Surface Tension and Density of Liquid Lead

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New measurements of the surface tension of 99.999% lead from 344–652°C with an improved maximum bubble pressure (MBP) system indicate that data reported in the literature many years ago are probably better than more recently reported measurements. Results show that the surface tension of liquid lead (γ) is given by γ(ergs/cm^2) = 467.7 − 0.066 T (°C) with a standard deviation from regression of 2.1 ergs/cm^2. Density of liquid lead was also obtained with the MBP system over the range from 384–551°C. The density of lead (ρ) is given by ρ(g/cm^2) = 11.13 − 0.14 × 10^{-2} T (°C) with a standard deviation from regression of 0.24 g/cm^2. A table of experimental and calculated values is given with graphs for comparison with data reported in the literature.

During investigations on the properties of solders and soldering systems, and while trying to relate such items as wetting and adhesion to soldering, questions about surface tensions of liquid metals became important. The literature shows that although many have measured the surface tensions of tin and lead, and all claim a certain amount of accuracy for their data, no two experimenters agree. A maximum bubble pressure (MBP) system having remarkable precision was developed (*11*) to measure these questionable surface tensions for ourselves. The surface tension and density of tin have been reported previously (*10*). This report gives our results for lead.

Normally, one would take the latest measurements of surface tension to be the most accurate because modern methods, higher purity materials, and more precise measurement and error analysis would be expected to produce superior data. For lead, those considerations do not hold. The latest measurements for lead by Melford and Hoar (*8*), dated about 1956, show a large disagreement with earlier data. Measurements by Mima and Kuranuki (*9*) also about 1957, although showing a temperature coefficient for surface tension similar to some earlier work, are much too high to be considered logical. Data reported by Matuyama in 1927 (*6*) also seem to be out of place. A fairly thorough discussion on surface tension of pure metals, including lists of numerical data from other experimenters, has been written by Semenchenko (*12*). The data for lead that Semenchenko reports are, with the exception of three numbers, the only data given in the tables in the 50th edition (1969-70) of the "Handbook of Chemistry and Physics" (*15*). The wide disagreement among these figures in the Handbook is confusing and thus required that we make new measurements. The new data for the surface tension of lead over the temperature range from 344-652°C indicate that the work by Bircumshaw in 1926 (*1*) and 1934 (*2*), or the data by Greenaway in 1947 (*3*) were, perhaps, more suitable than later measurements.

The density of liquid lead has been measured with high precision by many others and little disagreement is evident in the reported values. However, because density is needed in the calculations for surface tension, and the MBP apparatus was designed to include a rather precise measurement of density, the density of lead from 384-551°C is also given in this report. The density-measuring ability of the MBP apparatus was indispensable for measurements on other metals or alloys so that the determinations of density for lead authenticate the precision of the method.

EXPERIMENTAL

The MBP system uses a modified form of the Sugden twin capillary method (*13*), where two capillaries of different radii are placed side by side at the same depth in the liquid. The original Sugden method used concentric capillaries. The twin-tube system overcomes the experimental problem of locating the depth of immersion of the capillaries.

Other features of the MBP system that contribute to reliability and precision include: silica capillary tips ground internally in a cone shape so that a fairly sharp edge (~0.03 mm) is formed on the outside diameter, electronic differential pressure transducers with a digital readout to 0.005 torr, a micrometer screw reading to 0.0001 in. to adjust the depth of immersion of the capillaries allowing for density measurements, and a fast response recorder to monitor the pressure attained for each bubble. For nonwetting liquid metals the sharp edge on the outside of the capillary tip assures that the bubbles form on the outside diameter of the tube. The gas used to form the bubbles was commercial high-purity helium further purified by passing it through a drying column and through a train of heated titanium chips.

Corrections for nonsphericity of the bubbles resulting from the pressure head of the liquid metal were made by the method proposed by Sugden (*13*). [A summary of Sugden's method is also given by White (*17*), pp 764-5.] The correction method involves a series of successive approximations so a digital computer was used to reduce the data and derive equations for surface tension and density.

A total of 71 data points from three separate samples of lead were obtained for the surface tension measurements. For the density, eight pairs of determinations (16 data points) were made on the first lead sample only. Different sets of capillaries were used for each of the three different lead samples. For sample 1, the radii were 1.0552 mm and 0.5898 mm; for sample 2, 1.6165 mm and 0.9625 mm; for sample 3, 1.8576 mm and 0.9752 mm. These radii represent the average of four measurements of diameter on each tip (every 45°), and were made at 500× magnification with a metallograph calibrated for this purpose. Each pair of capillaries was checked before making measurements on lead by measuring the surface tension of triple-distilled mercury at room temperature (25°C). For this standardizing, the figure supplied by Ziesing (*18*), 484.9 ergs/cm^2, became the target value. The measurements made with all three sets of capillaries were within 1% of Ziesing's figure [and previous measurements by the authors (*11*)]; therefore the capillary preparation and radii measurements were considered adequate for the subsequent work on molten lead. The use of mercury at room temperature for a check on the MBP system is valid for higher temperatures because the thermal expansion of the capillary tips is practically self-canceling. In the twin-tube system the expansion coefficient is the same for both capillaries, and the numerical difference in expansion of the two tubes produces less than 0.05% error in the radii at 650°C. This error is much smaller than the scatter of data points, so that no corrections are necessary.

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The lead used for the tests was obtained as 99.999% pure. Spectrographic analyses of the lead showed only traces of silicon and copper as the detectable impurities. Analyses were made before and after the surface tension was measured. The reference to trace amounts indicates that the spectral lines were just barely visible on the spectrographic film—of the order of a few parts per million. The presence of these small amounts of copper or silicon would tend to increase the surface tension of the lead slightly, because both elements have much higher surface tensions than lead. The usual behavior of the surface tension of mixtures, plus the point that the MBP method minimizes the influence of surface active impurities *(11)*, indicates that the purity of the molten lead is not a major factor in the accuracy of the results given.

Temperatures in the melt were measured using a type K thermocouple in a silica protection tube positioned close to the two capillary tips. The thermocouple was checked for the temperature ranges of the tests with a set of melting point standards. The temperatures given in the data are considered to be within ±0.5°C of the true temperature.

The bubble pressure measurements for the first run were made with the capillaries immersed at two different depths for each of the eight different temperatures. This results in two surface-tension measurements and two density measurements for each temperature. The slight changes in liquid level resulting from the changes in the immersion of the capillaries and thermocouple tube were calculated from the dimensions of these parts and the crucible. These changes in liquid level were included in the calculations for density. They do not affect the surface tension calculations.

RESULTS

The experimental values for the surface tension and density of liquid lead over the temperature ranges used are given in Table I, along with the values calculated from the linear equations obtained by a least-squares analysis of the data.

The straight line density-temperature relationship for liquid lead is shown in Figure 1 along with data from the literature. The equation for the density (ρ) of liquid lead vs. temperature (T,° C) is:

$$\rho(\mathrm{g/cm^3}) = 11.13 - 0.14 \times 10^{-2}\, T$$

from the melting point to above 551°C. The standard deviation from regression is 0.024 g/cm^3. The temperature coefficients for density reported by others are virtually the same as obtained in this work, −0.0014/°C. The vertical scale for the graph has been expanded significantly so that the various lines could be separated on the graph. All the curves (straight lines) shown are actually close together. The methods for obtaining these density figures, however, are decidedly different. Hogness *(4)* used a U-tube manometer system; Thresh et al. *(14)* used a graphite pycnometer; Kirshenbaum et al. *(5)* employed the Archimedean principle with a graphite sinker. Only Greenaway *(3)* used the MBP system, as did the authors.

A graph of surface tension vs. temperature is given in Figure 2 which includes graphical representations of data taken from the literature. The equation of the line for this work on the surface tension of lead (γ) vs. temperature (T, °C) is:

$$\gamma(\mathrm{ergs/cm^2}) = 467.7 - 0.066\,\mathrm{T}$$

Table I. Surface Tension and Density of Liquid Lead

Test no.	Temp, °C	Surface tension, dyn/cm		Density, g/cm^3	
		Exptl	Calcd	Exptl	Calcd
2	344	443.6	444.9		
2	344	442.7	444.9		
2	346	444.6	444.8		
2	350	445.6	444.5		
2	360	444.6	443.9		
3	360	447.0	443.9		
2	375	445.7	442.9		
1	384	444.0	442.3	10.62	10.59
1	384	444.2	442.3	10.61	10.59
2	386	441.6	442.2		
2	400	443.5	441.2		
1	407	439.2	440.8	10.59	10.56
1	407	439.4	440.8	10.58	10.56
2	408	441.4	440.7		
2	410	439.4	440.6		
3	418	438.6	440.1		
2	422	438.3	439.8		
2	426	441.4	439.5		
1	432	439.1	439.1	10.15	10.53
1	432	439.1	439.1	10.51	10.53
2	433	437.4	439.1		
3	436	439.0	438.9		
2	448	439.4	438.1		
2	462	434.3	437.2		
1	463	437.2	437.1	10.45	10.48
1	463	438.0	437.1	10.45	10.48
2	470	436.2	436.6		
3	476	434.3	436.2		
1	480	435.0	436.0	10.45	10.46
1	480	434.9	436.0	10.45	10.46
2	480	436.1	436.0		
2	486	435.1	435.6		
2	488	438.2	435.4		
2	488	437.1	435.4		
3	492	429.9	435.2		
2	494	437.1	435.0		
1	499	433.4	434.7	10.41	10.43
1	499	432.7	434.7	10.46	10.43
2	500	431.0	434.6		
3	504	436.2	434.4		
3	512	429.1	433.8		
2	515	432.0	433.7		
2	515	434.0	433.7		
2	518	436.1	433.5		
1	523	433.9	433.1	10.39	10.40
1	523	433.4	433.1	10.41	10.40
3	526	432.4	432.9		
3	526	432.4	432.9		
2	528	430.1	432.8		
2	530	434.0	432.7		
2	534	431.9	432.4		
2	550	431.9	431.3		
1	551	431.6	431.3	10.37	10.36
1	551	431.4	431.3	10.39	10.36
2	556	435.2	430.9		
2	559	433.9	430.7		
3	568	434.3	430.2		
2	570	424.7	430.0		
3	572	429.7	429.9		
3	578	428.1	429.5		
2	582	432.9	429.2		
2	582	433.9	429.2		
3	584	425.4	429.1		
2	588	428.8	428.8		
2	602	426.7	427.9		
2	610	425.6	427.4		
3	628	426.2	426.2		
2	640	425.6	425.4		
2	640	425.6	425.4		
2	650	425.6	424.7		
2	652	424.5	424.6		

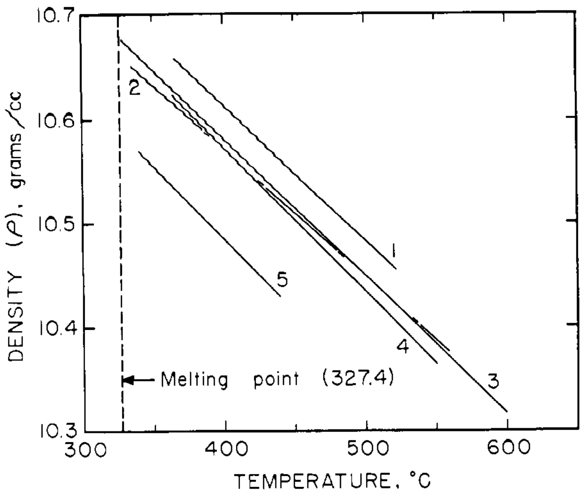

Figure 1. Density vs. temperature for liquid lead

1, Hogness (*4*), 1921, U-tube manometer; 2, Thresh et al. (*14*), 1968, pycnometer; 3, Kirshenbaum et al. (*5*), 1961, Archimedean; 4, This work, MBP; 5, Greenaway (*3*), 1947, MBP

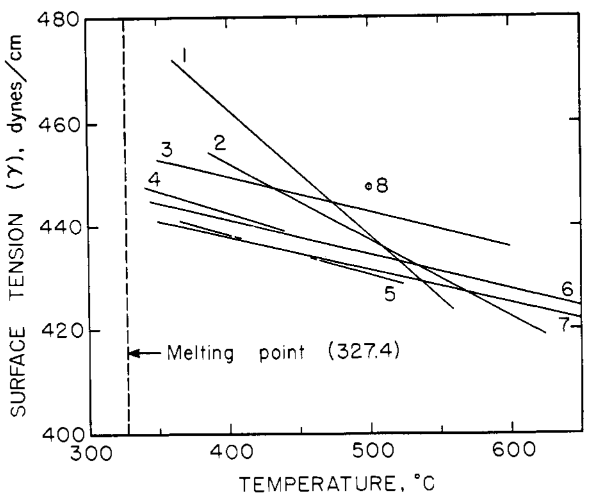

Figure 2. Surface tension vs. temperature for liquid lead

1, Melford and Hoar (*8*), 1956, capillary rise; 2, Motuyama (*6*), 1927, drop weight; 3, Bircumshaw (*1*), 1926, MBP; 4, Greenaway (*3*), 1947, MBP; 5, Hogness (*4*), 1921, maximum pressure in drops; 6, This work, MBP; 7, Bircumshaw (*2*), 1934, MBP; 8, Mayer (*7*), 1961, calculation from model

from the melting point to approximately 650°C. The standard deviation from regression for all the data (shown in Table I) is 2.1 ergs/cm^2. Test number 1 showed the smallest variance giving a standard error of 1.2 ergs/cm^2.

Data by Mima and Kuranuki (*9*) are not shown in Figure 2 because they fall above the limits of the graph. The temperature coefficient of surface tension for Mima and Kuranuki's data is about twice that shown in the equation above, but slightly less than the coefficient given by Matuyama (*6*). Matuyama's drop weight method produced some rather large deviations from the linear relationship near the melting point (not shown in Figure 2). The measurements made by Bircumshaw on two different occasions, 1926 (*1*) and 1934 (*2*), lie on both sides of the data given for this work. In addition, they exhibit almost identical temperature coefficients (-0.059 and -0.070 ergs/cm^2/°C). Over the short temperature range that Greenaway (*3*) reports, his results are close to ours.

A tabulation of the various methods used for measuring the surface tension of lead is rather revealing. Bircumshaw and Greenaway used the MBP method used here as well. This might explain the close agreement in values and coefficients. Hogness (*4*) obtained his data by measuring the pressure required to force a drop of liquid metal out the top of a capillary tube. This system resembles a reversed or "upside down" MBP method and his values, although on the low edge of the rest, are close to all the MBP data.

The fact that molten lead will react with silica under proper conditions is well known. The reactivity will increase with rising temperatures. In a system dependent upon contact angles, such as that used by Melford and Hoar, even a slight reaction of the lead with the silica tube would result in a lowering of the observed surface tension. Thus, Melford and Hoar's excessively high temperature coefficient (-0.24 erg/cm^2/°C) could be explained by slight unobservable reactions.

White (*16*) has commented that the MBP method is "not independent of the contact angle," but Semenchenko (*12*) and others consider the "absence of the contact angle in the final formula" one of the main advantages of the MBP method. Although it was not considered important to the experimental procedure, during the MBP work with lead, if capillaries were immersed in molten lead for periods of more than about 24 hr, even if bubbling constantly, a deposit would accumulate on the tip to prevent further measurements. For the measurements reported. the capillaries always came out of the molten metal in a "clean" condition, and onset of contamination (reaction), if it occurred, was easily detected in the pressure recordings.

The single value for surface tension by Mayer (*7*) is of interest because it was obtained through calculation from a model for molten salt mixtures.

The authors are in full agreement with White's comment (*16*) that accurate values for the surface tension of metals other than mercury may exist, but none is *known* to exist. Nevertheless, the values for the surface tension of lead over the given temperature range shown in this work, and those obtained by Bircumshaw in 1926 and 1934, seem to be more logical under theoretical considerations such as those given by White (*16, 17*). In addition, the values obtained by this work agree with observations on tin-lead alloys (to be reported) and correlate as well with the tin results (*10*).

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