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THERMODYNAMICS OF SOLID AND LIQUID AuSn AND HEAT CONTENTS OF GOLD AND TIN

Author
Plaza, Elias Meyer.

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(M.S. Thesis)

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THERMODYNAMICS OF SOLID AND LIQUID AuSn AND HEAT CONTENTS OF GOLD AND TIN

Elias Meyer Plaza

Inorganic Materials Research Division
Lawrence Radiation Laboratory
and
Department of Mineral Technology
College of Engineering
University of California
Berkeley, California

February, 1967

ABSTRACT

Using a diphenyl ether drop calorimeter, high temperature heat contents, $H_T - H_{298.15}$, of gold, in the range 404° -1486°K; tin, in the range 405° -924°K; and AuSn, in the range 416° -917°K, have been measured. Smooth curves have been drawn through the experimental points, within a scatter of ±20 cal/g. at., joining smoothly with data at low temperatures. Heats of fusion have been derived and tables of smoothed heat contents are presented.

The data have been used to calculate the heat of formation of the alloy AuSn as a function of temperature, taking as a basis the heat of formation at 273°K determined by Misra et al. The agreement obtained with heats of formation at 623°K reported by Kleppa, and at 696°K reported by Masse et al. is within 45 cal/g. at., which is much less than the combined experimental uncertainties of the heats of formation

and present data. This resolves discrepanices of 300 cal/g. at. or more, which existed among the mentioned heats of formation when previously available data for heat contents of AuSn were used. This is the significant evidence that indicates that the previous heat content data for AuSn were not accurate.

I. INTRODUCTION

Heat content or heat capacity data for alloys are necessary in order to extend the values of thermodynamic properties measured at one temperature to other temperatures of interest. Changes in atomic bonding and configuration of an alloy with temperature are also reflected in its heat capacity which permits the possible evaluation of such important factors in alloy theory as ordering; clustering; and magnetic, electronic, and Brillouin zone effects.

According to Hansen[1] the AuSn phase exists over a very narrow range of homogeneity and melts congruently at 691°K. The solid phase has been shown to have the completely ordered hexagonal ($B8_1$) structure isotypic with NiAs. A sketch of the phase diagram taken from Hansen is shown in Figure 1.

The available thermodynamic information on AuSn consists of heats of formation at several temperatures in the range 273° - 873°K and heat contents and heat capacities in the range 373° - 908°K.

An evaluation of then existing data was made by Hultgren et al.[2] in 1963.

The heat content of AuSn has been measured by Bottema and Jaeger[3] in the range 373° - 581°K, and by Kubaschewski[4] in the range 496° - 908°K. Misra, Howlett, and Bever[5] have measured heat capacities in the range 613° - 753°K.

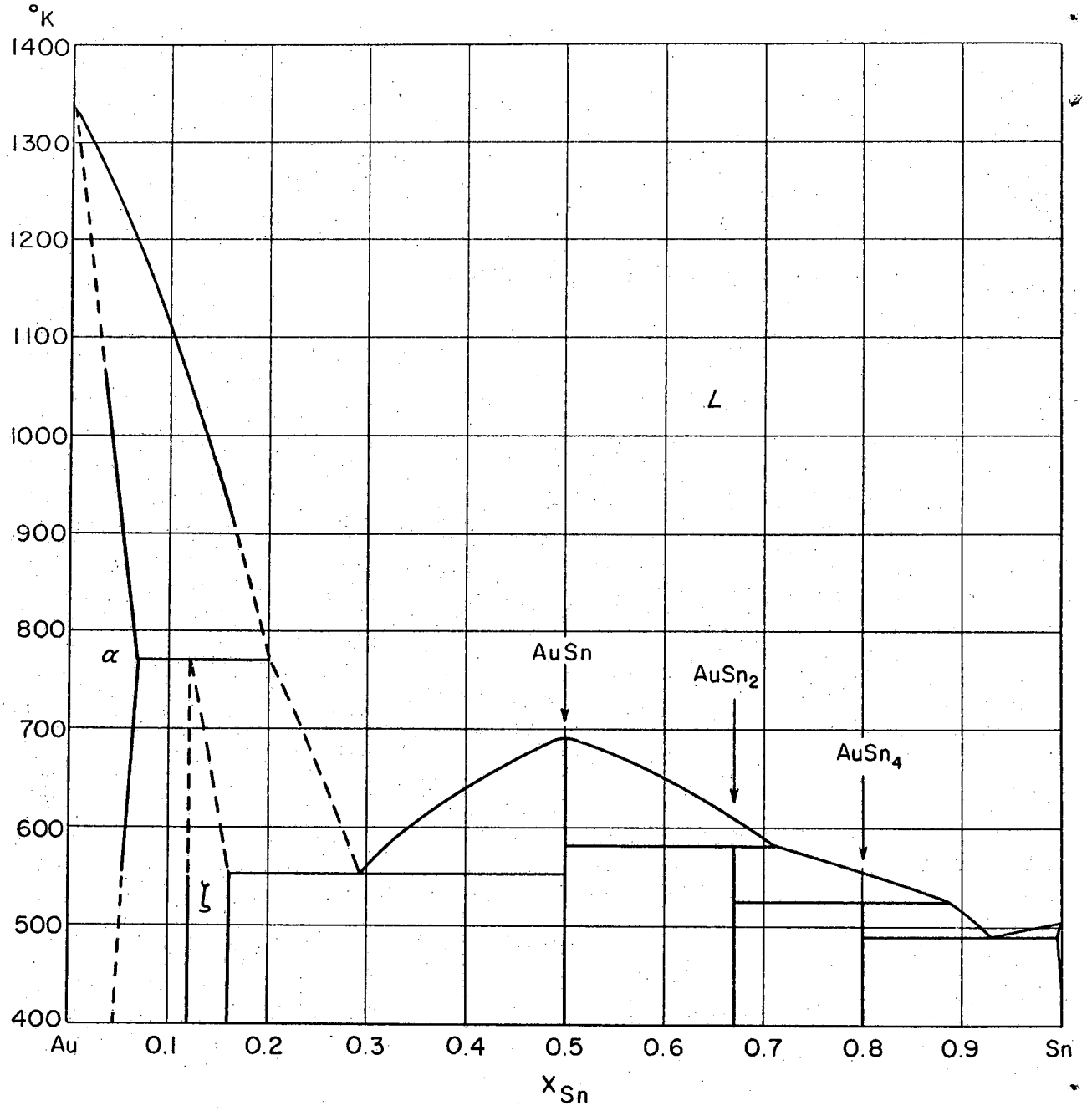

FIG. 1. PHASE DIAGRAM OF THE AuSn SYSTEM.

Several discrepancies exist in the data reported by these investigators; for example the heat contents reported by Kubaschewski are much higher than those of Bottema and Jaeger. Also the heat capacities reported by Misra, Howlett, and Bever, are much higher than those derived from the data of Bottema and Jaeger. Kubaschewski reports a melting temperature of 691°K and a heat of fusion of 3060 ± 80 cal/g. at.; whereas Misra et al. report a melting temperature of 692.4°K and a heat of fusion of 3370 ± 50 cal/g. at.

The following heats of formation have been reported in the literature:

Investigator	Method used	T, °K	ΔH_f, cal/g.at.	Ref. State
Misra et al.[5]	Metal Solution Calorimetry	273	-3645	$Au_{(s)}, Sn_{(s)}$
Biltz et al.[6]	Aqueous Solution Calorimetry	363	-4100	$Au_{(s)}, Sn_{(s)}$
Kleppa[7]	Metal Solution Calorimetry	623	-3580*	$Au_{(s)}, Sn_{(s, superheated)}$
Masse et al.[8]	Metal Solution Calorimetry	696	-3000	$Au_{(1, supercooled)}, Sn_{(1)}$
Kleppa[9]	Emf	873	-2316	$Au_{(1, supercooled)}, Sn_{(1)}$

* The value determined by Kleppa was -4250 cal/g. at. referred to solid gold and liquid tin. The value -3580 is referred to solid gold and solid superheated tin and has also been corrected to account for the calibration error found in Kleppa's calorimeter, which was determined to be 6.4% too low for the exothermic heats of solution.

These heats of formation can be compared using as a basis the heat of formation at 273°K determined by Misra et al.[5] and the heat content of AuSn determined by Kubaschewski.[4] Masse et al.,[8] for example, found that the value for the heat of formation of AuSn at 696°K, derived in this manner, was 300 calories less exothermic than his experimental value.

In order to resolve some of these discrepancies it was decided to measure the high temperature heat contents of the AuSn phase. Additionally it was also decided to measure the heat contents of the elements gold and tin.

II. EXPERIMENTAL

Materials

The gold used in this investigation was obtained from American Smelting and Refining Company with a reported purity of 99.999+ and the tin from Vulcan Detinning Company, Sewaren, New Jersey with a reported purity of 99.9998+.

Sample Preparation

The samples of pure metals were placed in spherical silica glass capsules of a diameter of about 7/8 inch, which were evacuated and then sealed, after which they were annealed at about 100 degrees below the melting point.

The alloys were prepared by placing the appropriate amounts of pure elements in the silica glass capsules, evacuating, and sealing. The sealed alloys were heated above the melting point to about 750°K for about 24 hours, with frequent shaking to allow reaction and homogenization. The samples were then slowly furnace cooled to room temperature. In each case the capsules were filled less than half full to avoid possible capsule failure.

Sample and capsule weights are recorded in Table 1.

Experimental Procedure

The heat contents were measured in a diphenyl ether Bunsen type drop calorimeter (Figure 2), similar in principle to one previously

TABLE 1

Weights and Composition of Samples and Weight of Silica Capsules

Platinum

Sample	Weight metal, gm.	Weight capsule, gm.
1	13.7850	1.9407
2	13.7850	2.0899
3	11.8108	3.0083

Gold

Sample	Weight metal, gm.	Weight capsule, gm.
1	15.0340	2.1477
2	15.0302	2.1465
3	9.9816	3.2728
4	16.5758	3.3051
5	18.1802	2.9705

Tin

Sample	Weight metal, gm.	Weight capsule, gm.
1	7.2820	2.1493

AuSn

Sample	Weight Au, gm.	Weight Sn, gm.	Weight capsule, gm.	At. fraction, Au
1	7.2814	4.3903	2.0070	0.500
2	7.3027	4.4005	1.7393	0.500

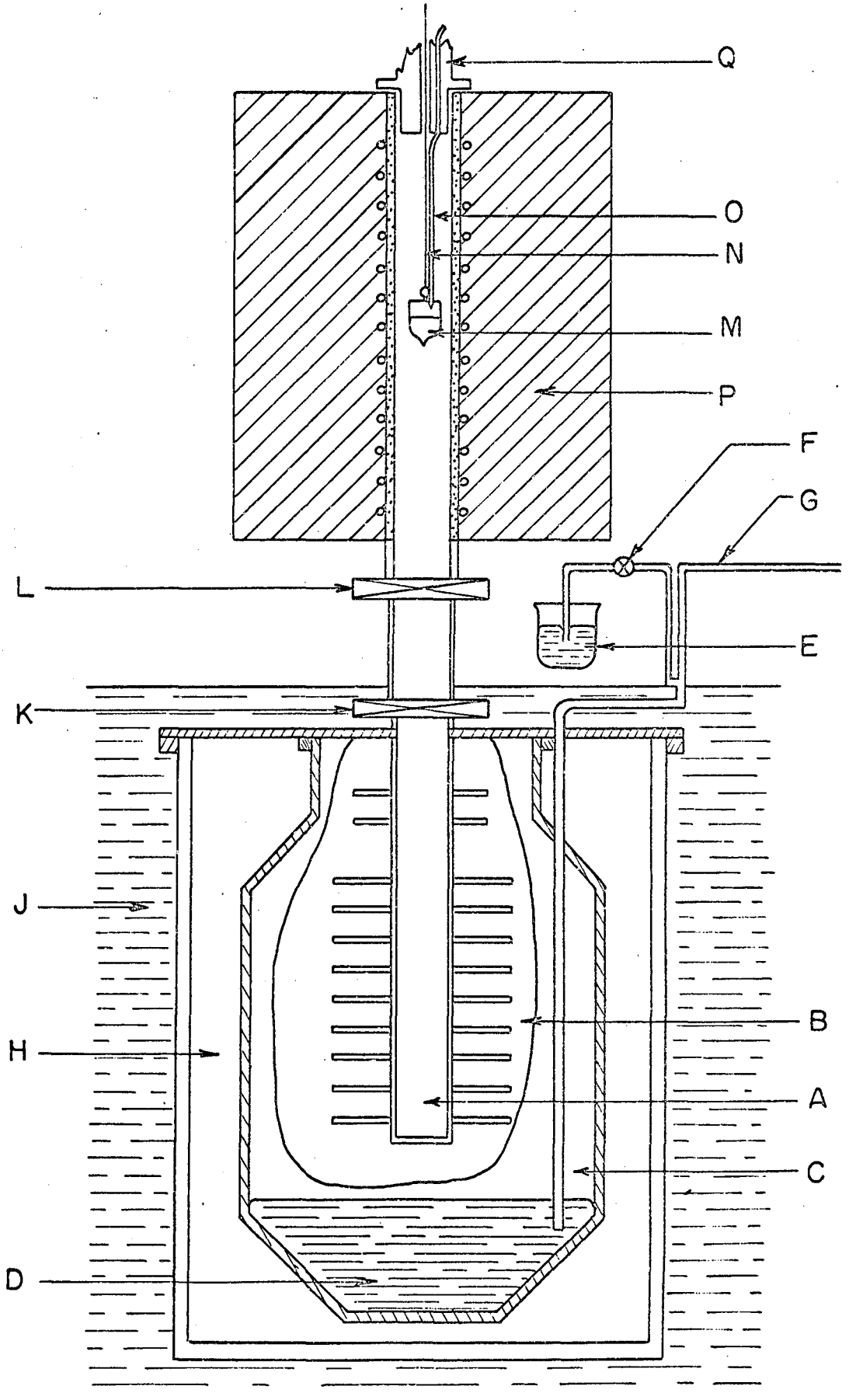

FIG. 2 DIPHENYL ETHER CALORIMETER.

Schematic Drawing of the Diphenyl Ether Calorimeter

A: Calorimeter well

B: Solid diphenyl ether

C: Liquid diphenyl ether

D: Mercury

E: Mercury reservoir

F: Stopcock

G: Calibrated capillary

H: Insulating air space

J: Constant temperature bath

K: Lower gate

L: Upper gate

M: Encapsulated sample

N: Platinum suspension wire

O: Thermocouple

P: Platinum wound furnace

Q: Dropping system

described in the literature.[10]

The encapsulated sample is suspended by means of a platinum-rhodium wire in a platinum wound vertical tube furnace until it reaches the desired equilibrium temperature, after which it is dropped into the calorimeter. Heat from the specimen enters a surrounding chamber containing liquid and solid diphenyl ether at its melting point, 300.0°K, isothermally melting some of the solid. The resulting change in volume is measured by the displacement of mercury from the bottom of the chamber into a horizontal calibrated capillary tube plus the amount received into a beaker. The heat effect is calculated from the amount of mercury displaced using the calibration factor determined by Jessup.[11]

Sample temperatures were measured by means of a Pt-Pt+10% Rh thermocouple. The accuracy of the thermocouple was checked during the runs on the same apparatus against the melting points of gold and tin. The agreement in both cases was closer than 0.5°C.

The results obtained for each temperature were corrected to account for the heat loss during the drop and for the heat content of the silica glass capsule.

To evaluate the heat loss, a series of runs in the range 400° - 1500°K was made on silica glass capsules filled with platinum, for which the heat content is known quite accurately.[12] The heat contents of the silica glass capsules were calculated using the values tabulated by Kelley.[13]

TABLE 2

Heat Loss of Platinum Samples

Sample 1		Sample 2		Sample 3	
T, °K	Heat loss, cal.	T, °K	Heat loss, cal.	T, °K	Heat loss, cal.
357.55	1.13	1067.06	7.58	1194.82	12.12
402.55	1.88	1239.23	14.83	1198.07	9.84
490.65	2.74	1290.98	13.24	1200.51	12.86
604.25	1.78	1292.82	11.60	1278.70	7.75
697.45	2.78	1537.82	31.81	1280.40	13.48
780.85	1.64			1303.98	9.79
782.15	3.03			1351.82	9.94
791.45	1.94			1354.42	10.37
923.95	5.33			1355.57	13.96
995.95	8.96			1361.57	16.46
998.85	5.57			1424.15	15.56
1217.15	12.08			1426.23	14.81
1399.25	19.31			1497.32	18.65
1512.65	33.39			1502.57	20.54
1527.80	24.32				

TABLE 3

Smoothed Heat Loss of Samples

T, °K	Heat Loss, cal.
300	0.00
400	1.60
500	1.63
600	1.65
700	2.25
800	2.95
900	4.00
1000	5.35
1100	7.10
1200	9.35
1300	12.10
1400	15.45
1500	19.80

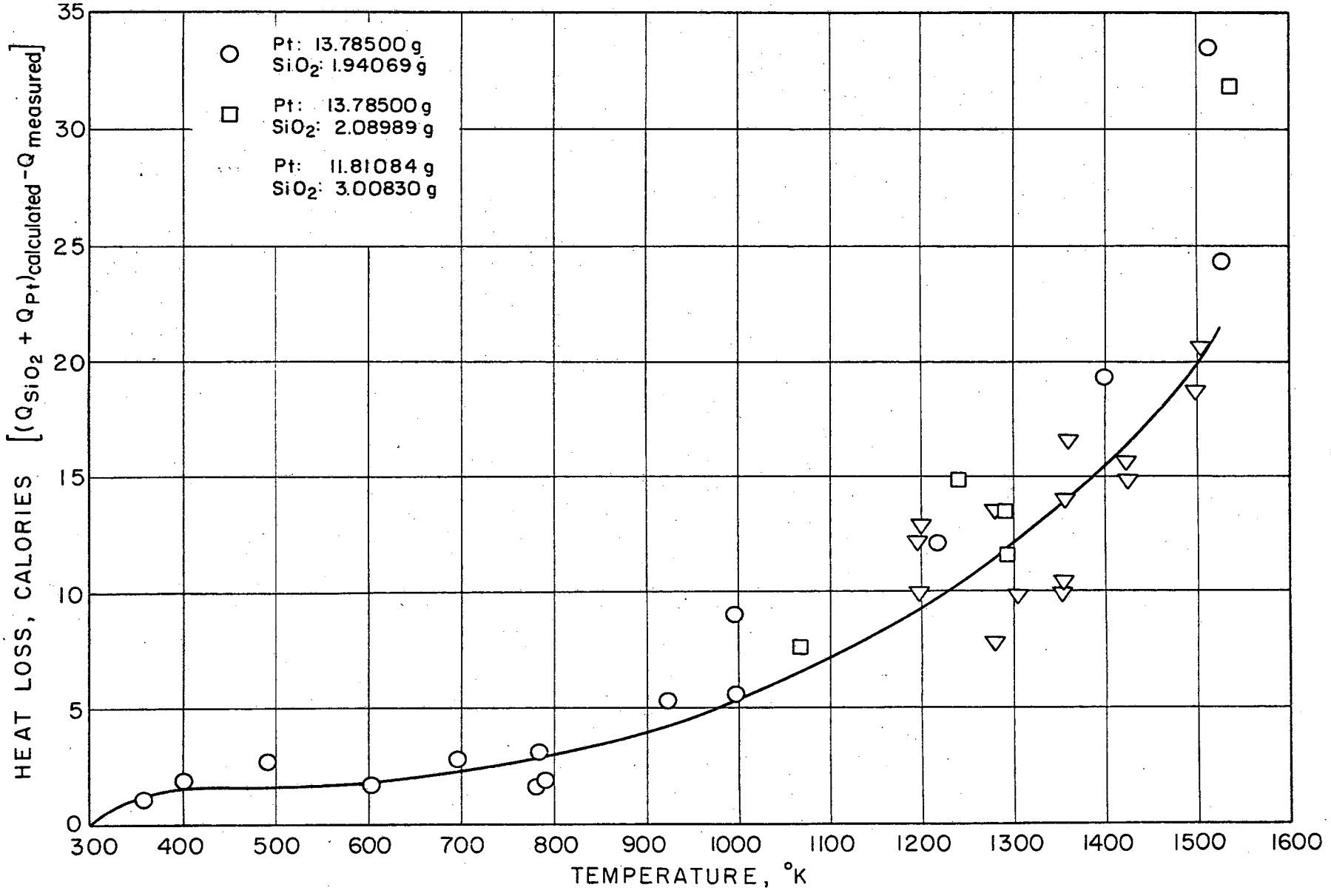

FIG. 3. HEAT LOSS OF SPECIMENS DURING DROP.

The experimental heat loss data are presented in Tables 2 and 3 and in Figure 3.

All the measured heat contents have been corrected to account for the difference between the calorimeter temperature 300°K and the standard reference temperature 298.15°K. For gold, this correction, $H_{300} - H_{298.15}$, amounts to 11.21 cal/g.at.; for tin it amounts to 11.93 cal/g.at.; and for AuSn it amounts to 11.15 cal/g.at.

III. EXPERIMENTAL RESULTS

The measured heat contents of Au, Sn and AuSn are presented in Tables 4-6. These results are plotted in Figures 4-6 as a graph of the function $Y = \frac{H_T - H_{298.15}}{T - 298.15}$ vs. T, together with the experimental values reported by other investigators. Smooth curves have been drawn which agree with the present data within a scatter of ±20 cal, and which join smoothly with the data at low temperatures in the case of gold and tin. For AuSn this has not been possible because of the lack of data at low temperatures.

Smoothed values for the heat contents are presented in Table 7.

TABLE 4(a)

Measured Heat Contents of Gold

Sample 1

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$ cal/g. at. °K
404.15	633.01	5.972
405.78	662.88	6.159
406.15	653.84	6.054
406.40	653.71	6.039
406.65	671.13	6.186
456.55	954.34	5.968
457.82	969.19	6.070
458.16	968.67	6.054
466.35	1045.21	6.214
466.45	1026.57	6.100
466.59	1022.38	6.070
484.65	1149.07	6.161
484.90	1140.56	6.107
484.48	1138.07	6.075
485.59	1138.72	6.075
502.05	1250.48	6.133
502.65	1253.62	6.130
503.70	1257.55	6.118
507.65	1280.48	6.112
507.78	1265.41	6.036
508.48	1281.27	6.092
532.67	1426.17	6.080
533.26	1442.15	6.134

TABLE 4(a) cont'd.

Measured Heat Contents of Gold

Sample 1

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$, cal/g. at. °K
596.48	1845.02	6.184
596.93	1850.00	6.190
693.75	2462.36	6.224
694.45	2476.12	6.248
810.85	3214.65	6.270
811.35	3216.09	6.267

TABLE 4(b)

Measured Heat Contents of Gold

Sample 2

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$, cal/g. at. °K
858.15	3534.82	6.312
859.35	3561.43	6.346
919.45	3951.82	6.361
919.85	3963.35	6.375
999.05	4497.76	6.417
1000.78	4509.95	6.419
1139.70	5455.46	6.483
1140.32	5484.95	6.513
1299.82	6607.50	6.596
1301.79	6600.69	6.577
1358.48	10,141.60	9.563

Sample 3

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$, cal/g. at. °K
1295.65	6634.97	6.652
1327.60	6902.75	6.705
1327.70	6895.05	6.697

TABLE 4(c)

Measured Heat Contents of Gold

Sample 4

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$, cal/g. at. °K
1116.88	5319.60	6.497
1221.73	6067.86	6.570
1224.73	6115.16	6.600
1313.15	6756.11	6.656
1313.24	6744.47	6.644
1313.69	6788.20	6.684
1321.73	6906.79	6.748
1329.74	6989.37	6.775
1331.25	6819.81	6.601
1466.40	10954.89	9.377

Sample 5

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$, cal/g. at. °K
1323.25	6891.32	6.723
1324.65	6885.90	6.708
1326.57	6921.54	6.730
1328.90	6897.92	6.692
1340.15	10029.31	9.625
1340.82	9963.55	9.556
1343.32	9998.33	9.556
1423.23	10635.27	9.453
1428.57	10640.25	9.413
1485.98	11121.18	9.363

TABLE 5

Measured Heat Contents of Tin

Sample 1

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$, cal/g. at. °K
405.27	703.01	6.563
405.40	701.55	6.541
406.15	722.08	6.686
407.05	735.11	6.750
456.40	1073.17	6.781
457.15	1064.36	6.694
457.60	1061.10	6.655
465.52	1138.04	6.800
465.65	1125.16	6.717
465.67	1127.61	6.731
466.05	1154.66	6.877
485.26	1275.76	6.818
485.48	1267.45	6.766
485.90	1290.11	6.871
486.15	1284.89	6.835
501.48	1415.29	6.961
502.15	1406.16	6.893
502.78	1406.97	6.876
503.26	1422.13	6.933
509.82	3103.71	14.663
509.93	3159.94	14.921
509.93	3142.99	14.841
513.82	3181.78	14.753

TABLE 5 (Cont'd.)

Measured Heat Contents of Tin

Sample 1

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$, cal/g. at. °K
535.15	3329.13	14.047
595.60	3759.43	12.639
596.26	3741.66	12.551
692.37	4408.29	11.182
810.35	5158.87	10.072
920.65	5889.89	9.462
923.95	5879.45	9.395

TABLE 6(a)

Measured Heat Contents of AuSn

Sample 1

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T - 298.15}$, cal/g. at. °K
406.40	681.32	6.294
406.50	677.26	6.251
406.65	676.72	6.237
455.65	982.73	6.240
456.52	998.28	6.303
457.15	985.98	6.201
465.15	1062.11	6.360
466.37	1043.04	6.200
467.40	1085.50	6.414

TABLE 6(b)

Measured Heat Contents of AuSn

Sample 2

T, °K	$H_T - H_{298.15}$, cal/g. at.	$\frac{H_T - H_{298.15}}{T-298.15}$, cal/g. at. °K
502.40	1307.41	6.401
502.77	1301.34	6.360
502.90	1303.40	6.366
504.05	1310.11	6.363
508.60	1332.09	6.330
508.60	1350.30	6.416
508.82	1316.18	6.248
509.82	1331.69	6.291
533.05	1480.98	6.305
533.95	1495.14	6.341
535.05	1529.12	6.455
595.60	1921.56	6.460
596.15	1907.94	6.402
633.26	2196.13	6.553
651.93	2325.33	6.673
664.05	2420.13	6.614
664.25	2409.84	6.582
680.59	2564.03	6.704
682.25	2582.37	6.723
693.35	3816.73	9.658
693.65	2870.29	7.257
694.15	5504.89	13.901
694.95	5493.56	13.855
704.05	5573.54	13.731
751.95	5946.42	13.104
791.35	6236.91	12.646
791.35	6246.08	12.664
915.79	7290.83	11.804
916.65	7268.31	11.752

TABLE 7

Smoothed Heat Contents of Au, Sn, and AuSn

Au		Sn		AuSn	
T, °K	$H_T-H_{298.15}$, cal/g. at.	T, °K	$H_T-H_{298.15}$, cal/g. at.	T, °K	$H_T-H_{298.15}$, cal/g. at.
298.15	0	298.15	0	298.15	0
400	620	350	340	400	635
500	1237	400	679	500	1279
600	1865	450	1030	600	1948
700	2508	500	1391	630	2160
800	3162	505(s)	1428	660	2388
900	3825	505(ℓ)	3103	690	2651
1000	4502	550	3413	693(s)	2681
1100	5192	600	3764	693(ℓ)	5492
1200	5907	700	4453	700	5545
1300	6662	800	5094	750	5930
1318	6818	900	5718	800	6322
1336(s)	7005			850	6710
1336(ℓ)	9951			900	7141
1400	10425				
1500	11237				

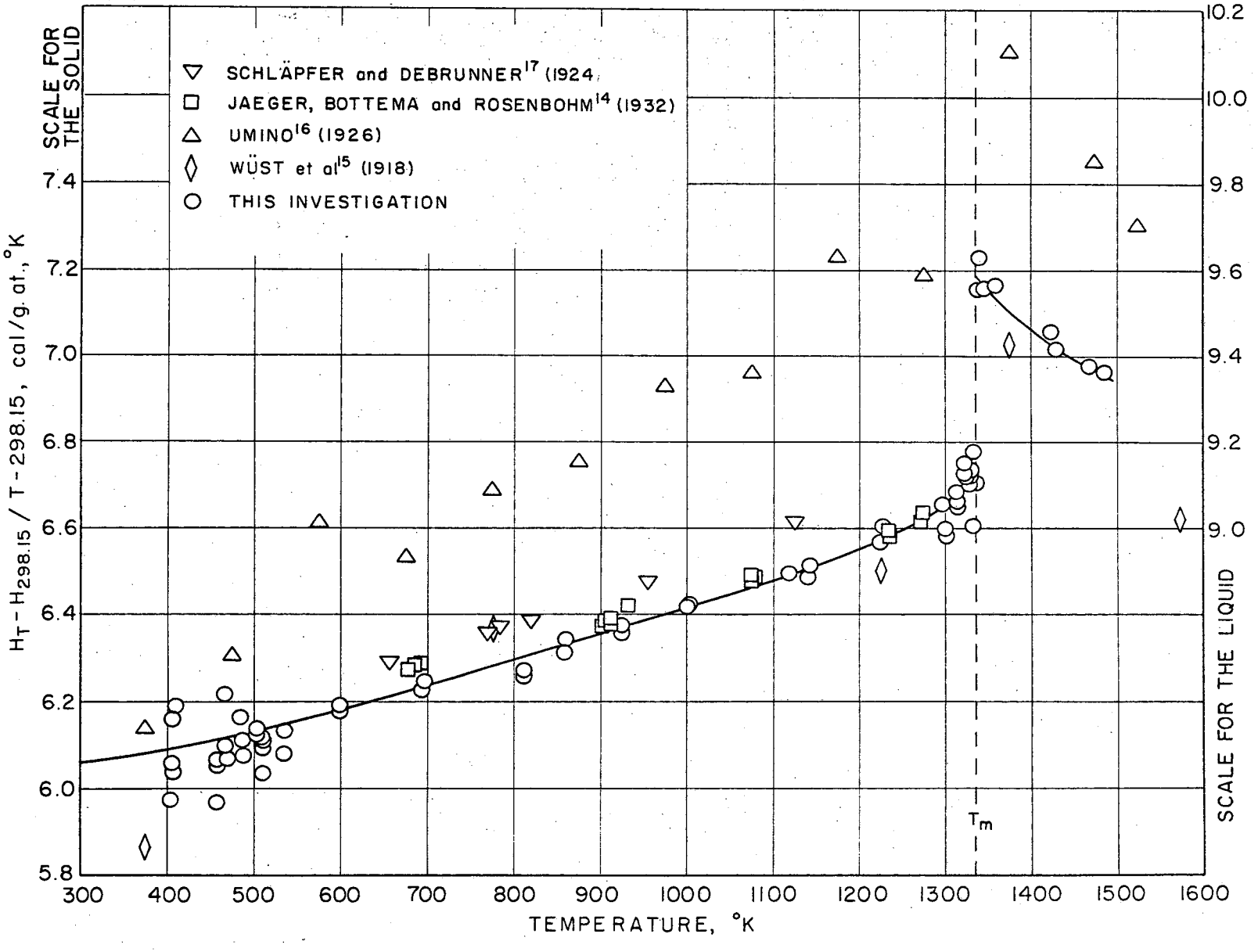

FIG. 4. HEAT CONTENTS OF GOLD EXPRESSED IN TERMS OF THE FUNCTION $(H_T - H_{298.15})/(T-298.15)$.

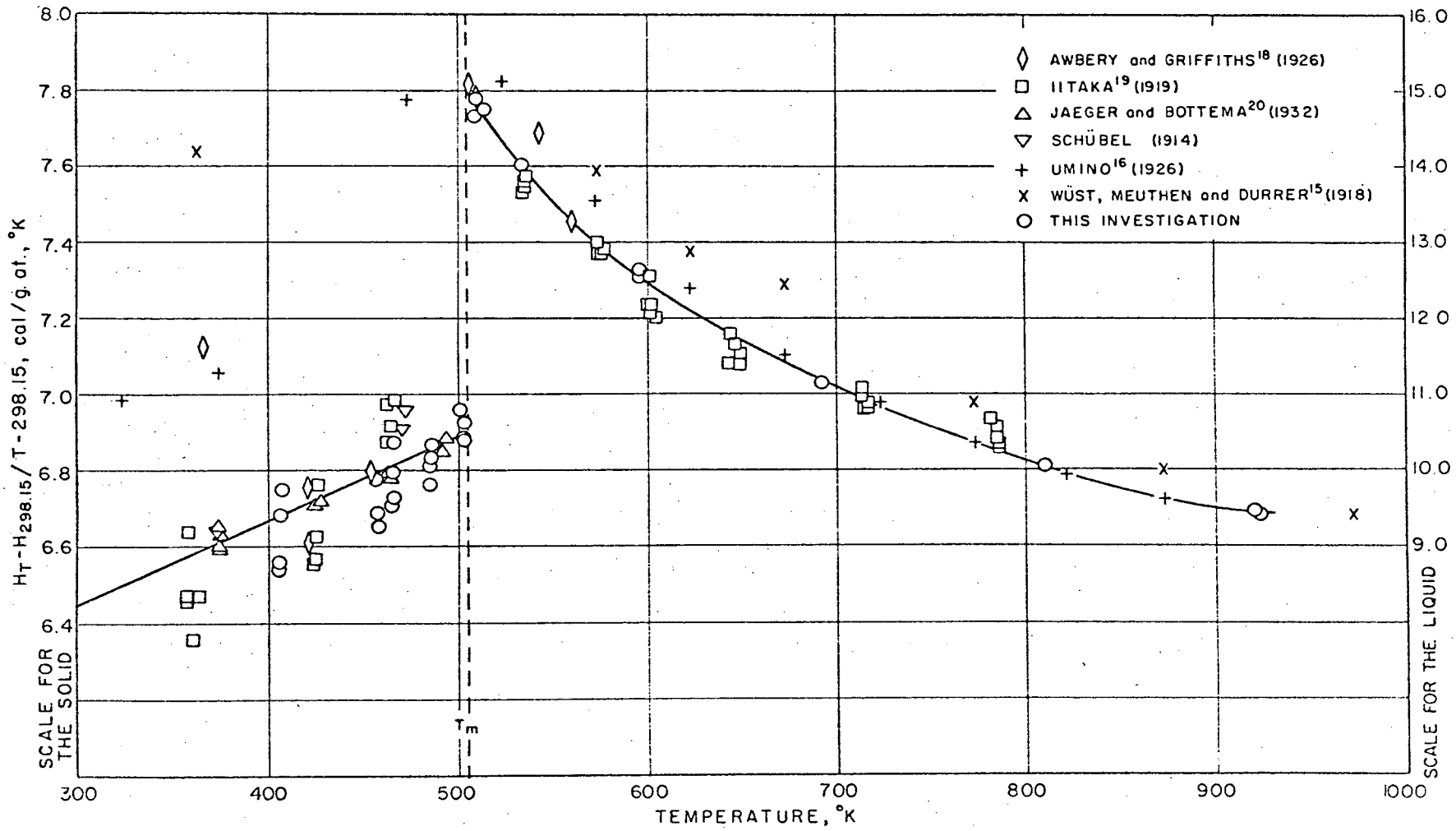

FIG. 5. HEAT CONTENTS OF TIN EXPRESSED IN TERMS OF THE FUNCTION $(H_T - H_{298.15})/(T-298.15)$.

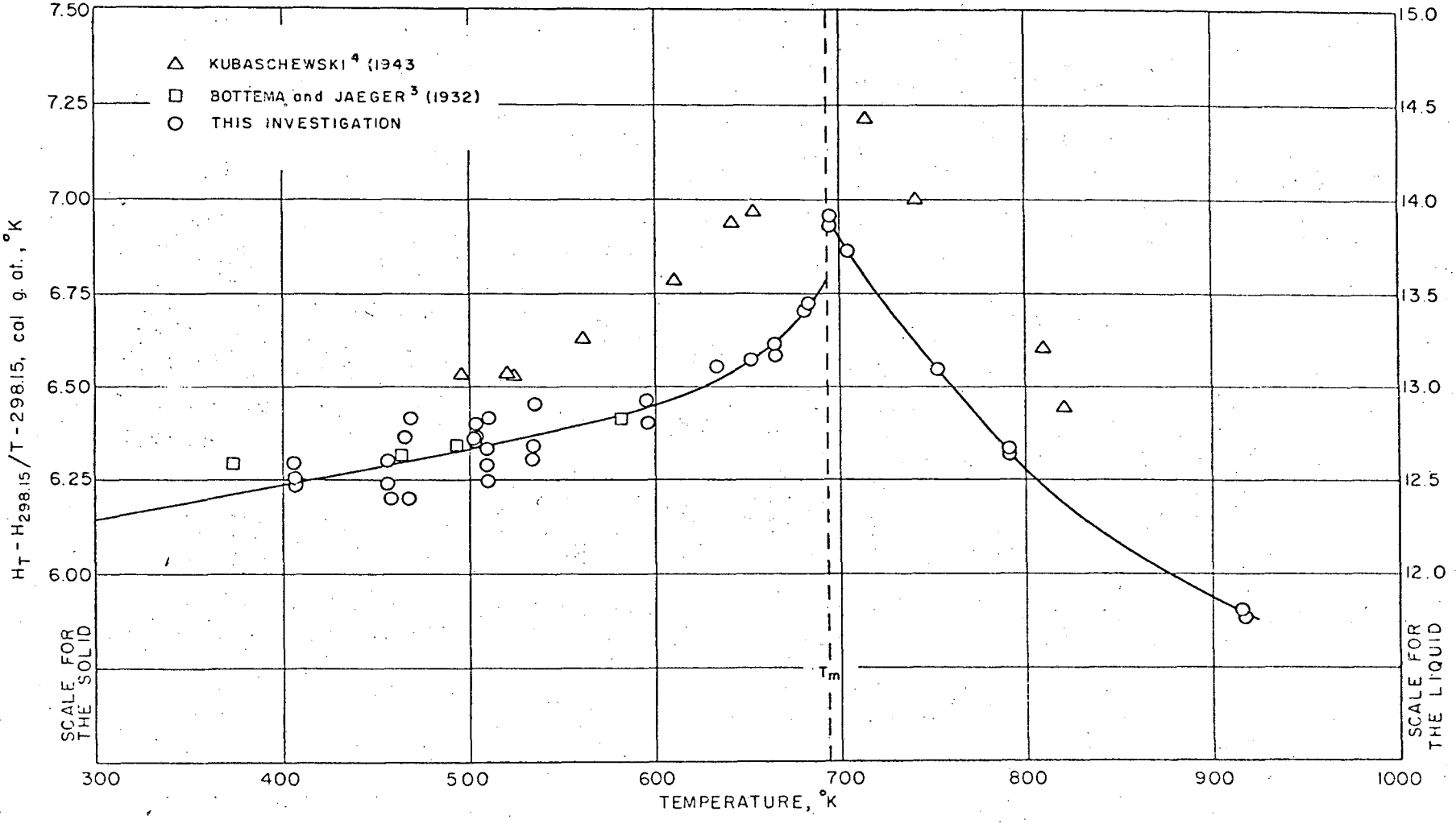

FIG. 6. HEAT CONTENTS OF Au Sn EXPRESSED IN TERMS OF THE FUNCTION $(H_T - H_{298.15})/(T - 298.15)$.

IV. DISCUSSION OF RESULTS

Gold

Heat contents of gold were measured in the range 404° - 1486°K. Previous measurements have been reported by Jaeger, Bottema and Rosenbohm[14] (692° - 1273°K); Wüst, Meuthen and Durrer[15] (373° - 1573°K); Umino[16] (373° - 1523°K); and Schläpfer and Debrunner[17] (665° - 1124°K). Heat content measurements of Jaeger et al. are slightly higher up to 900°K, but agree quite well with the present data at the higher temperatures. The measurements of Wüst et al. scatter, are higher for $T < 1000$°K and lower at higher temperatures. Those of Umino are higher at all temperatures. Those of Schläpfer and Debrunner are slightly higher at all temperatures.

A pronounced increase in the heat content values has been observed to occur, beginning at about 30 degrees below the melting point. It is difficult to explain this effect on the basis of impurities since the high purity of the samples used precludes large impurity effects. Also no evidence of pre-melting was found in the samples. It seems that this may be an effect due to a real non-linear increase of the heat capacity below the melting temperature. A value for the heat of fusion was found by taking the difference in the heat contents of the liquid and solid gold at the melting point, the heat content of the solid including the above mentioned rise. The value thus obtained was $\Delta H_m = 2946$ cal/g. at.

yielding an entropy of fusion ΔS_m = 2.20 eu, slightly lower than literature values.[2]

Tin

Heat contents of tin have been measured in the range 405° - 924°K. Previous measurements have been reported by Awbery and Griffiths[18] (366° - 560°K); Iitaka[19] (356° - 786°K); Jaeger and Bottema[20] (373° - 493°K); Schübel[21] (373° - 473°K); Orr, Heffan and Hultgren[22] (505° - 821°K); Umino[16] (323° - 873°K); Wüst, Meuthen and Durrer[15] (373° - 1273°K).

Results of Awbery and Griffiths are sligtly higher than the present data. Results of Iitaka scatter but in general are in good agreement with the present results. Heat contents of Jaeger and Bottema are in excellent agreement with present data. Those of Schübel are slightly higher. Those of Umino are much higher for the solid and liquid up to 600°K, however at higher temperatures are in excellent agreement with the present results. Results of Wüst et al. are higher at all temperatures. Heat contents of Orr, Heffan and Hultgren[22] are in excellent agreement with present data up to 700°K. At higher temperatures the present data tend to be lower than those derived from Cp measurements of Orr et al. More heat content measurements would be desirable at temperatures above 700°K in order to resolve this slight discrepancy.

The heat of fusion at the melting temperature 505°K was found to be ΔH_m = 1675 cal/g. at. and the entropy of fusion, ΔS_m = 3.31 eu, in good

agreement with the following previous reported values:

Investigator	ΔH_m, cal/g. at.
Oelsen[23]	1730-1660
Oelsen, Oelsen and Thiel[24]	1690
Oelsen, Rieskamp and Oelsen[25]	1720
Bartenev[26]	1660
Cavallaro[27]	1710
Person[28]	1690

AuSn

Heat contents of AuSn have been measured in the range 416° - 917°K. Previous measurements have been reported by Bottema and Jaeger,[3] (398° - 581°K) and Kubaschewski[4] (495° - 908°K). Results of Bottema and Jaeger are in excellent agreement with the present data. Those of Kubaschewski are much higher at all temperatures.

As in the case of gold a rapid increase in the heat content values, beginning at about 30 degrees below the melting point has been observed. A similar effect was observed by Bottema and Jaeger.[3] Misra, Howlett and Bever[5] have observed a rapid non-linear increase in the heat capacity beginning also at about 30 degrees below the melting point. In this case also it seems that this is a real effect and not due to impurities or pre-melting or thermal gradients in the samples.

The melting temperature was found to be 693°K which is in fair

agreement with 691°K quoted by Kubaschewski[4] and 692.4°K quoted by Misra, Howlett and Bever.[5]

The heat of fusion was found to be ΔH_m = 2811 cal/g.at. yielding an entropy of fusion ΔS_m = 4.05 eu. Here again the heat content of the solid includes the sudden rise below the melting point.

The heat of fusion reported by Kubaschewski[4] is 3060 cal/g.at., and that reported by Misra, Howlett and Bever[5] is 3370 cal/g.at. For reasons given below it is believed that Kubaschewski's heat contents measurements are in error, causing the heat of fusion derived from his results to be also in error. Misra et al. measured the thermal properties of AuSn in the range 613° - 753°K, using a constant temperature gradient calorimeter. They observed a rapid non-linear increase in the heat capacity of the solid, beginning at about 30 degrees below the melting point, and a rapid drop in the heat capacity of the liquid just above the melting point. In the heat of fusion reported by them, these two effects are considered as belonging to the melting process. Their value for the heat of fusion is about 550 calories greater than the value found in the present investigation. The mentioned effects would add only about 60 calories in the present investigation. We cannot account for the large deviation of Misra et al.

Biltz et al. measured the heat of formation of solid AuSn at 363°K using aqueous solution calorimetry. They found $\Delta H_{f,\ 363°K}$ = -4100 cal/g.at. referred to solid gold and tin. Kleppa[9] using emf techniques measured the heat of formation of liquid AuSn at 873°K. He found

$\Delta H_{f,\ 873°K}$ = -2316 cal/g. at. referred to liquid tin and "supercooled" liquid gold. Kleppa[7] by metal solution calorimetry later found the heat of formation of solid AuSn at 623°K to be $\Delta H_{f,\ 623°K}$ = -4250 cal/g. at. referred to solid gold and liquid tin. Later Kleppa called attention to a calibration error found in his calorimeter,[7, 29] the nature of the error being such that all the measured exothermic heats of solution were about 6.4% too low. Making the appropriate correction, the value becomes $\Delta H_{f,\ 623°K}$ = -3580 cal/g. at. referred to solid gold and "superheated" solid tin. Misra, Howlett and Bever[5] by metal solution calorimetry found $\Delta H_{f,\ 273°K}$ = -3645 cal/g. at. referred to solid gold and tin; and Masse et al.[8] also by metal solution calorimetry found $\Delta H_{f,\ 696°K}$ = -3000 cal/g. at. referred to liquid tin and "supercooled" liquid gold.

In order to compare these different measurements the heat of formation at 273°K determined by Misra et al.[5] has been taken as a basis and the heat contents found in the present investigation have been used to find the heat of formation as a function of temperature. The results are presented in Table 8. In Figure 7 these results are presented together with the previous reported values. Care has been taken to refer the heats of formation to the same reference state.

From these results it is seen that the heat of formation reported by Biltz et al.[6] at 363°K differs by more than 400 calories from the calculated one, but this is not surprising since heats of formation obtained by

TABLE 8

Heats of Formation of AuSn

T, °K	ΔH_f, cal/g. at.	Ref. state
298.15	-3640	$Au_{(s)}, Sn_{(s)}$
400	-3655	$Au_{(s)}, Sn_{(s)}$
500	-3665	$Au_{(s)}, Sn_{(s)}$
600	-3670	$Au_{(s)}, Sn_{(s, superheated)}$
693(s)	-3555	$Au_{(s)}, Sn_{(s, superheated)}$
693(ℓ)	-3045	$Au_{(\ell, undercooled)}, Sn_{(\ell)}$
700	-3040	$Au_{(\ell, undercooled)}, Sn_{(\ell)}$
800	-2900	$Au_{(\ell, undercooled)}, Sn_{(\ell)}$
900	-2735	$Au_{(\ell, undercooled)}, Sn_{(\ell)}$

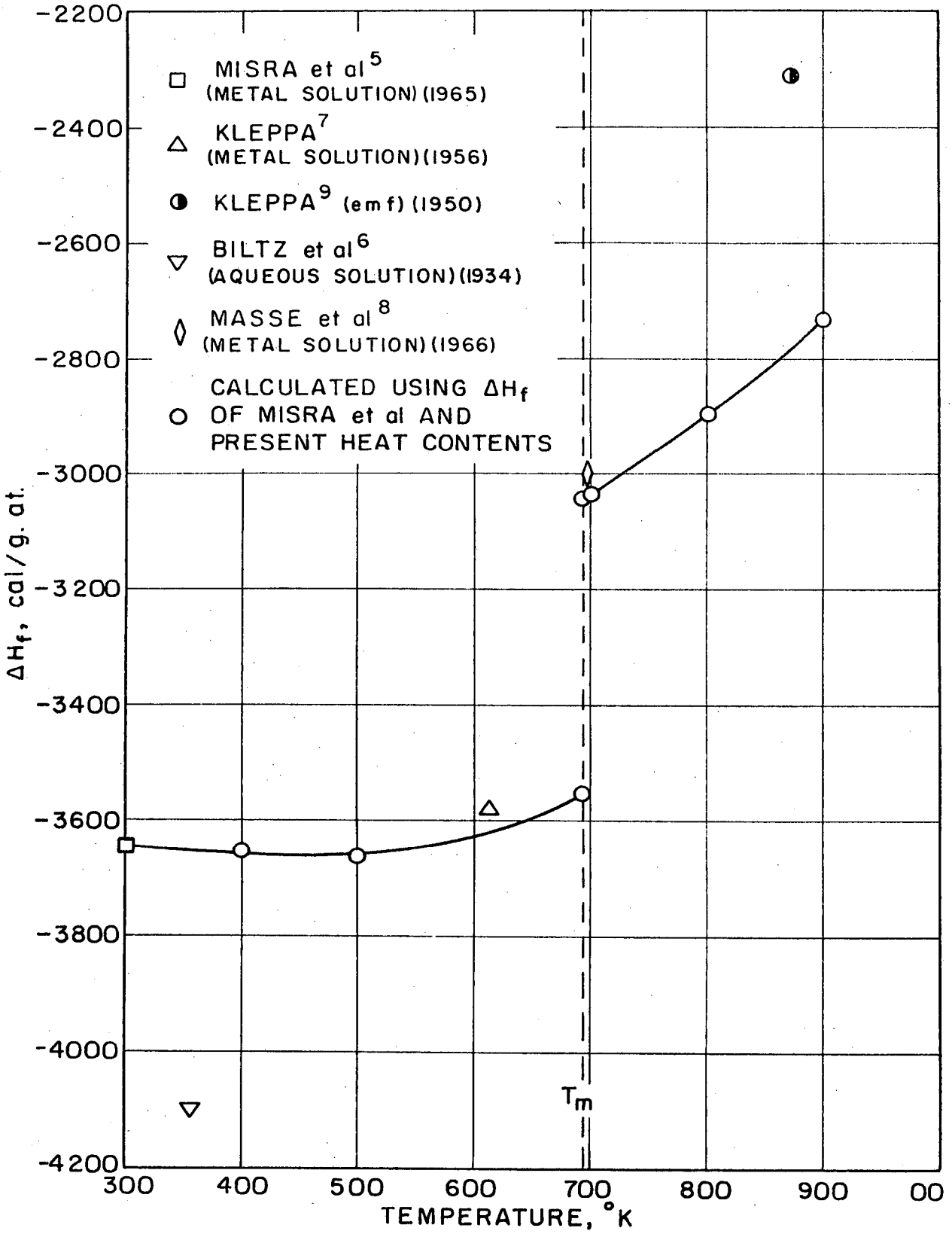

FIG. 7. HEATS OF FORMATION OF AuSn AS A FUNCTION OF TEMPERATURE.

aqueous solution calorimetry in general are inaccurate. The same applies to the heat of formation at 873°K determined by Kleppa,[9] using emf techniques, which differs by about 500 calories from the calculated one. It is also seen that there exists a fairly good agreement between the calculated heat of formation at 623°K with the experimental value of Kleppa,[7] using metal solution calorimetry. It can also be observed that the heat of formation evaluated in this manner differ from Masse et al.'s[8] metal solution calorimetry value by about 45 calories which is much less than the combined experimental uncertainties in Misra et al., Masse et al., and present data.

Thus, the discrepancy of 300 calories between Masse's and Misra et al. values no longer exists, if, in order to make the comparison, the present data is used instead of using Kubaschewski's values. This is the significant evidence that gives more validity to our results and which indicates that the previous measurements of the heat contents of AuSn made by Kubaschewski are in error.

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