# HEAT CAPACITY OF A LIQUID INDIUM-TIN ALLOY

by

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# ABSTRACT

The heat capacity of a liquid indium-tin alloy containing 47.22 atomic percent tin has been measured as a function of temperature in an isothermal calorimeter. The data extend from 394° K, slightly above the alloy eutectic temperature, to 758° K. The measured Cp values decrease with temperature, the rate of decrease becoming smaller as the temperature increases, resembling the behavior shown by pure liquid metals for which precise data are available. The magnitude of the decrease in Cp for the alloy above its eutectic temperature has been found to be considerably greater than those found in previous investigations on the pure liquid components.

Above the melting temperature of Sn, the alloy Cp data are compared with values calculated from Kopp's Law using previously reported data for the pure liquid components. It is found that, well within the overall accuracy of the data, $\Delta Cp = 0$ for the formation of the liquid alloy from the liquid elements at temperatures where it can be evaluated. This is consistent with the results of reported heat of formation and activity data for the liquid solution which indicate it to approach closely the properties of an ideal solution and suggest the absence of strong unlike atom interactions. The rapid change of Cp with T for the liquid alloy above its eutectic temperature is interpreted as being due primarily to the same mechanisms responsible for similar behavior in pure metals and not to an increase in $\Delta Cp$ with decreasing temperature.

Assuming $\Delta Cp = 0$ for the liquid alloy at temperatures below the melting point of Sn, Cp values for supercooled liquid In and supercooled liquid Sn have been calculated. The postulated Cp curves so derived join smoothly with those for the liquid metals above their melting temperatures.

# INTRODUCTION

Very few accurate heat capacity data have ever been measured for either pure metals or alloys in their liquid states. Most of the available heat capacity values for pure liquid metals have been obtained from high temperature heat content measurements, where the experimental scatter is such that trends with temperature are not apparent and a heat capacity which is constant with temperature is usually inferred.[1] Those few metals whose liquid heat capacities have been directly measured or obtained from heat content data of unusually high precision, namely, Bi, Hg, In, K, Li, Na, Pb, Sn and Zn, show Cp values decreasing with temperature in the temperature range near the melting point. The temperature coefficient of Cp usually has been found to become less negative with increasing temperature. In some cases where measurements have been extended to temperatures far above the melting point, the Cp has reached a minimum followed by increasing values.

Heat capacity measurements should sensitively reflect such phenomena as changes in liquid structure with temperature, and so be valuable in consideration of theoretical models for the liquid metallic state. The decreasing Cp above the melting point has been usually ascribed to the breakup of quasi-crystalline atomic associations or to changes in the vibrational potential functions with temperature, or to both.

Heat capacities of liquid alloys have been studied even less. These have been obtained in some cases from heat content measurements, but mostly from the variations of measured heats of formation with temperature, which give $\Delta Cp$ for formation of the alloy from the liquid elements. The only direct determinations for liquid alloy heat capacities which were found are those for the

liquid $KNa_2$ alloy[2] extending about 20°C above its liquidus temperature and for a series of Hg-Tl amalgams at room temperature.[3] Lacking sufficient data, thermodynamic calculations involving liquid alloys usually require the assumption of Kopp's law of additivity of heat capacities, namely that

$$Cp_{A_xB_{(1-x)}} = xCp_A + (1-x)Cp_B, \text{ i.e., } \Delta Cp = 0$$

It therefore seems important to measure Cp values for a number of representative liquid alloys to determine their general behavior and to contribute to the knowledge of their structures. From these the values of $\Delta Cp$ for the formation of liquid alloys from liquid elements can be calculated. These values are directly related to the temperature dependence of the heat and excess entropy of formation, $\Delta H$ and $\Delta S^{xs}$:

$$\Delta Cp = \frac{d\Delta H}{dT} = \frac{d\Delta S^{xs}}{d\ln T}$$

For an ideal solution $\Delta H = 0$, $\Delta S^{xs} = 0$, and $\Delta Cp = 0$. For a regular solution, $\Delta S^{xs} = 0$, and $\Delta Cp = 0$. If the solution is non-regular but $\Delta S^{xs}$ is constant with temperature, $\Delta Cp$ is also zero.

In an exothermically formed solution, breakups of non-random associations of unlike atoms (ordering) with increasing temperature would yield a positive contribution to $\Delta Cp$. The same would be expected to be true of breakups of like atom associations (clustering) in an endothermically formed solution. The nature and degree of associations in the liquid solution just above its liquidus temperature would be expected to be greatly influenced by the nature and stability of the solid phases at lower temperatures. Negative contributions to $\Delta Cp$ might result from a lesser vibrational or translational energy absorption in the alloy as compared with that in the pure liquid components. This contribution

would depend on the strength of the alloy bonding and might be expected to be greatest in solutions for which $\Delta H$ and $\Delta S^{xs}$ are large and negative.

For the present investigation it was decided to measure directly the heat capacity of a liquid indium-tin alloy. The phase diagram for this system as chosen by Hansen[4] is shown in Figure 1; those phase boundaries which are uncertain are shown as dashed curves. The composition chosen was that of the $\beta$-$\alpha$(Sn) eutectic, 47.2 at.% Sn, as this permitted measurements to approach the lowest temperature of liquid stability, 390°K, the eutectic temperature. The In-Sn system seemed especially favorable for study as the heat capacities of both liquid In[5] and liquid Sn[6] had previously been measured using the same apparatus and techniques. Thus comparisons of the data obtained for the alloy with those for the pure metals should yield highly reliable values of $\Delta C_p$.

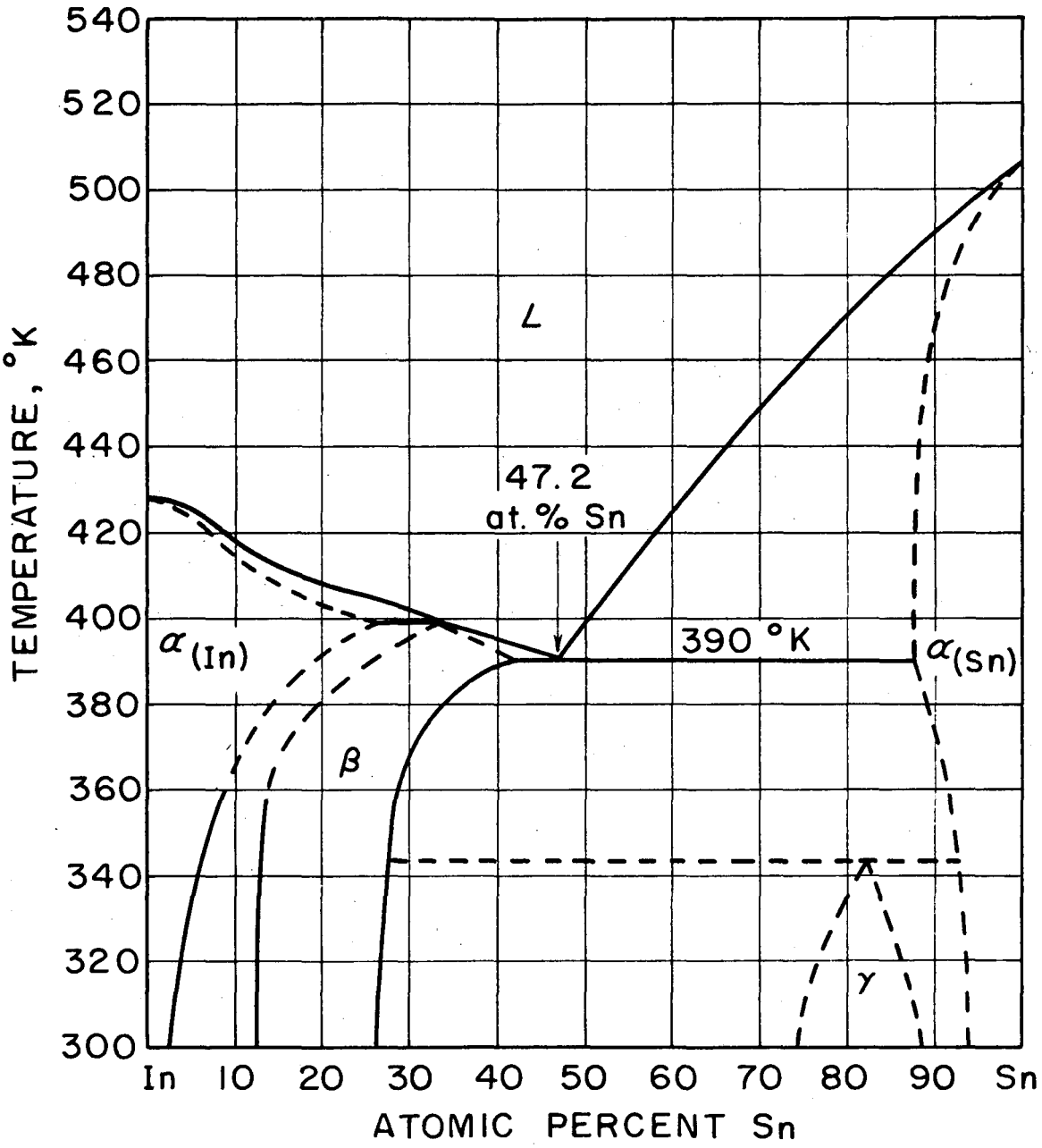


FIG. 1 PHASE DIAGRAM FOR In - Sn SYSTEM.
(HANSEN[4])

# EXPERIMENTAL

## Method and Apparatus

Measurements were made using essentially the same experimental methods and apparatus used in previous measurements on liquid In[5] and liquid Sn.[6] Approximately 450 gms. of alloy were contained in a thin-walled Mo crucible weighing 32.5 gms. The crucible was supported on three sharp points of a lavite refractory within the isothermal copper jacket of a slightly modified liquid tin solution calorimeter which has been described in detail previously.[7] At each of a series of elevated temperatures above the eutectic temperature of the alloy a known endothermic heat effect was introduced into the alloy crucible by means of Pt or Mo pellets dropped from the calorimeter dispenser unit as will be described later. The temperature difference between the crucible and jacket during the cooling and return to steady state periods was measured as a function of time by means of a copper-constantan differential thermocouple. From these data the heat transfer correction was evaluated and applied to the measured temperature change according to methods previously established and described.[7] From the total heat capacity of the crucible and contents thus determined, the heat capacity of the liquid alloy was obtained by subtracting the known heat capacities for the crucible and its component parts. The measurements were conducted under a vacuum of about $10^{-5}$ mm Hg in order to prevent oxidation of the alloy or the crucible and to reduce the heat transfer coefficient between the crucible and jacket.

At the higher temperatures of measurement, 527° to 758°K, small Pt pellets (0.8 - 1.4 gms.) were used to provide the known heat effects. Since

Pt is soluble in the alloy, the pellets were dropped into a closed Ta tube immersed in the alloy. The crucible arrangement, including the Ta tube, Mo funnel, tube support and thermocouple well, is shown in Figure 2.

At lower temperatures of measurement, however, it was found that the smaller rates of heat transfer between the platinum pellet and the alloy resulted in progressively longer equilibrium times for the runs. It was decided, therefore, to drop inert Mo pellets (0.5 - 1.1 gms.) directly into the liquid. This, of course, greatly increased the rate of heat transfer and reduced the equilibrium times. For these runs the Ta tube was replaced by a larger Mo tube, open at the bottom, the purpose of which was to direct the Mo pellet to the center of the liquid alloy, thus yielding a more consistent and even distribution of the heat effect introduced in each run. The tube acted as a shield preventing cold convection currents from causing erratic thermocouple readings during the initial part of a run.

All pellets were dropped from the calorimeter dispenser unit where their initial temperatures were measured by a calibrated Pt-Pt+10%Rh thermocouple. These initial temperatures varied from 296° to 320°K. The temperature of the liquid alloy was determined from the calibrated leg of the differential copper-constantan thermocouple extending into the crucible thermocouple well. The corrected temperature changes of the alloy during the runs were of the order of 0.1° to 0.5°C, and the measured heat capacities were referred to the mean alloy temperatures for each run. In order to convert temperature changes of the liquid alloy, measured in micro-volts with the copper-constantan thermocouple, to degrees, a smooth curve of copper-constantan temperature coefficients was derived from the NBS tables of

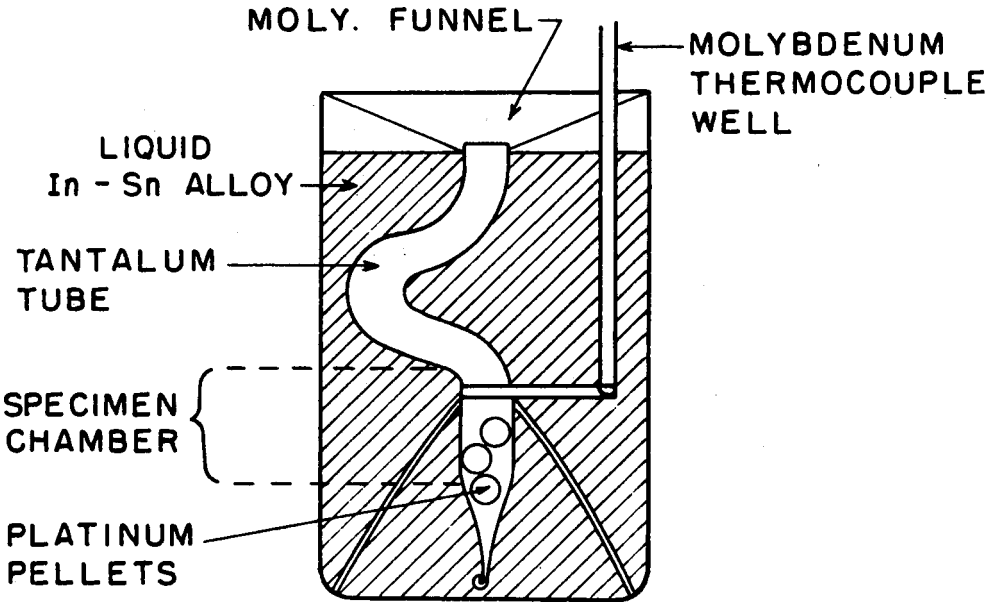


FIG. 2 CALORIMETER CRUCIBLE.

1938.[8] Calibration of the thermocouple wire being used at a number of fixed points (melting points of In, Sn, and Bi) substantiated the chosen values.

The heat effects introduced by the Pt pellets were calculated from a set of recently tabulated heat content values for that element evaluated from new experimental data from this laboratory as well as previous data.[9] Heat contents for Mo were taken from the selected values of Stull and Sinke.[10] Determinations made using both Mo pellets and Pt pellets at approximately 525°K were in good agreement, indicating the Mo heat content data to be consistent with those for Pt. The heat content data employed in the calculations are given in Table I.

TABLE I

Heat Content Values Employed

in Determinations of Known Heat Effects

| T, °K | $H_T - H_{298.15}$, cal/g-atom | |
|---|---|---|
| | Pt | Mo |
| 298.15 | 0 | 0 |
| 300 | 11 | 11 |
| 400 | 636 | 595 |
| 500 | 1273 | 1203 |
| 600 | 1924 | 1825 |
| 700 | 2587 | 2460 |
| 800 | 3263 | 3100 |

Materials

The alloy was prepared by melting the appropriate amounts of 99.99% pure In and 99.998% pure Sn into the molybdenum crucible under a protective reducing atmosphere of $N_2$ and $H_2$. The alloy contained 47.22 at.% Sn and had a gram-atomic weight of 116.65 based on the International atomic weights of 1955.[11] For the Pt runs the weight of alloy was 454.2868 gms. (3.8944 gm. atoms). In changing the set up for the Mo runs, a small amount of alloy was lost, leaving 452.0853 gms. (3.8756 gm. atoms). Corrections for the contributions to the total measured heat capacities by the crucible materials and the Pt or Mo pellets previously added were of the order of10% of the total value and were made using values derived from tabular data.[9, 10]

# RESULTS

Successful measurements were obtained for ten Mo-drop runs (393.8° - 524.1° K) and for eight Pt-drop runs (527.0° - 757.9° K). The results are summarized in Table II, which for each run lists the following quantities:

| | |
|---|---|
| $T_m$ | Mean temperature of liquid alloy for measurement |
| q | Heat effect introduced by Pt or Mo pellet |
| $\Delta T$ | Corrected temperature change for alloy and crucible |
| $Cp_{total}$ | Total measured heat capacity for alloy and crucible |
| $Cp_{alloy}$ (cal° K) | Heat capacity of alloy corrected for contributions of crucible materials |
| $Cp_{alloy}$ (cal/° K, gm. atom) | Heat capacity of one gram atom of alloy |

The results are shown plotted in Figure 3 together with values calculated assuming Kopp's Law using previously measured data for In[5] and Sn[6] given in Figure 4. Smooth Cp values for the liquid alloy taken from the curve drawn for the measured data are listed in Table III.

TABLE II

Summary of Experimental Data

| Run | $T_m$ °K | q cal | ΔT °K | $Cp_{total}$ cal/°K | $Cp_{alloy}$ cal/°K | $Cp_{alloy}$ cal/°K, gm. atom |
|---|---|---|---|---|---|---|
| 25(Mo) | 393.8 | 6.336 | 0.2008 | 31.554 | 28.557 | 7.37 |
| 24 | 394.4 | 6.383 | 0.2012 | 31.725 | 28.795 | 7.43 |
| 21 | 400.7 | 3.470 | 0.1102 | 31.488 | 28.663 | 7.40 |
| 20 | 400.8 | 3.918 | 0.1256 | 31.194 | 28.408 | 7.33 |
| 22 | 428.3 | 5.214 | 0.1677 | 31.091 | 28.208 | 7.28 |
| 23 | 428.2 | 4.712 | 0.1503 | 31.351 | 28.427 | 7.33 |
| 16 | 475.7 | 9.010 | 0.2970 | 30.337 | 27.649 | 7.13 |
| 26 | 497.5 | 8.490 | 0.2775 | 30.595 | 27.433 | 7.08 |
| 14 | 524.1 | 9.769 | 0.3272 | 29.856 | 27.227 | 7.02 |
| 15 | 524.1 | 10.133 | 0.3387 | 29.917 | 27.243 | 7.03 |
| 3(Pt) | 527.0 | 10.226 | 0.3420 | 29.901 | 27.257 | 7.00 |
| 4 | 527.0 | 10.083 | 0.3358 | 30.027 | 27.337 | 7.02 |
| 6 | 596.2 | 9.039 | 0.3026 | 29.871 | 27.055 | 6.95 |
| 8 | 597.5 | 13.162 | 0.4404 | 29.886 | 27.157 | 6.97 |
| 9 | 693.4 | 15.716 | 0.5265 | 29.850 | 27.044 | 6.94 |
| 10 | 693.3 | 11.996 | 0.4018 | 29.856 | 27.007 | 6.93 |
| 11 | 757.9 | 13.102 | 0.4452 | 29.429 | 26.523 | 6.81 |
| 12 | 757.9 | 12.594 | 0.4194 | 30.029 | 27.092 | 6.96 |

TABLE III

Smoothed Heat Capacities for Liquid In-Sn Alloy, $x_{Sn} = 0.4722$

| T, °K | Cp cal/°K, gm. atom | T, °K | Cp cal/°K, gm. atom |
|---|---|---|---|
| 390(eut. temp.) | 7.42 | 600 | 6.95 |
| 400 | 7.38 | 650 | 6.93 |
| 450 | 7.22 | 700 | 6.93 |
| 500 | 7.07 | 750 | 6.92 |
| 550 | 6.99 | | |

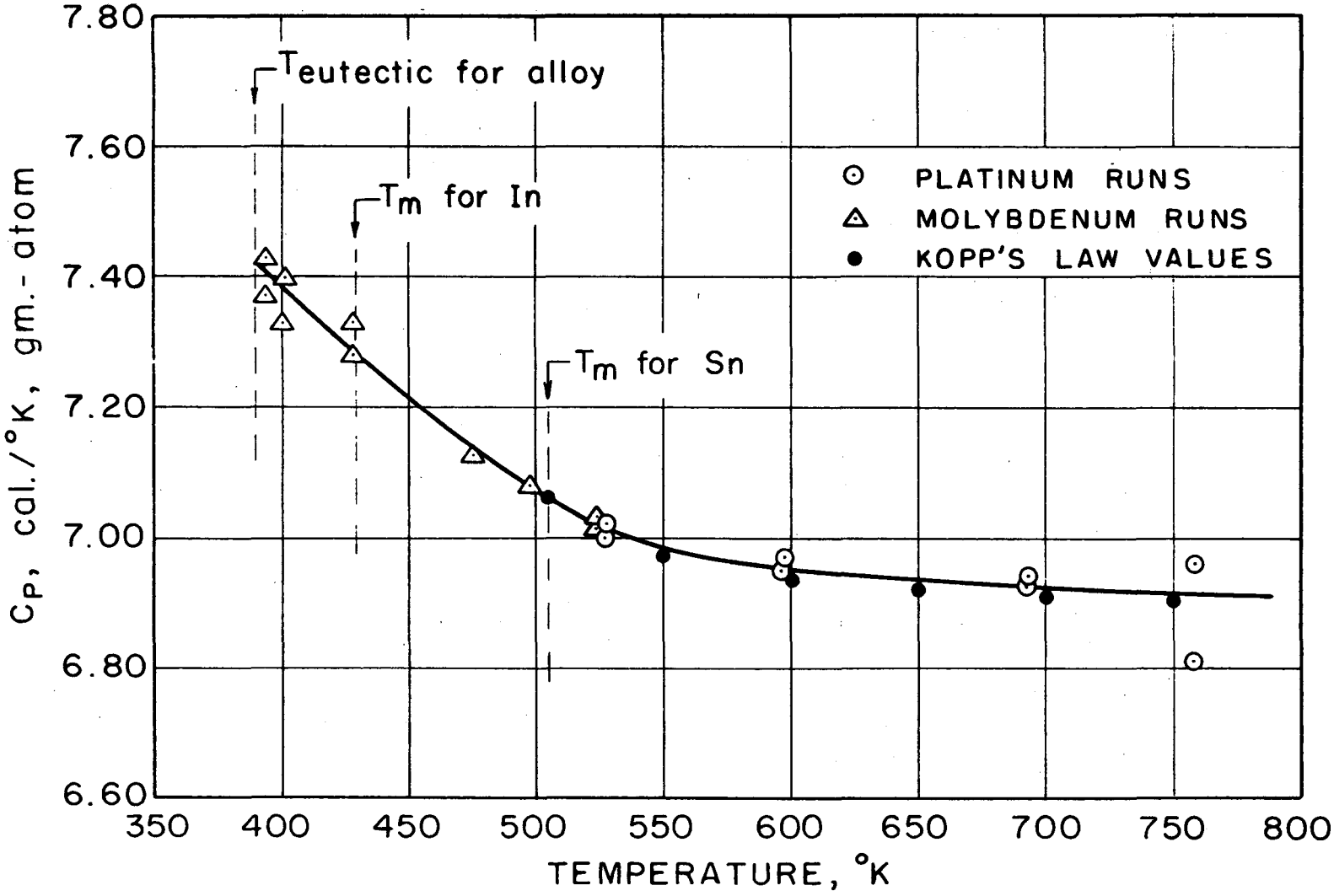


FIG. 3 HEAT CAPACITY DATA FOR THE LIQUID In-Sn ALLOY. (47.22 at. % Sn)

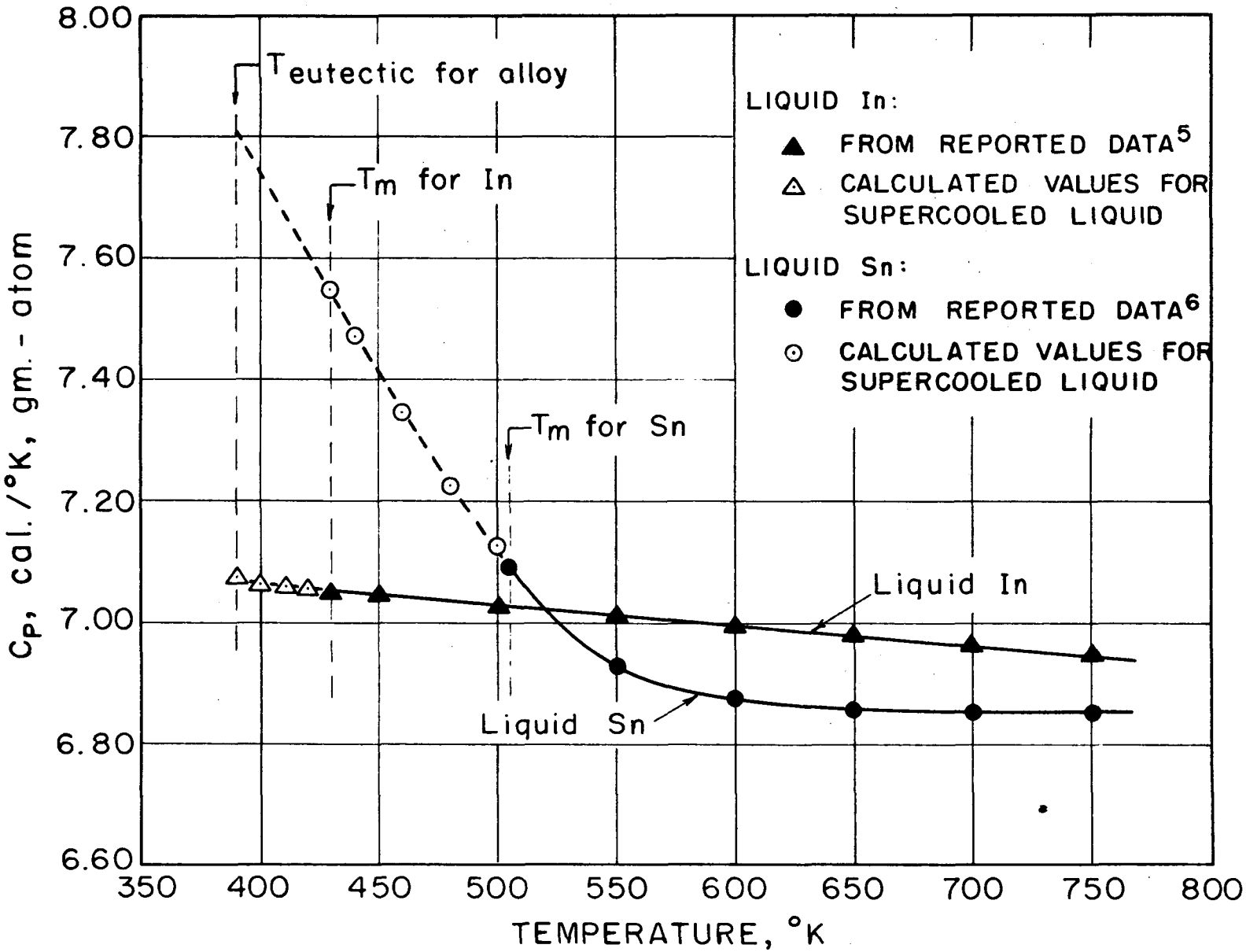


FIG. 4 HEAT CAPACITIES OF LIQUID In AND LIQUID Sn.

# DISCUSSION

In the 360° range above its eutectic temperature, the behavior of the heat capacity of the liquid In-Sn alloy resembles that found for pure liquid metals for which precise data are available. The Cp decreases with temperature, the temperature coefficient becoming less negative as the temperature increases. The magnitude of the initial rapid decrease in the 200° range above the eutectic temperature is considerably greater than those found for the pure components, as can be seen by comparing the measured curve in Figure 3 with the solid curves for liquid In and Sn in Figure 4. The reasons for this behavior will be considered later in the discussion.

For temperatures above the melting point of Sn the deviations of the measured values from those calculated assuming Kopp's Law, shown in Figure 3, are extremely small ( less than 0.02 cal/°K, gm. atom) and less than the overall precision. The absolute uncertainties in the measured Cp values for In, Sn, and the alloy are of the order of ±0.5% or approximately ±0.04 cal/°K, gm. atom. Thus well within the overall accuracies of the data, $\Delta Cp = 0$ for the formation of the liquid alloy from the liquid elements at temperatures where $\Delta Cp$ can be evaluated.

The observation that $\Delta Cp = 0$ is supported by other thermodynamic data available for the system. Data for the heats of mixing of the liquid alloys obtained by Wittig and Scheidt[12] (644°K, $x_{Sn} = 0.0\text{-}1.0$) and Kleppa[13] (723°K, $x_{Sn} = 0.76\text{-}0.94$) are in good agreement revealing no measurable temperature dependence on $\Delta H$. The heat of mixing of the liquid eutectic alloy is only -45 cal/gm. atom, the maximum exothermic value for any composition. This

extremely small value for the heat of mixing would indicate that the liquid solution approaches closely the behavior of an ideal solution, and that any unlike atom interactions beyond those between the like atoms themselves are quite feeble in character. Kopp's Law behavior of the heat capacity might be expected for such a solution.

Further indication of the near ideal character of the liquid solution is given by the data of Terpilowski and Przezdziecka-Mycielska,[14] who studied the liquid alloys by emf cell measurements between 663° and 883° K. These investigators found only slight negative deviations for the activities of In and Sn ($a_{In} = a_{Sn} = 0.45$ at $x_{Sn} = 0.50$, 773° K). Their free energies of mixing when combined with the calorimetric heats of mixing yield slightly positive values for the excess entropies of mixing ($\Delta S^{xs}_{mix} = +0.24$ cal/° K, gm. atom at $x_{Sn} = 0.50$, 773° K). Thus these data also indicate the absence of strong unlike atom interactions.

The large increase in the heat capacity of the liquid alloy with decreasing temperature below the melting point of Sn could be interpreted as resulting from two possible causes:

1) An increase in the interactions or non-random associations between unlike atoms as the temperature approaches the eutectic temperature yielding a positive value for $\Delta Cp$.

2) Changes in structure or in the vibrational and translational energy distributions such as those postulated to explain the similar Cp variations shown by pure liquid metals. This effect would not be expected to contribute to $\Delta Cp$ and $\Delta Cp$ would remain equal to zero with decreasing temperature.

Throughout this discussion $\Delta Cp$ for the formation of the liquid alloy is considered always to refer to liquid In and liquid Sn, even below their respective melting temperatures, 429.3°K for In and 505.0°K for Sn.

It could be that both effects described in (1) and (2) are operative in the liquid In-Sn alloy studied, and it is not possible from the present data alone to make an absolute distinction between them. Because of the near-ideal character of the liquid solution, however, it would seem most likely that by far the main contribution to the observed rapid decrease of Cp with T is due to the second cause mentioned above. The remarkably good agreement found between the curvature of the measured Cp curve and that shown by the Kopp's Law values in the temperature range just above the melting temperature of Sn is also indicative that this is a valid assumption.

The assumed adherence to Kopp's Law by the liquid alloy between its eutectic temperature and the melting point of Sn leads to a unique opportunity to calculate the heat capacities of supercooled liquid In and Sn. Between the melting points of In and Sn, the heat capacities of supercooled liquid Sn were calculated from the Cp values for the alloy and liquid In and the relationship:

$$Cp_{alloy_{(\ell)}} = 0.5278\, Cp_{In_{(\ell)}} + 0.4722\, Cp_{Sn_{(\ell)}}$$

The calculated curve was extrapolated to the alloy eutectic temperature, and the resulting values were used with the measured alloy data to similarly calculate the heat capacities of supercooled liquid In between its melting point and the eutectic temperature. The results of the calculation are shown by the dashed curves of Figure 4.

The calculated Cp curves for the supercooled liquid metals join smoothly

with the measured data for the liquids above their melting temperatures. The heat capacity behavior postulated for the supercooled liquids does not appear unreasonable. The Cp curve for supercooled liquid Sn indicates that the formation of quasi-crystalline associations and/or changes in the vibrational potential functions which initiate the increase in Cp with decreasing temperature at about 650° K occur continuously to a progressively greater extent within the supercooled liquid. The derived Cp curves for the supercooled liquids thus appear consistent with the models employed to explain the heat capacity variation in the real liquids. This tends to support the conclusion that the large increase in Cp found for the liquid In-Sn alloy with decreasing temperature is due primarily to the same mechanisms responsible for similar behavior in pure metals and not to an increase in $\Delta Cp$.

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