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STUDIES ON BISMUTH ALLOYS. I. LIQUIDUS CURVES OF THE Bi-Cu, Bi-Ag, AND Bi-Au SYSTEMS

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ABSTRACT

The liquidus curves of the Bi-Cu, Bi-Ag, and Bi-Au systems were redetermined by means of a sampling method. The Bi-Ag curve was somewhat shifted from the previously determined location. The eutectic was found at 262.5 ± 0.2°C at 4.95 ± 0.05 atom % silver (2.62 wt %). The Bi-Cu liquidus agreed fairly well with Kleppa's data over the range investigated by him. The discrepancies in the literature in regard to higher copper concentrations were resolved. The eutectic was determined to be at 270.6 ± 0.1°C at 0.46 atom % copper (0.14 wt %). The Bi-Au liquidus did not agree well with the few experimental data available. Below the peritectic temperature, a completely new liquidus curve was established. The peritectic was found to be at 371 ± 2°C by means of differential thermal analysis. The composition is 23.1 atom % gold (24.1 wt %). The eutectic is at 13.4 ± 0.2 atom % gold (14.1 wt %) at 241.5 ± 0.5°C.

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* Work performed under the auspices of the U. S. Atomic Energy Commission.

The heats of fusion of the four elements agreed reasonably well with the literature values, except that of bismuth.

The results show that the sampling method is, for many cases, well adapted for the determination of liquidus curves.

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Introduction

During an investigation of the distribution of small amounts of ternary additions to binary systems involving bismuth, it was found that liquidus data were obtained which differed from those reported in the literature. It was, therefore, considered useful to examine the systems involved a little more in detail. We are reporting here the results of our liquidus determinations of the binary systems of bismuth with copper, silver, and gold.

These three systems were investigated many years ago by means of thermal analysis. The results are summarized by Hansen and Anderko.[1] The Bi-Cu system has been investigated by Jeriomin,[2] Hiorns,[3] Portevin,[4] and Heycock and Neville[5] as well as by Kleppa[6] and others.

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[1] M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd edition, McGraw Hill, New York, 1958.

[2] K. Jeriomin, Z. anorg. Chem., 55, 412 (1907).

[3] A. H. Hiorns, Trans. Faraday Soc., 1, 179 (1905).

[4] A. Portevin, Rev. met., 4, 1077 (1907).

[5] C. T. Heycock and F. H. Neville, Phil. Trans. Roy. Soc. London, A189, 46 (1897).

[6] O. J. Kleppa, J. Am. Chem. Soc. 74, 6050 (1952).

Although the oldest, Heycock and Neville's work stands among the most precise thermal analyses ever done. Unfortunately, their investigations cover only very dilute solutions.

Kleppa used a sampling method which was quite adequate, but he, too, did not cover the complete liquidus range. Among the various determinations by thermal analysis, the work of Jeriomin and of Heycock and Neville is the most consistent. Kleppa's data do not entirely agree with those of Jeriomin. The sampling data lie above Jeriomin's liquidus.

The eutectic point has been reported at about 0.6° below the melting point of bismuth[7] and about 0.7 atom % bismuth by Heycock and Neville,[7] and at 0.48 atom % bismuth by Kleppa.[6]

The Bi-Ag liquidus has been investigated by Heycock and Neville[5,7,8] and by Petrenko.[9] Only the latter author covered the entire liquidus range. Recently a portion has been examined by Kleppa.[10] Petrenko reports a eutectic at 262°C and 95.3 atom % bismuth.

The Bi-Au system was investigated by Vogel,[11] who reported a eutectic at 240°C and 81.1 atom % bismuth. Later, an incongruently melting compound, Au_2Bi, was found by de Haas and Jurriaanse.[12] The peritectic was

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[7] C. T. Heycock and F. H. Neville, J. Chem. Soc., 61, 893 (1892).

[8] C. T. Heycock and F. H. Neville, J. Chem. Soc., 65, 73 (1894).

[9] G. I. Petrenko, Z. anorg. Chem., 50, 136 (1906).

[10] O. J. Kleppa, J. Phys. Chem., 60, 446 (1956).

[11] R. Vogel, Z. anorg. Chem., 50, 145 (1906).

[12] W. J. de Haas and F. Jurriaanse, Naturwissenschaften, 19, 706 (1931).

stated to be at 373° C.[13] The fact that Vogel did not observe the peritectic can be explained by the small number of his data and the apparent sluggishness of the formation of Au_2Bi.

The method which we have used consisted of sampling the liquid phase and analyzing the sample. In all cases known to us, sampling yields liquidus curves which, at best, coincide with curves obtained from thermal analysis. Generally, however, curves obtained by sampling lie higher than those obtained by thermal analysis. (See, for example, a number of cases cited by Nathans.[14]) We believe that the sampling method yields more reliable data, because it is a direct measurement under equilibrium conditions, provided that the existence of equilibrium can be ascertained and that a clear separation of the two phases can be effected.

Experimental Equipment

The apparatus was a stainless-steel furnace tube with a gas inlet at the bottom, a cooling coil at the top, a flanged head having an opening for a stirrer, a thermocouple well, and a sampling tube. All seals were made by means of O-rings or garlock gaskets. Sampling was done with 2- or 3-mm i.d. pyrex or quartz tubes with a piece of porous graphite (National Carbon Co. grade 60) press-fitted into one end to serve as a filter. Figure 1 shows the arrangement for inserting and withdrawing the sample tube from the melt. A Norton high-purity alumina crucible contained the melt. The crucible was located inside a graphite secondary with a heavy graphite top as an oxygen getter. The top had suitably located holes for the stirrer etc. The assembly

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[13] F. Jurriaanse, Z. Krist., <u>90</u>, 322 (1935).

[14] M. W. Nathans, AEC Rept. No. ANL-5753, July 1957.

was inserted in a Kanthal-wound Hevi-Duti clam shell type furnace, 3-inches i.d. and 18-inches long placed on end. Provisions were made to evacuate or pressurize the furnace or the sampling tube.

Temperatures were measured with a Pt-Pt (10% Rh) thermocouple with its cold junction in an ice-bath. The thermocouple was calibrated at the melting points of copper, aluminum, zinc, lead, and tin (NBS certified), and at the boiling points of p-dichlorobenzene and water. The calibration was checked periodically, but no change greater than 0.2 μV was observed. The temperatures were read to 0.1°C with a Rubicon model 2745 potentiometer.

Procedure

A charge of between 400 and 500 grams was placed in the crucible. In a number of experiments, about 60 to 100 milligrams of a ternary addition was present as a radioactive tracer so that data of the type described in a subsequent article[15] could be obtained simultaneously. The effect of this small amount of impurity on the binary liquidus is negligible.

After loading and emplacement, the furnace was flushed with high-purity nitrogen. Throughout an experiment, the pressure in the furnace was kept about 250 mm above atmospheric by means of nitrogen in order to impede the diffusion of small amounts of air through small leaks. The Bi-Cu and Bi-Ag melts were stirred with a tungsten rod flattened at the lower end. Stirring was usually continued during sampling. Bi-Au melts were agitated periodically with the thermocouple well to prevent pick-up of the stirrer metal by the melt. Agitation by gas bubbling through a tube was tried, but later abandoned because the bubble rate was rather difficult to control.

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[15] M. W. Nathans and M. Leider, to be published.

Although no record was kept of whether the melt was stirred during sampling or not, it was concluded from plots of the data that it did not matter. No particles passed the filter to a detectable degree. This was also checked on a couple of occasions by taking a sample without filter after a suitable settling period.

The charge was generally heated to about 100° C above the estimated liquidus temperature and kept there for at least thirty minutes. One or two samples were taken to check the composition of the melt. Further samples were taken at successively lower temperatures by pressurizing the melt, by suction on the sampling tube, or both. Control of the sample size was usually poor. Most sample weights varied between 5 and 15 grams. The sample size usually became smaller when a large amount of precipitate had formed. This was probably caused by the increased viscosity of the mass.

Experiments in the Bi-Cu and Bi-Ag systems above 600°C were carried out under a layer of purified flake graphite as additional insurance against oxygen pick-up by the melt. In these experiments, it is often impossible to obtain good samples, probably in part because the filter became clogged when the sampling tube passed through the graphite layer. The filter could be reopened, however, by blowing nitrogen through it prior to forcing a sample through.

Analytical

In each case, the entire sample was dissolved in either 8N to 10N HNO_3 or in aqua regia (when gold was present). The samples were analyzed for both components except when a large excess of one interfered with the analysis of the other.

Bismuth was determined by titration with EDTA (about 0.01N). Aliquots containing about 20 mg of bismuth were added to a solution having a p_H less than 2, and containing a few grams of thiourea as indicator and complexing agent. The titrations were carried out at a p_H between 2.1 and 2.4. The accuracy was quite sensitive to the p_H.

Copper was determined electrolytically. A separation from bismuth must be carried out first. This was done by carefully neutralizing the solution with ammonia to a p_H of 6 to 7 followed by the addition of ammonium carbonate to complex the copper ion. The precipitate was filtered off. A complete separation from bismuth can be effected by redissolving the precipitate in nitric acid and treatment with ammonium hydroxide and ammonium carbonate, a second and a third time.

In later samples, copper was determined spectrophotometrically with a Carey recording spectrograph. The 807-millimicron band was found suitable. Bismuth did not interfere, but the intensity was dependent upon the nitric acid concentration. The acid variation was held small, however, by diluting a suitable aliquot with a forty-fold volume of 2N nitric acid in a volumetric flask. The effect of dust particles in the acid was eliminated by letting the solutions stand overnight and transferring them to the cells with a transfer pipette.

Silver was determined electrolytically in an ammoniacal solution from its EDTA complex. Bismuth did not interfere. Gold was determined coulometrically with a controlled-potential coulometer.[16]

All analyses had a precision of better than ±1%. Material balances were, in all but a few isolated cases, between 99 and 100.5 %.

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[16] J. Harrar, J. Electroanal. Chem., to be published.

Materials

Bismuth:	99.999% pure droplets from American Smelting and Refining Co., melting point 271.4°C.
Copper:	OFHC copper from stock, melting point 1083°C.
Silver:	99.99% pure needles from Fairmont Chemical Co., melting point 961°.
Gold:	99.95% pure scrap from stock. The major impurities are (spectrographic): 0.003-0.03% Ag, 0.003-0.03% Pd, 0.001-0.01% Pb, 0.001-0.01% Cu.

Results

The results are shown in Figs. 2 through 4. Rather than tabulating our actual experimental data, we show in Tables I through III data as read from the smoothed curves before reproduction. We have also indicated the mean deviation of the experimental data from the curves.

The few points obtained during reheating agree well with those obtained during cooling. The deviation from the curve of points obtained by thermal analysis is small.

It appears that at higher copper contents, the copper precipitate is rather fine and does not settle rapidly. Samples were taken without a filter from a composition containing about 95% copper. The analyses showed too high a copper content which indicates poor phase separation.

In the gold-bismuth system, the sampling data near the peritectic were quite erratic. Our explanation is that the rate of formation of the compound is slow, and that there is still some tendency for pure gold to precipitate as a metastable phase. This could explain why Vogel did not observe the change in slope of the liquidus.[11]

An attempt was made to obtain sampling data on the bismuth-rich side of the silver-bismuth eutectic. We got only one point by sampling but were able to get two points by thermal analysis. We feel that this was sufficient to establish this part of the liquidus to about 5% relative to the silver content.

The eutectic data are shown in Table IV. They are the average of three separate determinations, including in the case of Bi-Ag a determination from the bismuth-rich side.

The Au-Bi peritectic can be established by the intersection of the two parts of the liquidus. It was determined separately, however, with a sample containing about 80 wt % Au_2Bi and 20% gold. This sample was obtained by treating an ingot with 8N nitric acid. It was subjected to differential thermal analysis with aluminum powder as the inert in a dynamic argon atmosphere and at an upheat rate of 10°C per minute. Figure 4 shows the record. Concurrently, the temperature of the sample was measured with a potentiometer. The peritectic was established at 371 ±2 °C.

The agreement of the liquidus points with the older data is fair to poor, but the agreement is good with Kleppa's data. The validity of the data was checked by calculating the heats of fusion from the terminal slope of a log (atom % solute) vs 1/T plot. We estimated the distribution coefficient of Bi between solid and liquid Ag as 0.1 from the data given by Hansen and Anderko.[1] Solid solubility was neglected in the remaining cases. Table V shows a comparison between our calculated values and those found in Hultgren's compilation.[17] The data agree well, except for bismuth. This may warrant further investigation.

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[17] R. Hultgren, Project Supervisor, "Selected Values, Thermo-dynamic Properties of Metals," Prepared for the USAEC at the Minerals Res. Lab., University of California, 1956.

Acknowledgments. We wish to acknowledge the valuable help and suggestions afforded us by the following members of the analytical laboratory: Dr. R. Bystroff, for his help with the spectrophotometric copper determination, Dr. J. Harrar, for his help with the coulometric gold determination, and Mrs. G. Stephas.

TABLE I

SMOOTHED LIQUIDUS DATA FOR THE Cu-Bi SYSTEM[a]

Temp °C	Atom % Cu	Wt % Cu	Temp °C	Atom % Cu	Wt % Cu
1083	100	100	650	15.5	5.3
1070	98.9_5	96.6_7	600	11.1	3.6_6
1050	97.3_5	92.1	550	7.3	2.3_4
1025	95.2	85.8	525	5.9	1.8_7
1000	92.7	79.4	500	4.76	1.50
975	89.0	71.1	460	3.53	1.11
950	83.6	60.8	440	2.95	0.92
925	77.5	51.2	420	2.44	0.75
900	70.7	42.5	400	2.03	0.63
875	63.4	34.5	380	1.65	0.51
850	56.2	28.1	360	1.35	0.41
825	49.3	22.8	340	1.08	0.33
800	43.0	18.7	320	0.74	0.23
775	36.9	15.1	300	0.56	0.17
750	31.4	12.2	280	0.50	0.15
725	26.5	9.9	270.6	0.46	0.14[b]
700	22.1	7.9	271.4	0.00	0.00

[a] Standard deviation: 0.2 atom %, 450° - 700°
1.4 atom %, 700° - 1083°

[b] Eutectic

TABLE II

SMOOTHED LIQUIDUS DATA FOR THE Ag-Bi SYSTEM[a]

Temp °C	Atom % Ag	Wt % Ag	Temp °C	Atom % Ag	Wt % Ag
961	100	100	460	53.1	36.9
950	99.1	98.3	450	50.0	34.0
925	94.9	90.6	430	42.4	27.5
850	90.8	83.6	420	38.3	24.3
800	86.7	77.1	410	34.7	21.5
750	83.2	71.9	400	31.0	18.8
700	80.1	67.5	390	27.2	16.2
650	76.6	61.5	380	23.7	13.8
600	72.6	57.5	360	17.6	9.9
575	70.2	54.9	340	13.2_5	7.3
550	67.6	51.9	320	10.0_5	5.4_5
520	63.9	47.7	300	7.7_7	4.1_7
500	61.1	44.8	280	6.0_8	3.2_3
480	57.9	41.5	270	5.4_2	2.8_7
			262.5	4.95	2.62[b]

[a] Standard deviation: 0.3 atom %, 260° - 400°
0.1 atom %, 400° - 960°

[b] Eutectic

TABLE III

SMOOTHED LIQUIDUS DATA FOR THE Au-Bi SYSTEM[a]

Temp °C	Atom % Au	Wt % Au	Temp °C	Atom % Au	Wt % Au
1063	100	100	450	41.2	39.8
1050	98.8	98.7	400	35.9	34.6
1000	94.5	94.2	371	33.1	31.8[b]
950	90.4	89.9	350	27.0	25.9
900	86.4	85.7	325	23.0	22.0
850	82.5	81.6	300	19.8	18.9
800	78.5	76.5	270	16.4	15.6
750	74.4	73.3	241	13.2	12.6[c]
700	69.9	68.7	250	10.0	9.5
650	64.6	63.3	260	6.0	5.7
600	59.0	57.5	270	0.9	0.8_5
550	52.9	51.5	271.4	0	0
500	46.7	45.3			

[a] Standard deviation: 0.3 atom %, 240° - 371°
0.5 atom %, 371° - 700°
0.2 atom %, 700° - 1065°

[b] Peritectic

[c] Eutectic

TABLE IV

EUTECTIC TEMPERATURES AND COMPOSITIONS

	Temp °C	Composition Atom % Bi	Wt % Bi
Bi-Cu	270.6 ± 0.1	99.54	99.86
Bi-Ag	262.5	95.0_5	97.3_8
Bi-Au	241.1 ± 0.3	86.8 ± 0.2	86.1

TABLE V

HEATS OF FUSION OF Cu, Ag, Au, and Bi

Element	Cu	Ag	Au	Bi
$\Delta H_m{}^a$ Calculated	2940	2780	2870	3130[b]
$\Delta H_m{}^a$ Literature	3120	2855	2955	2600

[a] Calories per gramatom

[b] Average of values 3100, 3300, and 3000 from the Cu-Bi, Ag-Bi, and Au-Bi systems respectively

/mr

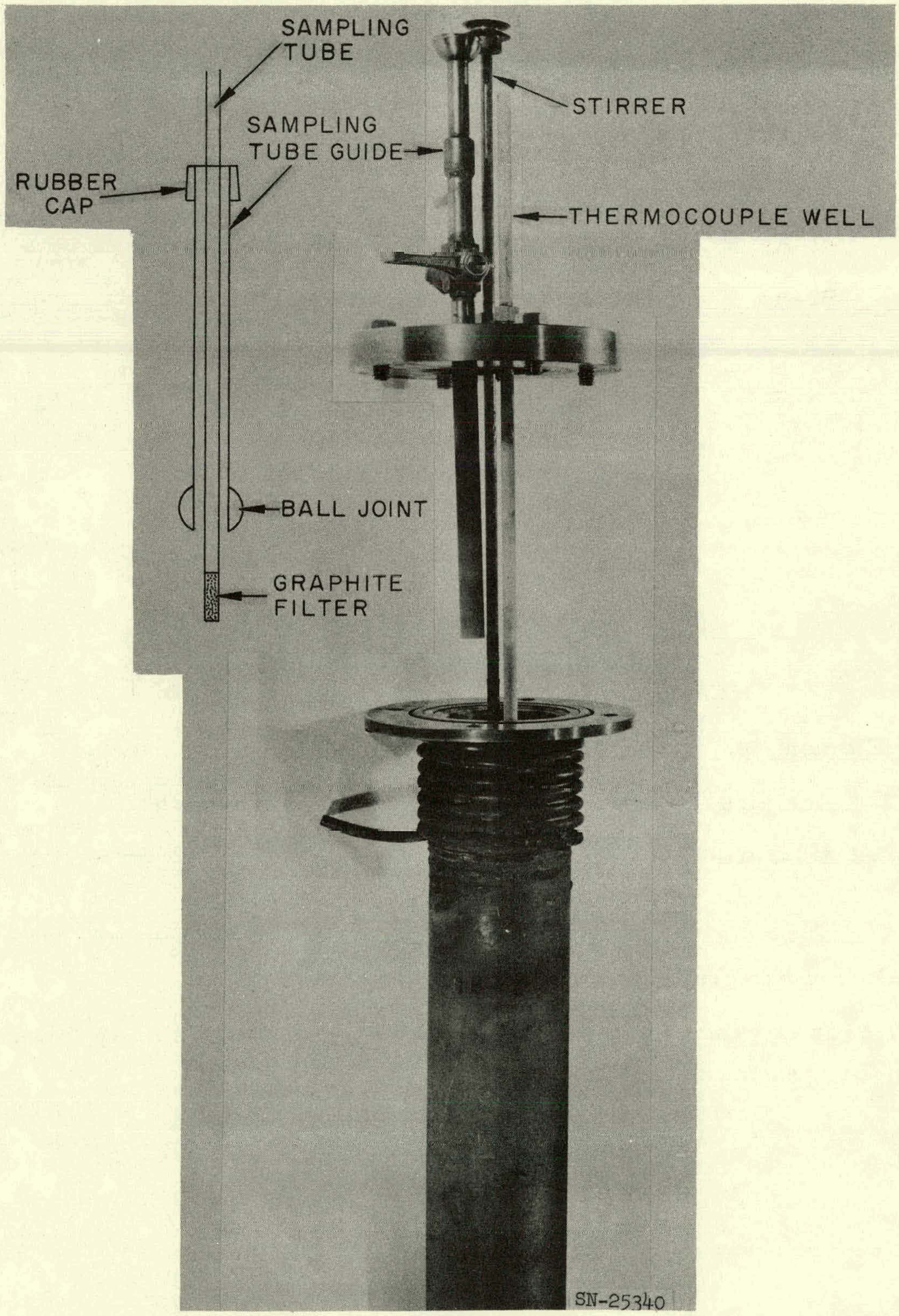

Fig. 1. Furnace closure with sampling arrangement.

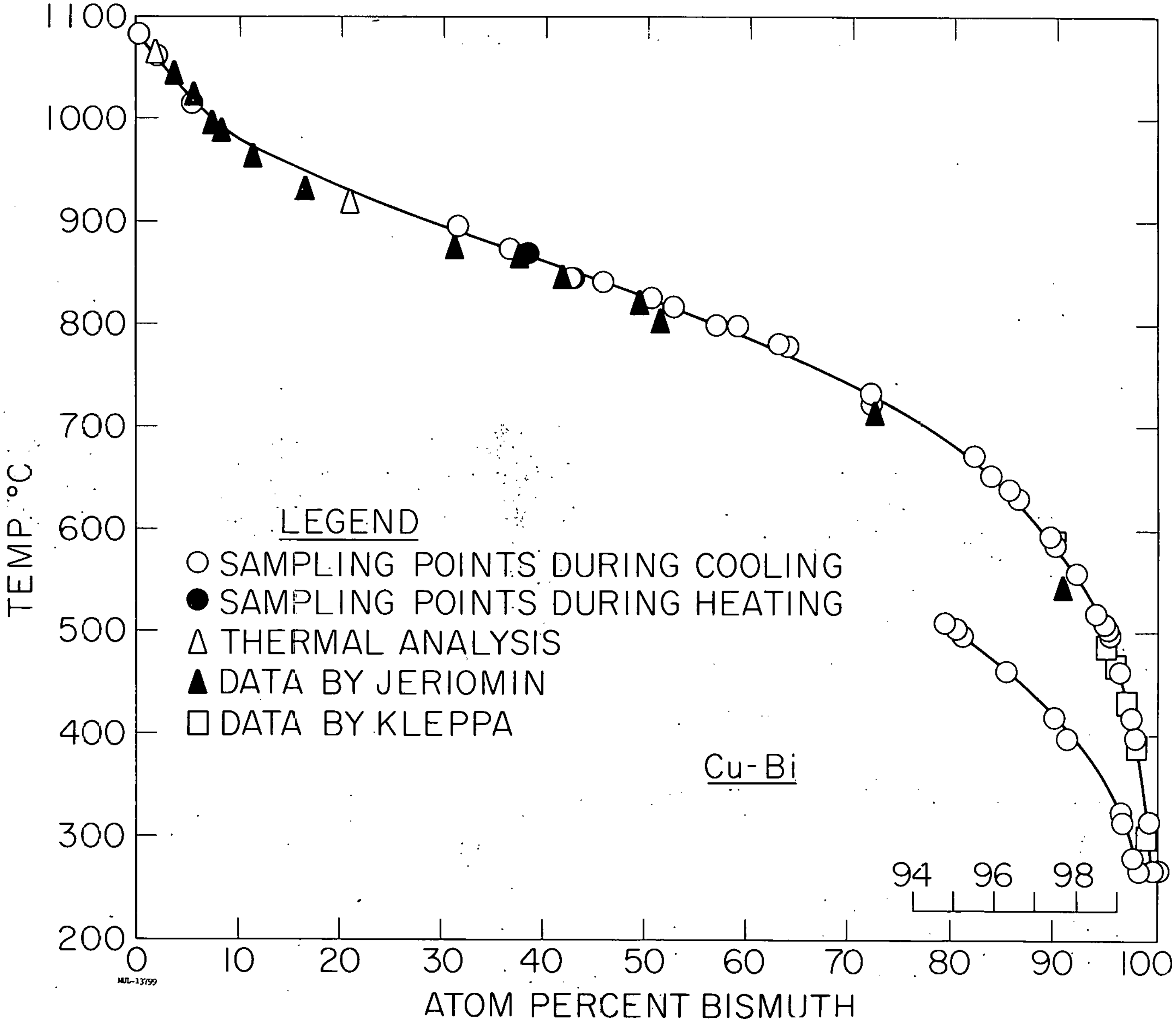

Fig. 2. Liquidus of the bismuth-copper system.

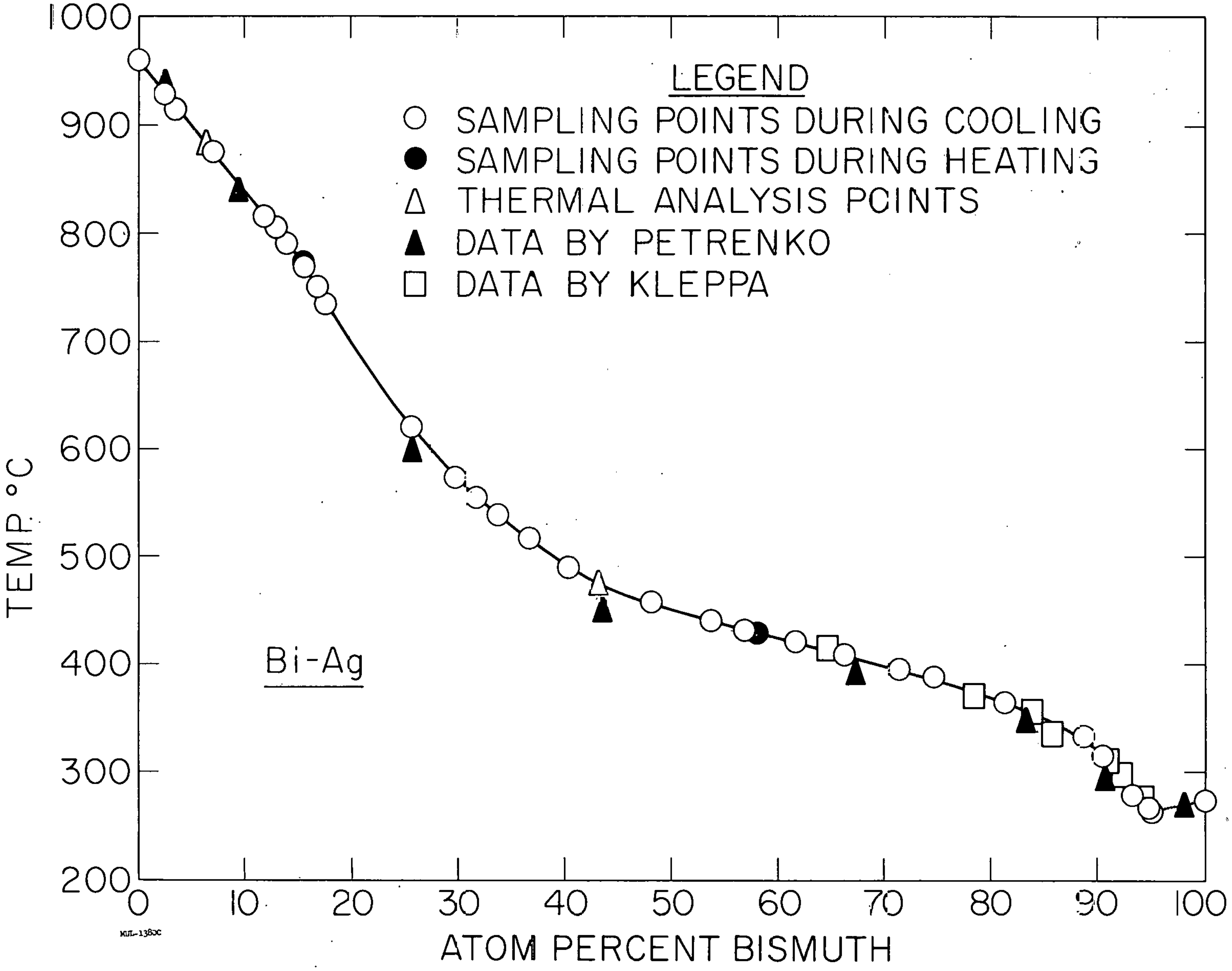

Fig. 3. Liquidus of the bismuth-silver system.

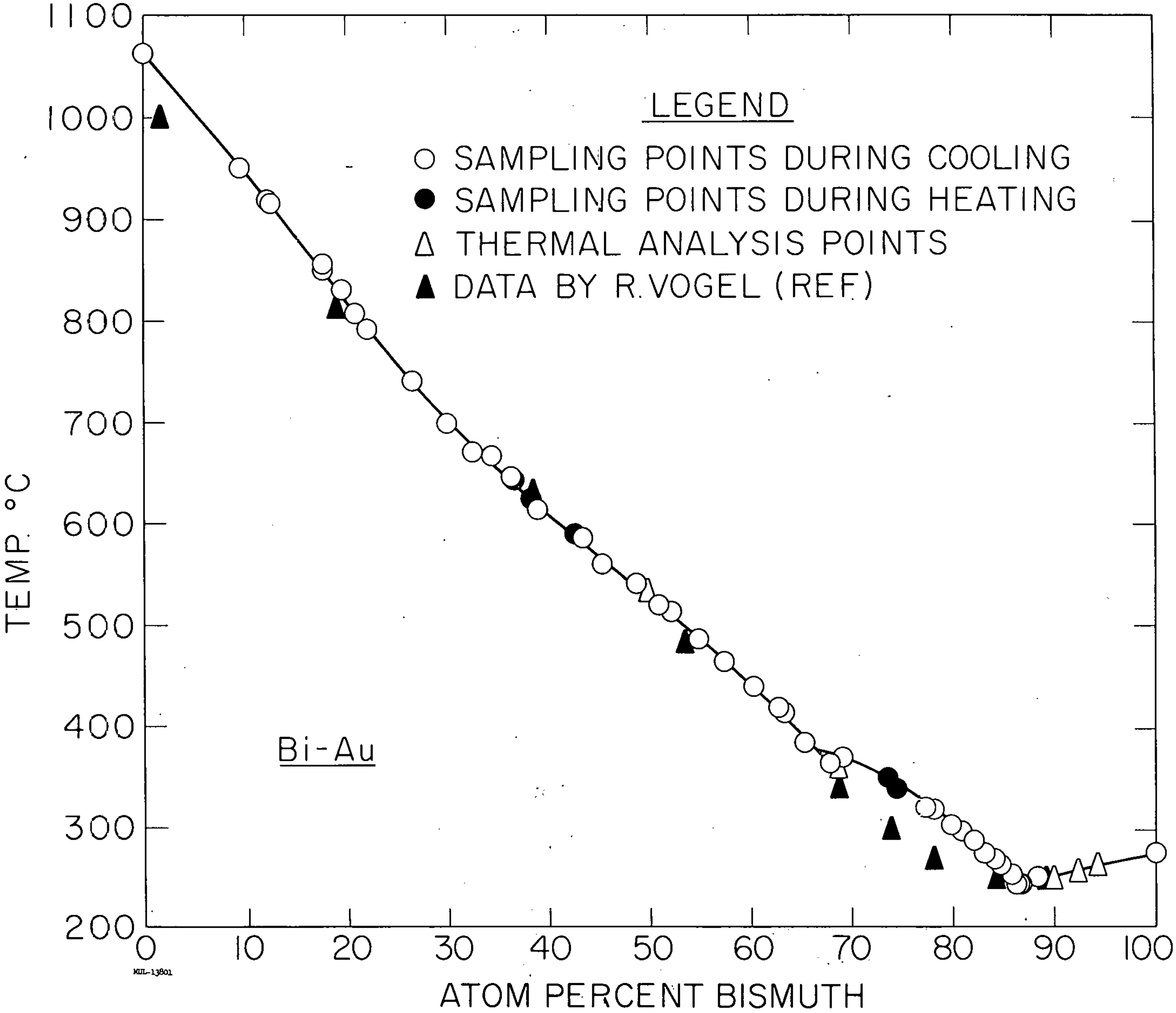

Fig. 4. Liquidus of the bismuth-gold system.