facet of interest in the study of properties of a binary system consisting of ternary salts with a common anion must involve speculation as to the extent to which molybdate anions, the metal cations, and oxide ions contribute to the total conductance of each mixture.

Surface tension is one property for which only a few reports have appeared in recent scientific literature for fused salt systems. In the course of planning research in this laboratory on the measurement of resistance in the fused salt system, lead molybdate–bismuth molybdate, the decision was made by the senior author to measure surface tension and density simultaneously for the same system. Density measurements are of value in both conductance and surface tension calculations. No data have been reported on either property for this system.

## ELECTRICAL CONDUCTANCE

**Experimental.** APPARATUS. A Marshall tubular testing furnace, 2.5-inch I.D., 12-inch O.D., 16 inches long, was employed for heating all samples. Furnace windings, on the outside of an impervious alumina core, were of platinum-rhodium alloy wire of a size that permitted a maximum sustained operation temperature of 1500° C. The presence of ten shunt taps, available through binding posts spaced vertically on the bright chromium plate exterior, made it possible to remove or impose thermal gradients along the entire length of the heating chamber. A high-purity alumina thermocouple well, located directly beneath the heating element and running the full length of the furnace chamber, held a Pt-Pt 13% Rh thermocouple. This thermocouple and a millivoltmeter pyrometer controller monitored the heating element temperatures.

A platinum–20% rhodium alloy crucible (diameter at top, 4.9 cm.; depth, 5.3 cm.) with reinforced rim and bottom and of 70-ml. capacity was used as container for the melts. The crucible rested on an alumina pedestal which could be raised or lowered through a vertical distance of 7 inches by a Cenco-Lerner Lab-Jack. When the pedestal was raised to the proper height into the furnace interior, it fitted flush against the lower open end of an alumina tube (2¼-inch O.D., 2-inch I.D., 16 inches tall) which, in turn, was supported within the alumina tube which lined the furnace chamber. The upper end of the first alumina tube was fitted with a Transite plug which held the following items as a unit: silica tubing for argon inlet, the handle part (an alternate thermocouple sheath) of the clear quartz conductance cell, platinum–10% rhodium wire (0.03-inch diameter) as electrode leads of the cell, and an alumina protection tube of thin wall which contained the Bristol platinum–platinum 10% rhodium measuring thermocouple for the melts. The upper end of this alumina tube assembly extended about 3 inches above the top of the furnace and was fixed in this position by means of a metal strap clamp. In the course of measuring melt temperatures with a Leeds and Northrup Type K-2 potentiometer, using a 0° C. ice reference junction, the lower end of the thermocouple protection tube was approximately ¼ inch above the surface of the melt. To provide an inert atmosphere, pure argon gas was circulated through the interior of the chamber continuously while each sample was heated from room temperature to elevated temperatures and cooled finally to room temperature.

The quartz dip-type capillary conductance cell used in the research was essentially identical in design and dimensions to that described by Van Artsdalen (*11*), except that the length of each capillary arm had to be limited to a little less than 2 inches by virtue of the height limitation of the platinum-rhodium alloy crucible which contained the samples. Platinum disk electrodes, each having a 3-mm. length of platinum-rhodium alloy wire welded to the center of the underside of the disk, rested on the shelf at the top of the capillary tubing of the cell.

Resistance measurements were made with a Leeds and Northrup precision Jones bridge. Principal accessories for the bridge were a Hewlett-Packard oscillator (20 cps. to 20 kc., Model 201-C), a General Radio amplifier and null detector (Model 1231-BMA), and a General Radio adjustable filter (Model 1231-P5M) for suppressing harmonics, noise, and hum. All leads were shielded. As an alternative means of determining bridge balance, the amplifier of the General Radio unit was used in conjunction with a DuMont cathode ray oscilloscope.

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[1] Present address, Department of Chemistry, Howard University, Washington 1, D. C.

[2] Present address, Space Systems Division, Air Force Unit Post Office, Los Angeles 45, Calif.

Early in the work, resistances of the melt were measured at several frequencies, to ascertain whether this was necessary to obtain polarization-free resistance. In aqueous solutions, a plot of measured resistance *vs.* the reciprocal of the square root of the frequency enables one to extrapolate to infinite frequency and thereby obtain a polarization-free resistance. However, polarization was not found to be significant for the capillary cells. Therefore, resistances of melts were all made at a frequency of 2000 cps. Demal aqueous potassium chloride solution at 25.0° C. was used to calibrate the conductance cell, using platinized electrodes, according to the recommendations of Jones and Bradshaw (*7*). No correction was made for the slight expansion of the quartz cells at elevated temperatures, because the correction is too small to be significant. Cell constants were of the order of 140 to 200 cm.$^{-1}$ To obtain higher cell constants, it would have been necessary to increase the capillary length and/or decrease its diameter. Neither adaptation was desirable for molybdate melts. At the first indication of devitrification (on the average, after use with two melts), cells were discarded and new ones calibrated and put into service.

Density data used in the calculations for equivalent conductance were obtained in connection with measurements described below.

CHEMICALS. The separate salts were obtained on special order from the S. W. Shattuck Chemical Co., Denver, Colo. Specifications for their preparation included use of best analytical reagent grade chemicals, heating of each product almost to sintering, cooling, and crushing to fine powder. Spectroscopic examination of the anhydrous salts revealed that both were of analytical reagent quality. For this research, the salts were dried at 200° C. for an hour. After cooling, mixtures were made by weighing appropriate amounts of the two chemicals and mixing thoroughly to ensure homogeneity.

All melts appeared to be homogeneous after cooling to room temperature in an atmosphere of pure argon. The results of complete analyses of representative samples of all melts were not available, at the completion of this article, from a cooperating Air Force laboratory and one of its heavily taxed analytical contractors.

**Results and Discussion.** The specific conductance, $\kappa$, of various compositions of lead molybdate and bismuth molybdate was determined, on the average, from about 50° to 150° above the melting point (Table I). No conductance data have been reported previously for this system. Although the pure salts are considerably poorer conductors than sodium chloride (about 4 ohm$^{-1}$ cm.$^{-1}$ for NaCl at 150° above the melting point), lead molybdate is a much better conductor than bismuth molybdate. Plots of specific conductance *vs.* temperature and of equivalent conductance *vs.* temperature are linear for all compositions. A quantitative explanation of the conduction process for this system must await the results of further studies that have just been begun by the senior author on other molten molybdate systems. A tentative speculation is that the principal current-carrying species in the melts are $MoO_4^{-2}$ and $Pb^{+2}$ and/or $Bi^{+3}$ and that most of the current is carried by molybdate ion. [Parsons (*9*) gives 0.96 and 1.20 A. as radii for $Bi^{+3}$ and $Pb^{+2}$ ions, respectively. Stern and Amis (*10*) give 2.54 A. for $MoO_4^{-2}$ ion. However, molybdate ion is the lightest of the three. Transference numbers are probably of the order $t_{MoO_4^{-2}} \gg t_{Pb^{+2}} > t_{Bi^{+3}}$.]

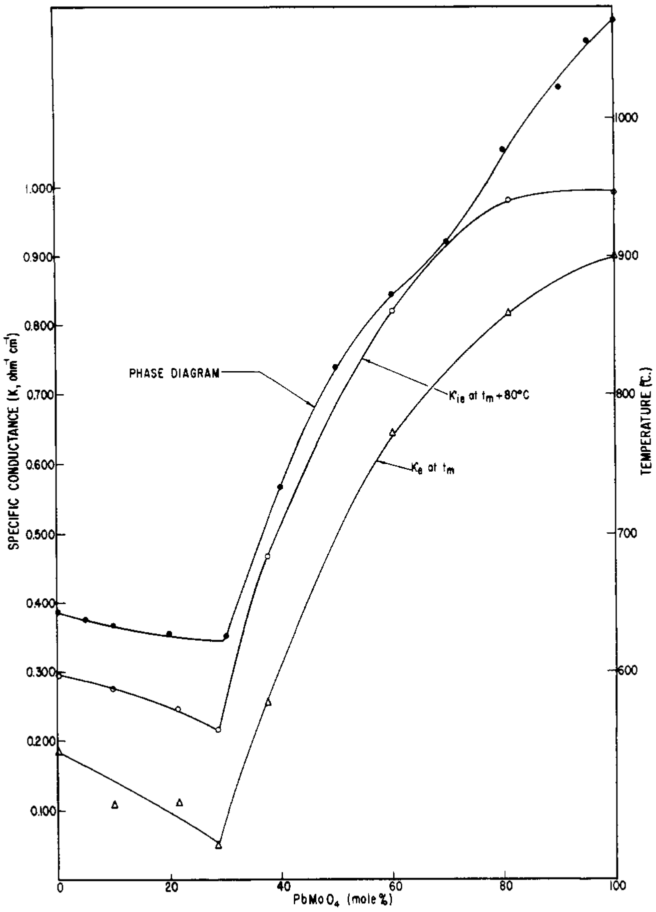

Figure 1. Specific conductance *vs.* composition for melts at corresponding temperatures

Under curve is temperature-composition diagram for system

Table I. Specific Conductance in the System $PbMoO_4$-$Bi_2(MoO_4)_3$

| Mole % $PbMoO_4$ | Temp., ° C. | Spec. Cond., $K$, Ohm$^{-1}$ Cm.$^{-1}$ | Mole % $PbMoO_4$ | Temp., ° C. | Spec. Cond., $K$, Ohm$^{-1}$ Cm.$^{-1}$ |
|---|---|---|---|---|---|
| 0.000 | 707.6 | $0.2735_9$ | 37.80 | 779.5 | $0.3841_7$ |
| | 746.6 | $0.3327_4$ | | 800.5 | $0.4350_3$ |
| | 793.7 | $0.4331_9$ | | 819.3 | $0.4704_4$ |
| | 817.4 | $0.4802_3$ | | 843.8 | $0.5241_1$ |
| | 847.3 | $0.5502_9$ | | | |
| 10.00 | 717.2 | $0.2815_9$ | 60.00 | 910.2 | $0.7270_1$ |
| | 743.4 | $0.3319_2$ | | 934.5 | $0.7781_2$ |
| | 767.3 | $0.3795_2$ | | 951.2 | $0.8165_4$ |
| | 788.8 | $0.4255_8$ | | 975.5 | $0.8694_4$ |
| 21.30 | 703.7 | $0.2371_9$ | 80.40 | 1023.7 | $0.9126_3$ |
| | 728.0 | $0.2886_0$ | | 1026.0 | $0.9161_5$ |
| | 748.9 | $0.3288_3$ | | 1035.9 | $0.9354_5$ |
| | 771.0 | $0.3706_8$ | | 1051.3 | $0.9658_8$ |
| | 789.5 | $0.4089_7$ | | 1060.8 | $0.9875_5$ |
| 28.50 | 718.3 | $0.2989_0$ | 100.00 | 1098.1 | $0.9375_8$ |
| | 735.7 | $0.3467_7$ | | 1107.4 | $0.9495_1$ |
| | 749.2 | $0.3766_0$ | | 1115.7 | $0.9583_3$ |
| | 769.1 | $0.4200_9$ | | 1117.5 | $0.9627_2$ |

Physical properties of different substances should be compared at "corresponding temperatures." Bloom and Heyman (*2*) compare conductances at 10% above the melting point in absolute degrees. Recently, others (*12*) have defined their corresponding temperatures in a slightly different manner and have compared conductances at equal fractions, $\theta$, above the melting point, where $\theta = T° K/T_m° K$. In the present research conductances are compared at the melting point and at 80° above the melting point. These data and the phase diagram data of Zambonini (*13*) are shown in Table II. When these data are plotted *vs.* composition, as in Figure 1, one observes a very striking resemblance between the two conductance curves and the phase diagram for the system. This suggests that for this system and for the temperature ranges employed, the structures of the melts are not vastly different from the structures of the corresponding solids. Moreover, this definition of "corresponding temperature" as employed here may be useful for other two-component systems possessing a common ion and which reveal only a simple eutectic in the phase diagram. Although specific conductances have been used on the plot, the same sort of resemblance would be observed if equivalent conductances were used for the same system. Molar or equivalent conductance concepts are usually more fundamental.

## SURFACE TENSION AND DENSITY

**Apparatus.** Density and surface tension measurements were based, respectively, on the Archimedean principle and the break-weight technique. The density-surface tension bob was of platinum and weighed 20.7 grams. When viewed in a plane, the cylindrical body was hexagonal and carried a pin of 0.051-inch diameter × 0.25 inch extending from the lower tip of the hexagon. The end of this pin was perfectly flat. The bob stem, 0.035 inch in diameter, extended 7/16 inch from the upper tip of the hexagon and ended in an eyelet for attachment to the suspension system. A volume correction for the bob because of expansion at high temperatures was made in all density calculations. The bob was suspended from the left end of the beam of a high-quality Chainomatic analytical balance by means of a Pt-10% Rh wire of 0.03-inch diameter. The procedures for making density and surface tension measurements almost simultaneously were essentially those described by Janz and Lorenz (*5*).

**Results and Discussion.** In the fused salt system, lead molybdate-bismuth molybdate, surface tension measurements were made for eight compositions (Table III). When surface tension is plotted as a function of temperature for the several compositions, some of the plots are linear while others are parabolic. Usually, with simple salts, surface tension varies with temperature, $t$, according to the linear relation, $\gamma = a - bt$, where $a$ and $b$ are empirical constants. A reader may wonder why the parabolic curves were not averaged as best straight lines. In a mixture such as the eutectic composition of 28.50 mole % $PbMoO_4$, alternate points were obtained for ascending temperatures and descending temperatures, respectively. The smoothness of the curve appears to support the validity of the data. In the case of the mixture consisting of 60.00 mole % $PbMoO_4$, temperature cycling gives essentially the same type of curve with a "wiggle." Future investigations involving use of the maximum bubble pressure method and of a third experimental method for the same system should enable one to compare the extents to which each method will yield precise data for fused salt systems.

If one constructs "best" straight lines for the surface tension-temperature plots and then compares surface tensions for the system at "corresponding temperatures," as is done above for conductance data, the surface tension *vs.* composition plots are inversions, in appearance, of the phase diagram. The surface tension is a maximum for the eutectic composition and corresponds to about 176.0 dynes $cm.^{-1}$ at $t_m$ (615° C.) and of about 170 dynes $cm.^{-1}$ at a temperature 80° higher. This fact lends further support to the usefulness of this definition of corresponding temperatures in comparing properties of various substances.

Density data for the system are given in Table IV. Density-temperature plots are all linear. If the densities for the several compositions are compared at the corresponding temperatures, density, like surface tension, is a maximum for the eutectic composition.

Recently, Bloom and his collaborators (*1*) have used total surface energy or surface heat content per unit area ($H^s/a$) in comparing melts. The relation is $H^s/a = \gamma - T(d\gamma/dT)$, where $\gamma$ is defined as surface free energy per unit area and $d\gamma/dT$ represents the negative of the surface entropy per

Table II. Specific Conductance and Phase Diagram[a] Data

| Mole % $PbMoO_4$ | Melting Point, $t_m$, ° C. (*13*) | Spec. Cond., $K_e$,[a] at $t_m$, $Ohm^{-1}Cm.^{-1}$ | Spec. Cond., $K_{ie}$,[b] at $t_m$ + 80° C., $Ohm^{-1}Cm.^{-1}$ |
|---|---|---|---|
| 0.00 | 643 | 0.185 | 0.295 |
| 5 | 638 | | |
| 10.00 | 634 | 0.110 | 0.275 |
| 20 | 628 | | |
| 21.30 | 628 | 0.110 | 0.245 |
| 28.50E | 615E | 0.050 | 0.215 |
| 30 | 627 | | |
| 37.80 | 733 | 0.255 | 0.465 |
| 40 | 734 | | |
| 50 | 820 | | |
| 60.00 | 872 | 0.645 | 0.820 |
| 70 | 910 | | |
| 80 | 977 | | |
| 80.40 | 977 | 0.815 | 0.980 |
| 90 | 1022 | | |
| 95 | 1054 | | |
| 100.00 | 1065 | 0.900 | 0.995 |

[a] Extrapolated to melting point, $t_m$.
[b] Interpolated or extrapolated to $t_m$ + 80° C.

Table III. Surface Tension in the System $PbMoO_4$-$Bi_2(MoO_4)_3$

| Mole % $PbMoO_4$ | Temp., ° C. | Surface Tension, Dynes /Cm. | Mole % $PbMoO_4$ | Temp., ° C. | Surface Tension, Dynes /Cm. |
|---|---|---|---|---|---|
| 0.00 | 680.8 | 161.8 | 37.80 | 747.1 | 162.5 |
| | 701.1 | 162.0 | | 767.3 | 162.7 |
| | 720.8 | 160.2 | | 791.3 | 159.7 |
| | 740.5 | 157.8 | | 834.0 | 155.1 |
| | 760.3 | 154.8 | | | |
| 10.00 | 727.9 | 164.7 | 60.00 | 899.7 | 159.3 |
| | 752.0 | 162.3 | | 917.8 | 159.0 |
| | 759.2 | 161.4 | | 935.0 | 156.6 |
| | 773.3 | 160.5 | | 953.5 | 155.8 |
| | 783.3 | 160.5 | | | |
| | 807.8 | 158.4 | | | |
| 21.30 | 680.7 | 163.7 | 80.40 | 1027.3 | 156.9 |
| | 707.3 | 161.7 | | 1037.8 | 155.6 |
| | 745.3 | 158.7 | | 1046.5 | 155.8 |
| | 777.2 | 155.8 | | 1059.6 | 154.3 |
| | 797.4 | 154.9 | | | |
| 28.50 | 697.1 | 169.7 | 100.00 | 1093.2 | 166.0 |
| | 720.8 | 168.4 | | 1106.3 | 163.5 |
| | 741.7 | 167.1 | | 1115.3 | 163.9 |
| | 760.6 | 165.5 | | 1124.5 | 163.8 |
| | 787.6 | 162.7 | | | |

Table IV. Density in the System $PbMoO_4$-$Bi_2(MoO_4)_3$

| Mole % $PbMoO_4$ | Temp., ° C. | Density, G./Cc. | Mole % $PbMoO_4$ | Temp., ° C. | Density, G./Cc. |
|---|---|---|---|---|---|
| 0.00 | 680.9 | 5.219 | 37.80 | 781.8 | 5.182 |
| | 702.8 | 5.191 | | 801.5 | 5.158 |
| | 722.9 | 5.170 | | 817.8 | 5.139 |
| | 744.2 | 5.155 | | 836.6 | 5.112 |
| | 761.1 | 5.128 | | | |
| 10.00 | 741.6 | 5.164 | 60.00 | 839.6 | 5.135 |
| | 762.1 | 5.144 | | 915.8 | 5.116 |
| | 786.2 | 5.115 | | 935.3 | 5.109 |
| | 811.9 | 5.087 | | 956.8 | 5.091 |
| 21.30 | 691.4 | 5.226 | 80.40 | 1015.8 | 5.112 |
| | 743.4 | 5.173 | | 1025.7 | 5.104 |
| | 778.1 | 5.138 | | 1037.5 | 5.097 |
| | 812.6 | 5.102 | | 1045.6 | 5.090 |
| | 851.1 | 5.070 | | 1058.5 | 5.079 |
| 28.50 | 741.6 | 5.203 | 100.00 | 1074.3 | 5.235 |
| | 749.1 | 5.192 | | 1089.6 | 5.226 |
| | 757.5 | 5.182 | | 1106.9 | 5.213 |
| | 787.6 | 5.147 | | 1128.2 | 5.199 |

unit area ($-S^s/a$). Those investigators point out that surface heat content per unit area is a constant and independent of temperature, if the temperature coefficient of surface tension is constant for the molten salts. The present authors hoped to test the applicability of this concept to the lead molybdate–bismuth molybdate system. However, they are unable to use the concept because the temperature coefficient of surface tension is not invariant for some of the mixtures of their system.

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# Vapor Pressure of Ammonium Nitrate

J. D. BRANDNER, NORMAN M. JUNK, J. W. LAWRENCE, and JACK ROBINS
Atlas Chemical Industries, Inc., Reynolds Experimental Laboratory, Tamaqua, Pa., and
Technical Center, Wilmington 99, Del.

FEICK(1) determined the vapor pressure of liquid ammonium nitrate from 190° to 270° C. using a modified boiling point apparatus. He showed that, at these temperatures, ammonium nitrate vaporizes by dissociation:

$$NH_4NO_3(l) \rightleftarrows NH_3(g) + HNO_3(g)$$

The object of this investigation was to extend the work of Feick on liquid ammonium nitrate to lower temperatures and to determine the vapor pressure of the solid.

## EXPERIMENTAL

The vapor pressure was measured by a transpiration method based on the relationship first derived by Regnault (5).

$$p = Pv/V$$

where $p$ is the vapor pressure in millimeters, $P$ the barometric pressure in millimeters, $v$ the volume in liters of ammonia and nitric acid produced by the dissociation of ammonium nitrate, and $V$ the total gas volume in liters.

A known volume of dry gas (air or nitrogen) was passed slowly over the heated sample (10 to 30 grams) of C.P. ammonium nitrate, then through an air-cooled condensation trap filled with glass wool, and successively through a solid carbon dioxide trap and a wet-test meter. Experiments were of 1 to 120 hours' duration. The temperature of the furnace was controlled by means of a Thermocap relay. The sample temperature was separately measured by a Chromel-Alumel thermocouple placed directly over the sample.

Repeated runs at different flow rates produced only small differences in vapor pressure and no consistent pattern in these differences other than that of experimental error. Calculations indicated that the carrier gas became saturated with ammonium nitrate in a fraction of a second. For solid ammonium nitrate, the gain in weight of the condensation trap (after the contents had been dried in vacuo at room temperature) was essentially equal to the weight loss of the sample, which was taken as the weight of vaporized ammonium nitrate. For liquid ammonium nitrate the weight gain in the condensation trap was less than the sample weight loss, this difference in weight being taken as the amount decomposed. The loss due to decomposition ranged from 0.12% of a 15-gram sample in 6 hours at 170° C. to 15% of the sample in 40 minutes at 240° C. With liquid ammonium nitrate virtually all of the water vapor resulting from the decomposition was retained by the system, part by the condensed ammonium nitrate, and the remainder by the solid carbon dioxide trap. Since this water vapor also made up part of the gas volume above the ammonium nitrate and was not measured by the wet-test meter, its volume was calculated from the amount of decomposed ammonium nitrate and used to correct the vapor pressure calculations. In addition, a method of iteration was used to correct for the period of time the sample was warming to temperature. The vapor pressures were calculated on the assumption that the ammonium nitrate dissociated completely to nitric acid and ammonia