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SURFACE TENSION AND DENSITY OF LIQUID TIN

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SURFACE TENSION AND DENSITY OF LIQUID TIN

by

Alfred E. Schwaneke[1] and Wilbert L. Falke[2]

ABSTRACT

The surface tension from 240° to 844° C and the density from 236° to 583° C of 99.999 percent purity liquid tin has been measured using the maximum-bubble-pressure method. Results for surface tension (γ) show γ (dynes/cm) = $566.84 - 4.76 \times 10^{-2}$ T (° C) with a standard error of ±1.9 dynes/cm. Results for density (ρ) show ρ (g/cm^3) = $7.16 - 6.3 \times 10^{-4}$ T (° C) with a standard error of 0.012 g/cm^3. Comparisons with other data found in the literature are discussed. The experimental results are considered to be as good as any data presently available.

INTRODUCTION

The surface tension and density of liquid tin have been measured by many investigators using different methods (1, 3-4, 6-7, 9-10).[3] Agreement between the reported values for surface tension, however, is poor. Recent data (1959, (1); 1964, (4)) for tin in the useful temperature range (melting point to 600° C) show differences of as much as 10 percent. Older data (1921, (6); 1934, (3)) are often dismissed as being too low because the purity of the tin or the method used for measurement was at fault. In Bureau of Mines studies of the properties of tin-lead solders the dilemma arose of whose data are better. Therefore, new measurements of the surface tension of high-purity tin were made using the maximum-bubble-pressure (MBP) method. The data resulting from these measurements appear very acceptable because they fall generally in the middle range between other data considered either too high or too low. Because the measurement of surface tension for a liquid metal involves a knowledge of the density, and because density data for alloys we intended to study were unavailable, this measurement was included in the design of the apparatus used to measure surface tension. The density values for liquid tin reported here are in close agreement with those reported by others (4-5, 7-8). Surface tension measurements were made from 240° to 844° C. Density was determined from 236° to 583° C. Experimental values are reported along with those

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

calculated from equations derived by a linear least-squares analysis of the experimental data. Comparison of these results with others reported in the literature is included.

APPARATUS AND PROCEDURE

The MBP apparatus is described elsewhere (13). The system uses a modified form of the Sugden twin-capillary method (14) 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 method overcomes the problem of accurately measuring the depth of capillary immersion. Improvements made in this system over other MBP systems described in the literature (17) include (1) internally ground silica capillary tubes which reduce the influence of "tip effects" for nonwetting liquid metals, (2) an electronic differential pressure transducer having a rapid response to replace the usual water or mercury manometer, (3) a micrometer to adjust the immersion depth of the capillaries for density measurements, and (4) recorder-readout of the maximum pressure attained for each bubble.

With the MBP method, gas is forced through a capillary tube immersed in a liquid until maximum gas pressure is achieved and the bubble formed at the capillary tip detaches. The maximum pressure occurs for a nonwetting system, such as tin and silica, when the diameter of the bubble is equal to the outside diameter of the capillary tip. Assuming that the bubble being formed is spherical the total maximum pressure, P_{max}, is equal to the pressure from the liquid metal head, P_h, plus the pressure required to hold the bubble surface against the collapsing force of surface tension, P_γ, thus:

$$P_{max} = P_h + P_\gamma = g\rho h + 2\gamma/r;$$

where g is the acceleration of gravity, h is the height of the liquid metal surface above the tip of the capillary, ρ is the density of the liquid metal, r is the radius of the bubble at maximum pressure, and γ is the surface tension of the liquid. In practice the bubble is not spherical, but is flattened by the pressure head of the liquid. Correction for nonsphericity of the bubbles was made by a method proposed by Sugden (14) in which the data of Bashforth and Adams (2) for liquid drops resting on a solid surface were applied to the case of a gas bubble in a liquid. By using two capillaries of different radii set at the same depth in the liquid, P_h and h cancel out, and γ can be calculated with the difference in bubble pressures from each tube, the density of the liquid, and the radius of each tube (14, 17) including, of course, the correction for bubble distortion. The correction method involves a series of successive approximations so a digital computer was used to reduce the data and derive the resulting equations for surface tension and density.

Three different sets of capillaries were used during the measurements on tin. The tip of each capillary was ground internally to a 60° cone shape so that the thickness of the outside edge of each tip was about 0.04 mm. The capillary pairs had outside tip diameters of 1.623 and 0.995 mm, 1.620 and 0.728 mm, and 1.178 and 0.781 mm, respectively. The density measurements were all made with the last pair of capillaries listed. The pressure transducer was of the "infinite resolution" type, but a digital potentiometer in the system limited the least count to 0.005 torr. The least count of the micrometer elevating screw used to change the capillary immersion for density measurements was 0.0001 inch. Temperatures of the liquid tin were measured with a standardized type K thermocouple inside a thin silica protection tube that was positioned in close proximity to the capillary tips. Certified high-purity grade helium, dried through a calcium chloride and calcium sulfate column 1 meter long, and then further purified through a tube 2 meters long packed with heated titanium chips, was used to form the bubbles in the molten tin.

The tin used for the molten charges was 99.999 percent pure as certified by the supplier. Spectrographic analyses of samples from the charges showed only trace amounts of silicon and calcium. The oxygen content of the tin was not determined. Prior to each experimental run the charge was heated to above 500° C and purged alternately with helium and a vacuum of 1×10^{-3} torr. Under these conditions the partial pressure of residual oxygen should be lower than 1×10^{-10} torr. Several measurements were made using hydrogen instead of helium and no differences in surface tension values were obtained. In addition, during early experiments with molten tin the effect of very low partial pressures of oxygen was determined through the use of Grade A helium (3.6 ppm oxygen, maximum) in the system. The presence of the oxygen was easily detectable as a decrease of surface tension with time. This was indicated by an approximately exponential decay of bubble pressures as the bubbling progressed. Agitating the molten charge by bubbling the helium rapidly through both capillaries for about 5 minutes reproduced the original high bubble pressures followed by their exponential decay. Using certified high-purity helium and increasing the length of the purifying column of heated titanium chips from 0.6 meter to 2 meters removed the apparent effect of oxygen and bubble pressures became constant and reproducible over long periods of time.

Although the capillary tip dimensions were measured with a filar eyepiece microscope, and the pressure transducer was calibrated against a precision mercury servo-manometer, the complete MBP system was always standardized by measuring the surface tension of mercury at room temperature before proceeding with other metals or alloys. The value for the surface tension of mercury used for standardizing was 484.9 dynes/cm at 25° C as reported by Ziesing (18).

With the twin-tube MBP system the actual depth of immersion of the capillaries' tips is not needed for the surface tension measurement, but changes in immersion depth are required for density values. Small corrections were made for the thermal expansion of the stainless steel crucible support and for the change in melt surface level as the immersion depth of the capillaries was changed.

RESULTS AND DISCUSSION

Surface Tension

The results for the surface tension of tin from 240° to 844° C are given in table 1. A linear least-squares analysis gave the following equation for surface tension (γ) versus temperature (T) in ° C:

$$\gamma \text{ (dynes/cm)} = 566.84 - 4.76 \times 10^{-2}\ T.$$

Calculated values of surface tension using the above equation are given in the last column of table 1. The standard error was ±1.9 dynes/cm. Standard error for the predicted values of surface tension can be obtained from the relationship:

$$\text{Standard error of } \gamma \text{ (dynes/cm)} = (0.03962 + 1.98 \times 10^{-6}\ (T - 565.84)^2)^{\frac{1}{2}}.$$

TABLE 1. - Surface tension of liquid tin

Temp., ° C	No. of observations	Observed[1] dynes/cm	Calculated[2] dynes/cm	Temp., ° C	No. of observations	Observed[1] dynes/cm	Calculated[2] dynes/cm
240	1	557.9	555.4	550	3	538.2±0.3	540.7
250	4	556.6±1.2	555.0	580	3	539.5± .8	539.3
346	2	551.2± .8	550.4	586	3	540.6± .8	539.0
355	1	549.8	550.0	600	7	537.9±2.3	538.3
365	2	549.1±1.4	549.5	610	6	537.8±1.4	537.8
397	2	547.1±1.4	548.0	644	1	536.1	536.2
402	3	550.2± .5	547.7	651	5	536.1±1.4	535.9
414	2	549.0± .4	547.2	660	3	532.5± .5	535.5
439	3	544.0± .8	546.0	680	5	534.2±1.4	534.5
450	2	543.3± .2	545.4	702	4	535.1± .1	533.5
478	2	544.0± .9	544.1	720	3	532.9± .5	532.6
502	6	541.3±1.1	543.0	730	2	534.4± .7	532.1
521	3	541.2± .5	542.1	753	3	532.1± .5	531.0
530	3	541.0± .5	541.6	778	2	531.3±0	529.8
538	3	541.7±0	541.3	804	2	528.5± .1	528.6
				844	2	527.3±0	526.7

[1] Value shown is the mean of the number of observations (n). The ± limits represent the estimate of the population standard deviation calculated from the sample

$$s(y) = \left[\frac{\Sigma(y - \bar{y})^2}{n-1}\right]^{\frac{1}{2}} \quad (\underline{16}).$$

[2] Calculated from the equation

$$\gamma = 566.84 - 4.76 \times 10^{-2}\ T\ (° \text{ C}).$$

A straight line representing the equation for surface tension is shown in figure 1 along with other surface tension data for tin found in the literature. As can be seen, the data from the literature show a wide range of disagreement in both specific values and in temperature coefficient (slope of the line). The data from this work fall generally in the center range between low and high data from other sources, although the temperature coefficient is slightly less than any shown.

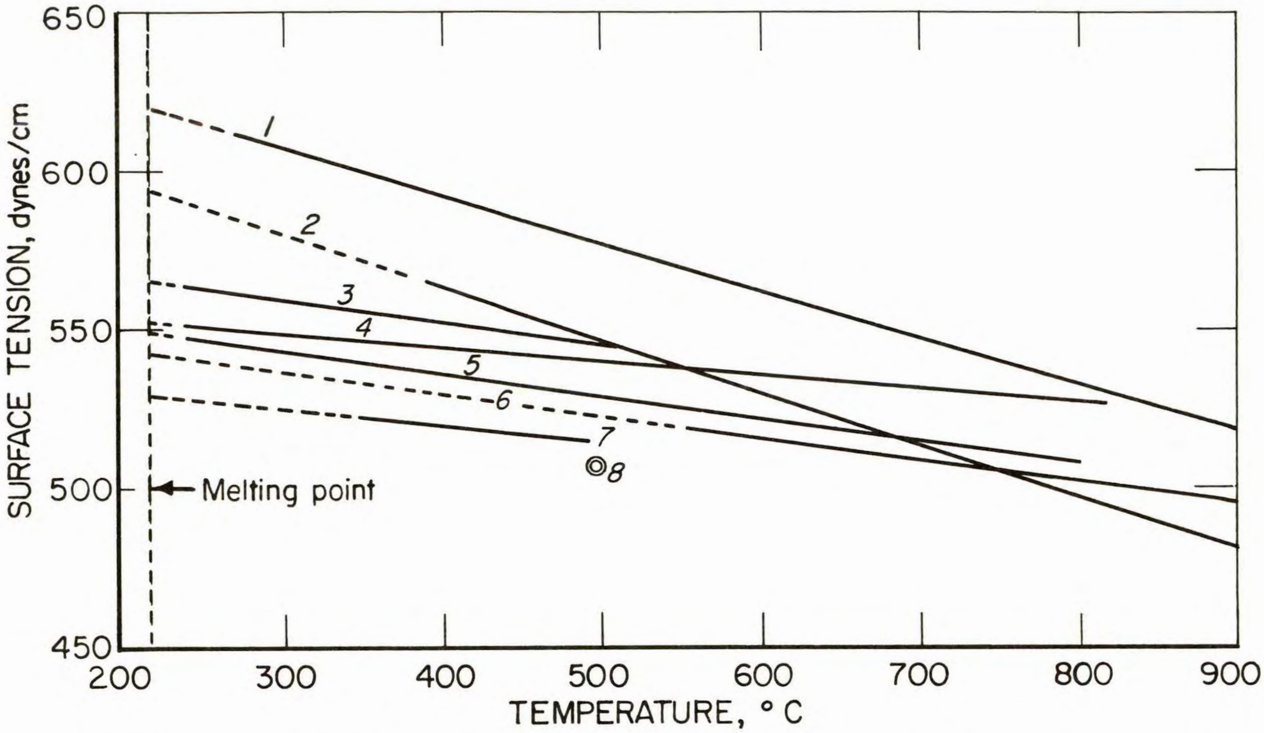

FIGURE 1. - Surface Tension Versus Temperature for Tin. 1, Pelzel, 1949, maximum bubble pressure (11). 2, Allen and Kingery, 1959, sessile drop (1). 3, Melford and Hoar, 1956, capillary rise (10). 4, This work, maximum bubble pressure. 5, Bircumshaw, 1934, maximum bubble pressure (3). 6, Cahill and Kirshenbaum, 1964, maximum bubble pressure (4). 7, Hogness, 1921, maximum pressure in drops (6). 8, Mayer, 1961, calculation from model (9).

For the data given on the graph, Hogness (6), Bircumshaw (3), Cahill and Kirshenbaum (4), and Pelzel (11) all used the MBP method. Pelzel's data give the highest values for surface tension, but according to White (17) his capillaries were too large in diameter which accounts for the erroneously high readings. The data by Hogness (6) and Bircumshaw (3) are usually considered low because the tin they used contained impurities. Cahill and Kirshenbaum (4) used 99.89 percent tin which was even less pure than that used by Hogness or Bircumshaw. The closest data to that of the present work were obtained by Melford and Hoar (10) using a capillary-rise method. The single value reported by Reiss and Mayer (12) was calculated from an ionic salt model. Considering the superior capabilities of the apparatus used, and the careful observance of the many precautions involved in surface tension determinations (17), the authors feel that the data given in table 1 and shown in figure 1 are as good as any available.

Density

Experimental and calculated values for the density of high-purity tin are given in table 2, and a straight line representing the calculated density is plotted in figure 2 along with a selection of older data found in the literature. A linear least-squares analysis of the density data resulted in the following density-temperature equation for liquid tin:

$$\rho\ (\mathrm{g/cm^3}) = 7.16 - 6.3 \times 10^{-4}\ T\ (°\ \mathrm{C}).$$

The standard error was 0.012 g/cm³. Standard error for the predicted values of density can be obtained from the relationship:

$$\text{Standard error of } \rho\ (\mathrm{g/cm^3}) = (8.576 \times 10^{-6} + 0.6151 \times 10^{-9}\ (T - 406.25)^2)^{\frac{1}{2}}.$$

A graph of the density equation is shown in figure 2 along with data from the literature. Kirshenbaum and Cahill (7) and Day, Sosman, and Hostetter (5) used an Archimedean method; Thresh, Crawley, and White (15) and Matuyama (8) used a pycnometer method. The majority of data found place the density of tin at the melting point between 6.95 and 7.01 g/cm³ with temperature coefficients very close to 6 × 10^{-4}. The data given here show a density at the melting point of 7.01 g/cm³ and a temperature coefficient of 6.3 × 10^{-4}. Figure 2 shows that density measurements with the MBP system compare favorably with values obtained by other methods.

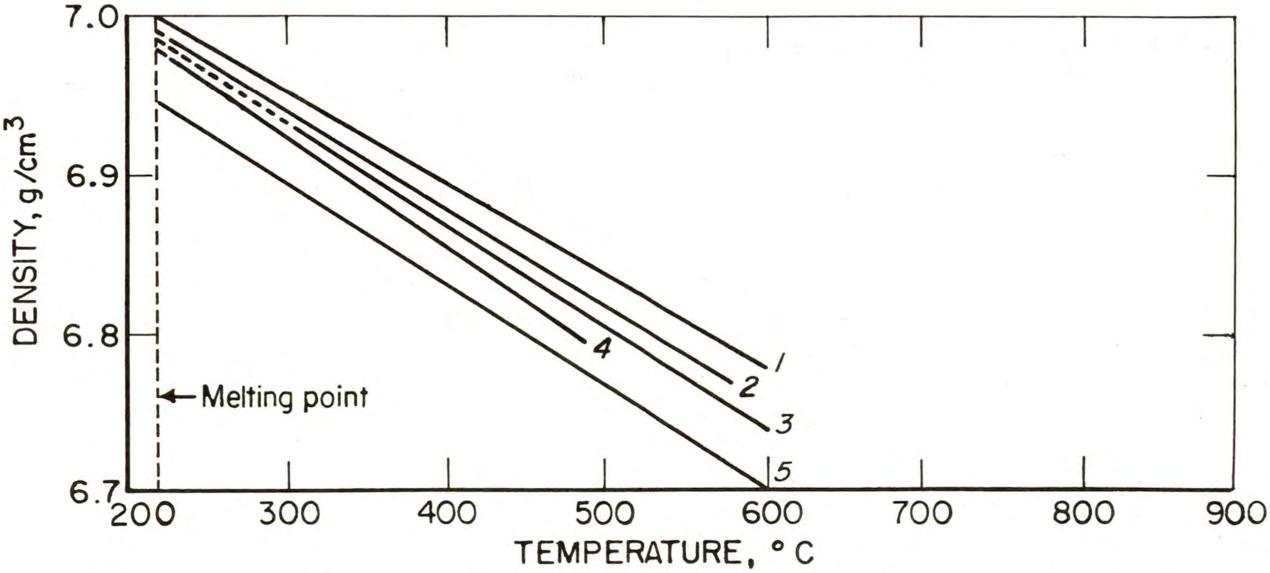

FIGURE 2. - Density Versus Temperature for Tin. 1, Kirshenbaum and Cahill, 1962, Archimedean (7). 2, This work, maximum bubble pressure. 3, Day, Sosman, and Hostetter, 1914, Archimedean (5). 4, Thresh, Crawley, and White, 1968, pycnometer (15). 5, Matuyama, 1921, pycnometer (8).

TABLE 2. Density of liquid tin

Temp., ° C	Observed[1] g/cm^3	Calculated[2] g/cm^3	Temp., ° C	Observed[1] g/cm^3	Calculated[2] g/cm^3
236	7.00±0.006	7.01	442	6.86±0	6.88
282	6.95± .004	6.98	487	6.83± .003	6.85
317	6.94± .004	6.96	541	6.81± .002	6.82
362	6.90± .001	6.93	583	6.76± .008	6.79

[1] Value shown is from 2 observations. The ± limits represent the range of observations.

[2] Calculated from the equation

$$\rho = 7.16 - 6.3 \times 10^{-4}\ T\ (^\circ\ C).$$

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