

The Rb-Sr (Rubidium-Strontium) System

85.4678

87.62

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The Rb-Sr system was found by Klemm and Kunze [67Kle] to exhibit virtually complete immiscibility in both solid and liquid states. No compounds were found by X-ray diffraction.

Crystal structure and lattice parameter data are given in Table 1.

Cited Reference

*67Kle: W. Klemm and D. Kunze, "Systems of Alkali and Alkaline Earth Metals," Proc. Int'l. Symp. on Alkali Metals, London Chem. Soc., Special Publ. No. 22, 3-22 (1967). (Equi Diagram; Experimental; #)

*Indicates key paper.

#Indicates presence of a phase diagram.

Table 1 Rb-Sr Crystal Structure and Lattice Parameter Data

| Phase | Composition, at.% Sr | Pearson symbol | Space group | Proto- type | Lattice parameter, nm | | Reference |
|------------------------|-------------------------|-------------------|----------------------|----------------|-----------------------|-----------|------------|
| | | | | | a | Comment | |
| (Rb)..... | 0 | cI2 | <i>Im</i> 3 <i>m</i> | W | 0.5703 | At 25 °C | [King1] |
| (α Sr)..... | 100 | cF4 | <i>Fm</i> 3 <i>m</i> | Cu | 0.6084 | At 25 °C | [King1] |
| (γ Sr)(a)..... | 100 | cI2 | <i>Im</i> 3 <i>m</i> | W | 0.485 | At 614 °C | [Pearson2] |

(a) Above 557 °C.

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The Au-Pt (Gold-Platinum) System

196.9665

195.08

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The equilibrium phases of the Au-Pt system are: (1) the liquid, L; and (2) the fcc, continuous solid solution, (Au, Pt), encompassing a miscibility gap (Au) + (Pt). The critical point of the miscibility gap is at about 61 at.% Pt and 1260 °C. The solid phase boundaries in Fig. 1 have been drawn according to the experimental data of [52Dar] as well as a tentative thermodynamic model similar to that of [71Kub]. The liquid phase boundaries were drawn from a subregular solution model derived from the experimental boundaries of [07Doe], [28Gri], [30Joh], [31Ste], [38Wic], [47Wic1], [47Wic2], [49Wic], [51Gru], [52Dar], [57Tie], [60Mun], and [64Rau]. Experimental data are not sufficient to establish a completely satisfactory thermodynamic model, but the features shown in Fig. 1 may only differ in very small detail from a true representation for this system. Earlier reviews were published by [62Dar], [78Sav], and [81Sin].

Equilibrium Diagram

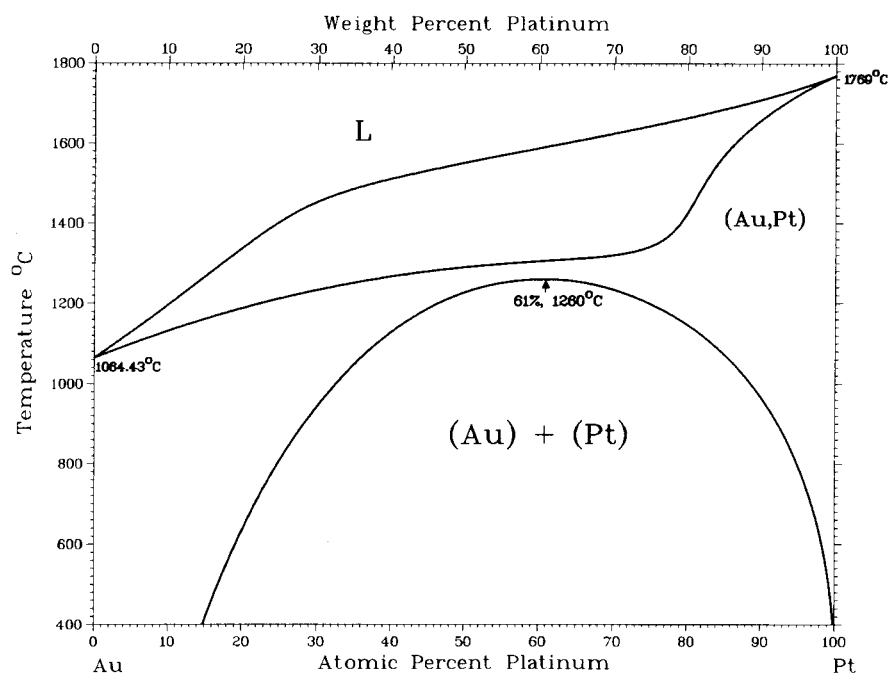
The Au-Pt phase diagram has been investigated extensively because of the experimental and theoretical interest in the miscibility gap occurring in the solid solution field, as well as the controversy regarding the form of the liquidus and solidus boundaries. Very early reports on this system, as early as in 1796, concerning the alloying characteristics are summarized in the review paper by [62Dar].

[07Doe] concluded from cooling curves using six alloys that a continuous series of solid solutions can be obtained following crystallization from the melt. The miscibility gap in the solid state was first observed by [30Joh], who used mainly resistivity measurements. Many supporting reports with better accuracy and more detail followed this work. In the mean time, probably misguided by the nearly horizontal form of the solidus (Fig. 1), [28Gri] and [51Gru] proposed a diagram with a peritectic reaction $L + (Pt) \rightarrow (Au)$. This was proved not to be true by [52Dar] from detailed thermal, microscopic, X-ray, and resistivity observations.

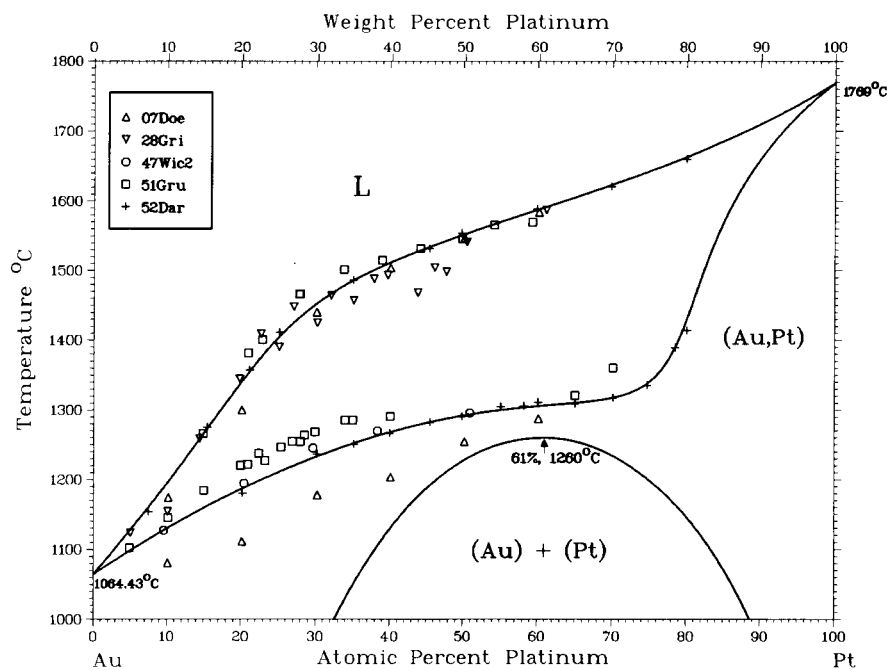
Liquidus. The melting points of Au and Pt are accepted as 1064.43 °C and 1769.0 °C, respectively [Melt]. All the liquidus data by [07Doe], [28Gri], [51Gru], and [52Dar] given in Table 1 were determined from cooling curves. Agreement between these data is fairly good, as can be seen in Fig. 1, although the melting point of Pt by [07Doe] and [28Gri] is considerably lower than the accepted value and a large experimental scatter can be seen in the data of [28Gri]. The liquidus line in Fig. 1 is based on the experimental data of [52Dar].

Solidus. The solidus data were obtained by [07Doe], [28Gri], and [51Gru] from cooling curves, by [47Wic2] and [51Gru] from electrical resistivity vs temperature curves,

Fig. 1 Assessed Au-Pt Phase Diagram



(a)

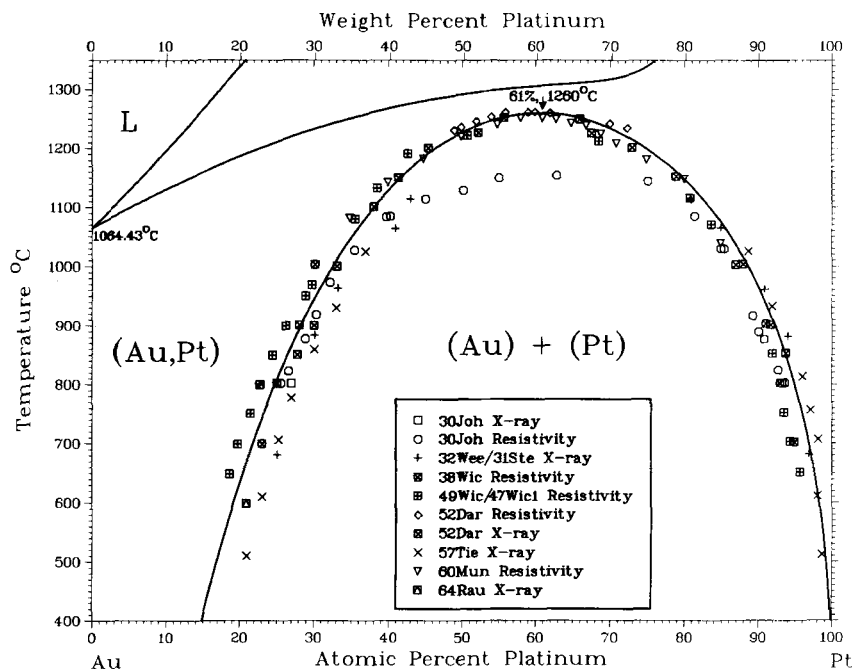


(b)

(a) Assessed diagram. (b) Assessed liquidus and solidus.

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Fig. 1 Assessed Au-Pt Phase Diagram (continued)



(c)

(c) Assessed miscibility gap.

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Table 1 Experimental Data on Liquidus

| Composition, at.% Pt | Temperature, °C | Composition, at.% Pt | Temperature, °C |
|----------------------|-----------------|----------------------|-----------------|
| [07Doe] | | [28Gri] (cont'd) | |
| 0 | 1064 | 22.7 | 1410 |
| 10.1 | 1174 | 25.2 | 1389 |
| 20.2 | 1299 | 27.2 | 1447 |
| 30.2 | 1437 | 30.17 | 1425 |
| 40.2 | 1503 | 32.2 | 1462 |
| 50.2 | 1544 | 35.2 | 1456 |
| 60.2 | 1579 | 37.86 | 1487 |
| 100 | 1744 | 39.98 | 1493 |
| [52Dar] | | 44.09 | 1467 |
| 7.6 | 1155 | 46.11 | 1502 |
| 15.1 | 1274 | 47.7 | 1496 |
| 20.21 | 1355 | 50.59 | 1540 |
| 25.2 | 1408 | 61.54 | 1582 |
| 35.2 | 1483 | 100 | 1755 |
| 45.47 | 1529 | [51Gru] | |
| 49.95 | 1550 | 10.2 | 1197 |
| 60.2 | 1584 | 15.0 | 1266 |
| 69.94 | 1617 | 21.0 | 1382 |
| 80.2 | 1655 | 23.0 | 1401 |
| [28Gri] | | 28.0 | 1466 |
| 0 | 1063 | 34.0 | 1502 |
| 5.0 | 1123 | 38.9 | 1513 |
| 10.14 | 1154 | 44.3 | 1530 |
| 15.1 | 1259 | 50.0 | 1544 |
| 19.91 | 1345 | 54.4 | 1562 |
| | | 59.3 | 1569 |

Table 2 Experimental Data on Solidus

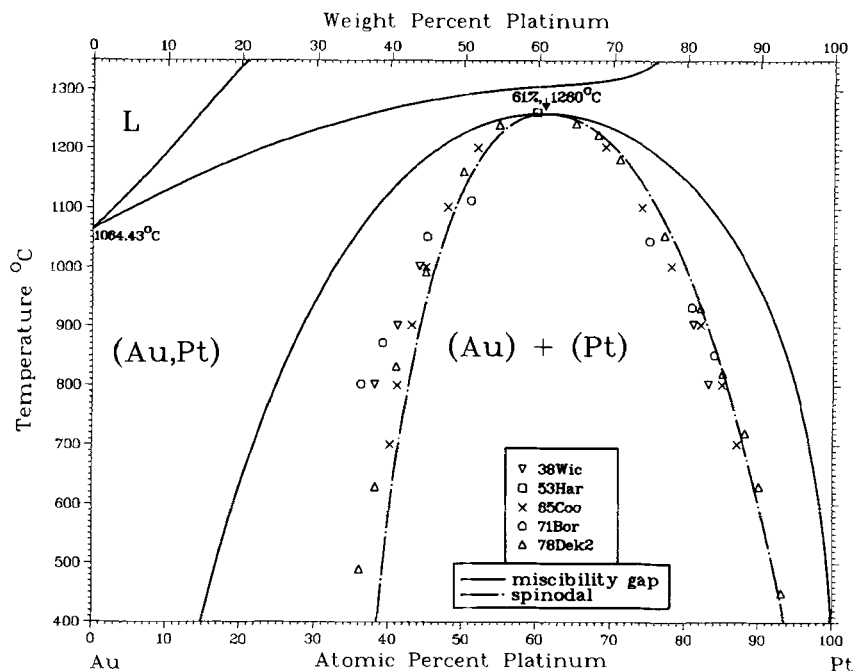
| Composition, at.% Pt | Temperature, °C | Composition, at.% Pt | Temperature, °C |
|----------------------|-----------------|----------------------|-----------------|
| [07Doe] (a) | | [47Wic2] (cont'd) | |
| 10.1 | 1079 | 29.5 | 1245 |
| 20.2 | 1109 | 38.5 | 1270 |
| 30.2 | 1177 | 51.0 | 1294 |
| 40.2 | 1203 | [51Gru] (a) | |
| 50.2 | 1253 | 10.2 | 1149 |
| 60.2 | 1285 | 15.0 | 1188 |
| [52Dar] (b) | | 21.0 | 1223 |
| 20.21 | 1180.5 ± 2.5 | 23.0 | 1229 |
| 30.22 | 1235 | 28.0 | 1255 |
| 35.2 | 1249.5 | 34.0 | 1286 |
| 40.2 | 1265 | 65.2 | 1314 |
| 45.47 | 1280 | 70.0 | 1357 |
| 49.95 | 1287.5 | [51Gru] (c) | |
| 55.2 | 1302.5 | 5 | 1105 |
| 58.2 | 1302.5 | 10 | 1147 |
| 60.2 | 1307.5 | 15 | 1187 |
| 65.2 | 1307.5 | 20 | 1219 |
| 69.94 | 1312.5 | 22.5 | 1240 |
| 74.72 | 1332.5 | 25 | 1247 |
| 78.03 | 1369.5 | 26.7 | 1254 |
| 80.2 | 1410 | 28.4 | 1263 |
| [47Wic2] (c,d) | | 30 | 1267 |
| 9.6 | 1128 | 35 | 1285 |
| 20.4 | 1196 | 40 | 1290 |

(a) Thermal. (b) Microscopic. (c) Electrical Resistivity. (d) From [Hansen].

and by [52Dar] from microscopic observations. The data by [07Doe], [47Wic2], [51Gru], and [52Dar] are listed in Table 2. The data by [28Gri] and part of the data by [51Gru] were omitted here because of the large experimental uncertainty involved, which presumably lead to

the erroneous conclusion about the occurrence of a peritectic reaction. The solidus temperatures by [07Doe] are too low, an error often encountered when the cooling curve method is employed. The solidus line in Fig. 2 is based on

Fig. 2 Au-Pt Spinodal Curve



Solid line is based on the present thermodynamic model.

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the data of [52Dar] for 0 to 80 at.% Pt and on the present thermodynamic model for 80 to 100 at.% Pt.

Incoherent Miscibility Gap. The incoherent (stable) miscibility gap in the solid state was experimentally observed mainly with electrical resistivity measurements [30Joh, 38Wic, 47Wic1, 49Wic, 52Dar, 60Mun] and X-ray measurements [30Joh, 31Ste(32Wee), 51Gru, 52Dar, 57Tie, 64Rau] (Table 3, Fig. 1). The earliest studies of resistivity in quenched alloys by [30Joh] indicated a fairly low critical temperature ($\sim 1150^\circ\text{C}$) when compared with later experiments ($\sim 1260^\circ\text{C}$), probably due to the insufficient quenching rate employed by [30Joh]. Later resistivity measurements carried out at high temperatures agreed with one another reasonably well (see Fig. 1). The miscibility gap boundary determinations with X-ray methods also are in generally good agreement. The composition corresponding to the critical temperature is about 61 at.% Pt. The miscibility gap curve in Fig. 1 is based on the present thermodynamic model.

Spinodal curves associated with the observed miscibility gap can be estimated from experimental data using different models or assumptions. These were discussed by [38Wic], by [65Coo] from the data of [52Dar] and [57Tie], by [71Bor] from the data of [49Wic], and by [78Dek2] from the van der Waals differential equation for coexisting phases and with assumed ideal entropy of mixing (Table 4). Some ambiguity regarding the shape of the spinodal is inevitable (Fig. 2). The spinodal can be also determined theoretically (see "Thermodynamics"). The kinetics of formation of the miscibility gap have been discussed by [37Joh], [38Bor], [38Wic], [51Bor], [60Too2], [67Car], [70Kra], [78Dek1], and [78Sin2].

Crystal Structures

The lattice parameters of pure Au and Pt at 25°C are accepted as 0.40784 nm [King1] and 0.39233 nm [King1] an obvious misprint in the table of lattice parameters has been corrected]. The Au-Pt system has only one stable structure (Au, Pt) based on the Cu-type fcc solid solution. The lattice parameters of the quenched alloys were measured by [30Joh], [51Gru], [52Dar], [55Rau], and [67Car] (Table 5). Annealing temperatures seem to have little effect on the lattice parameter (within experimental error). The deviation from an assumed Vegard's law is very slight (Fig. 3). Short-range order in dilute Pt alloys has been observed in 98 at.% Pt alloys [68Gol], and 96 and 99.38 at.% Pt alloys by [75Che]. The results by the latter for the 99.38 at.% Pt alloy may be incorrect [76Mac].

Metastable Phases

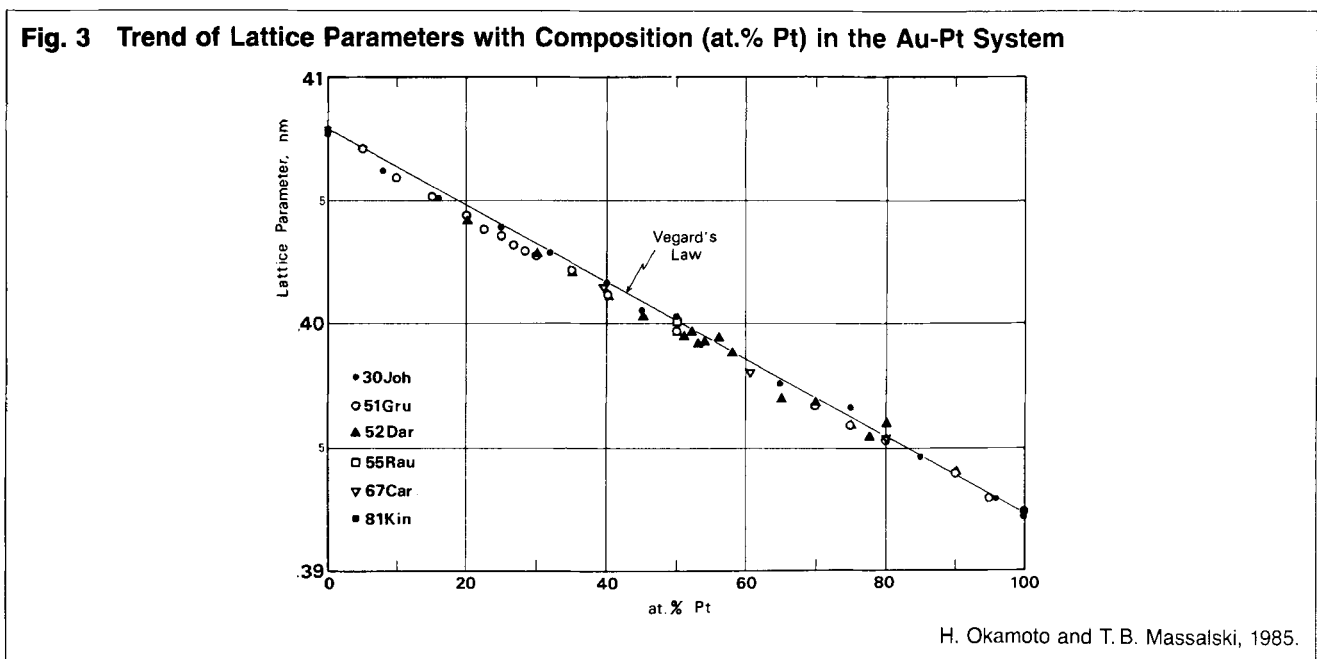
Intermetallic Compounds. The Au_3Pt phase is classified as a metastable phase here, although a definite conclusion on this has not yet been determined. The existence of this phase together with the AuPt and AuPt_3 phases was hinted at by [30Joh] on the basis of the change of slope in the magnetic susceptibility vs temperature curve. [51Gru] reported that the X-ray patterns showed the existence of the Au_3Pt superlattice in alloys up to 40 at.% Pt after severe cold working followed by annealing at 900°C . [64Rau] also reported two distinguishable lattice parameters in alloys with up to ~ 22 at.% Pt (phase boundary) at 600 and 800°C . On the other hand, X-ray diffraction studies of 10 and 25 at.% Pt alloys by [61San] showed that the Au_3Pt , AuPt, and AuPt_3 phases materialized as metastable phases during the heating of a two-phase mixture of (Au) and (Pt). [51Gru] could not confirm the existence of

Au-Pt

Table 3 Experimental Data on the Miscibility Gap

| Composition, at.% Pt | Temperature, °C | Composition, at.% Pt | Temperature, °C | Composition, at.% Pt | Temperature, °C | Composition, at.% Pt | Temperature, °C |
|----------------------|-----------------|----------------------|-----------------|-------------------------|-----------------|-----------------------------|-----------------|
| [30Joh](a) | | [52Dar](a) | | [57Tie](b, c) | | [64Rau](b, c) | |
| 25.5 | 800 | 49.2 | 1229 | 21.2 | 510 | 21 | 600 |
| 26.4 | 820 | 50.2 | 1238 | 23.2 | 610 | 23 | 800 |
| 28.7 | 875 | 52.2 | 1244 | 25.2 | 705 | [47Wic1]; [49Wic](a) | |
| 30.2 | 916 | 58.2 | 1252 | 27.2 | 755 | 18.7 | 650 |
| 35.5 | 1025 | 59.2 | 1260 | 30.2 | 810 | 20.0 | 700 |
| 39.5 | 1060 | 60.2 | 1258 | 33.2 | 930 | 21.7 | 750 |
| 81.3 | 1060 | 62.2 | 1257 | 37.2 | 1025 | 23.0 | 800 |
| 85.0 | 1025 | 65.2 | 1248 | 89.1 | 1025 | 24.5 | 850 |
| 89.4 | 916 | 70.2 | 1243 | 92.1 | 930 | 26.5 | 900 |
| 90.8 | 875 | 72.7 | 1233 | 96 | 810 | 29.0 | 950 |
| 92.7 | 820 | [52Dar](b) | | 97 | 755 | 30.0 | 970 |
| 93.7 | 800 | 27.9 | 850 | 98 | 705 | 36 | 1080 |
| 32 | 968 | 29.1 | 900 | 98 | 610 | 39 | 1130 |
| 40 | 1080 | 33.6 | 1000 | 99 | 510 | 45 | 1190 |
| 45 | 1108 | 38.5 | 1100 | [60Mun](a, c, d) | | | |
| 50 | 1125 | 41.8 | 1150 | 35.23 | 1080 | 51 | 1220 |
| 55 | 1145 | 47.0 | 1200 | 40.24 | 1140 | 60 | 1235 |
| 65 | 1150 | 52.8 | 1225 | 45.25 | 1180 | 69 | 1210 |
| 75 | 1140 | 56.3 | 1250 | 50.25 | 1217 | 75 | 1180 |
| 85 | 1025 | 66.4 | 1250 | 55.25 | 1238 | 81 | 1115 |
| 90 | 912 | 67.9 | 1225 | 58.25 | 1250 | 84 | 1070 |
| [30Joh](b) | | 73.4 | 1200 | 61.24 | 1249 | 87 | 1005 |
| 26.8 | 800 | 79.1 | 1150 | 63.24 | 1248 | 90 | 930 |
| 93.5 | 800 | 83.3 | 1100 | 65.23 | 1242 | 91.0 | 900 |
| [31Ste]; | | 87.1 | 1000 | 67.22 | 1237 | 92.0 | 850 |
| [32Wee](b, c) | | 91.9 | 900 | 69.22 | 1226 | 93.0 | 800 |
| 25 | 680 | 93.8 | 850 | 71.21 | 1208 | 93.5 | 750 |
| 30 | 880 | [38Wic](a) | | 75.19 | 1180 | 94.5 | 700 |
| 33 | 960 | 23 | 700 | 80.16 | 1148 | 95.5 | 650 |
| 41 | 1060 | 25 | 800 | 85.13 | 1035 | | |
| 43 | 1110 | 28 | 900 | | | | |
| 81 | 1110 | 30 | 1000 | | | | |
| 85 | 1060 | 88 | 1000 | | | | |
| 91 | 960 | 91 | 900 | | | | |
| 94 | 880 | 93 | 800 | | | | |
| 97 | 680 | 95 | 700 | | | | |

(a) Resistivity measurement. (b) X-ray measurement. (c) Read from graphs. (d) Same data points in different figures show ± 5 °C error.



the AuPt and AuPt₃ superlattices. [57Tie] detected no diffraction lines from a second phase or superlattice lines in a 10.1 at.% Pt alloy. However, they found sidebands, reportedly related to either a pre-precipitation or a superlattice, in alloys containing 40.2 and 80.2 at.% Pt. Similar sidebands were observed by [67Fie] in 11.3 and 22.9 at.% Pt alloys. Field-ion microscopy work on the Au-Pt alloy series by [74Pol] indicated that an alloy of composition Au₃Pt is ordered when quenched from 950 °C and disordered when quenched from 1050 °C. These facts suggest that the existence of ordered structures (such as Au₃Pt, AuPt, or AuPt₃) is observed convincingly only in transient states, or in thin films. Crystal structures of these stoichiometric compounds are listed in Table 6.

Coherent Miscibility Gap. The coherent (metastable) miscibility gap in the solid state was observed experimentally by [68Wei] and [69Kra]. The spinodal curve associated with the coherent miscibility gap determined by [70Kra] was treated theoretically by [80Sin] (see [81Sin]).

Amorphous Phase. [78Sin1] reported the formation of an amorphous phase by implantation of Au⁻ ions into the platinum matrix.

Table 4 Experimental Data on Incoherent Spinodal

| Composition, at.% Pt | Temperature, °C | Composition, at.% Pt | Temperature, °C |
|----------------------|-----------------|----------------------|-----------------|
| [38Wie] | | [65Coo] (cont'd) | |
| 38 | 800 | 52 | 1200 |
| 41 | 900 | 69 | 1200 |
| 42 | 1000 | 74 | 1100 |
| 76 | 1000 | 78 | 1000 |
| 81 | 900 | 82 | 900 |
| 83 | 800 | 85 | 800 |
| [71Bor] (a) | | 87 | 700 |
| 36 | 800 | [78Dek2] (a) | |
| 39 | 870 | 36 | 490 |
| 45 | 1050 | 38 | 680 |
| 51 | 1110 | 41 | 830 |
| 75 | 1040 | 45 | 990 |
| 81 | 930 | 50 | 1160 |
| 84 | 850 | 55 | 1240 |
| [65Coo] (a) | | 65 | 1240 |
| 40 | 700 | 68 | 1220 |
| 41 | 800 | 71 | 1180 |
| 43 | 900 | 77 | 1050 |
| 45 | 1000 | 82 | 930 |
| 48 | 1100 | 85 | 820 |
| | | 88 | 720 |
| | | 90 | 630 |
| | | 93 | 450 |

(a) Read from graphs.

Thermodynamics

Thermodynamic Data. The only relevant experimental thermodynamic data for a phase diagram calculation were measured by [70Jon], who used a mass spectrometric method for the solid phase in the temperature range 1340 to 1520 K. The excess Gibbs energy evaluated by [Hultgren, Binary] from the data of [70Jon] and the enthalpy of mixing by [70Jon] are shown in terms of the usual function $\Delta G^{ex}/X(1 - X)$ and $\Delta H/X(1 - X)$ in Fig. 4 and 5, respectively, where X represents the atomic fraction of Pt in the alloys. The heat of formation values proposed by [71Hay] from high-temperature calorimetric measurements in ternary Au-Pd-Pt alloys suggest that

Table 5 Experimental Data on the Lattice Parameter

| Composition, at.% Pt | Lattice parameter, nm | Composition, at.% Pt | Lattice parameter, nm |
|----------------------|-----------------------|----------------------|-----------------------|
| [30Joh](a) | | [51Gru](cont'd) | |
| 0 | 0.4077 | 40 | 0.40121 |
| 8 | 0.4062 | 50 | 0.39969 |
| 16 | 0.4051 | 70 | 0.39669 |
| 25 | 0.4039 | 75 | 0.39587 |
| 32 | 0.4029 | 80 | 0.39527 |
| 40 | 0.4017 | 90 | 0.39376 |
| 45 | 0.4006 | 95 | 0.39292 |
| 50 | 0.4003 | 100 | 0.39236 |
| 65 | 0.3976 | [67Car] | |
| 75 | 0.3966 | 39.65 | 0.4015 |
| 85 | 0.3946 | 60.78 | 0.3980 |
| 90 | 0.3938 | 80.15 | 0.3954 |
| 96 | 0.3929 | [52Dar] | |
| 100 | 0.3922 | 20.2 | 0.40416 |
| [55Rau] | | 30.2 | 0.40280 |
| 50.3 | 0.4001 | 35.2 | 0.40201 |
| [51Gru](a) | | 40.2 | 0.40119 |
| 0 | 0.40783 | 45.2 | 0.40026 |
| 5 | 0.40706 | 50.2 | 0.39963 |
| 10 | 0.40594 | 51.2 | 0.39950 |
| 15 | 0.40515 | 52.2 | 0.39967 |
| 20 | 0.40442 | 53.2 | 0.39916 |
| 22.5 | 0.40381 | 54.2 | 0.39923 |
| 25 | 0.40353 | 56.2 | 0.39941 |
| 26.7 | 0.40321 | 58.2 | 0.39980 |
| 28.4 | 0.40295 | 65.2 | 0.39700 |
| 30 | 0.40279 | 70.2 | 0.39685 |
| 35 | 0.40216 | 75.2 | 0.39590 |
| | | 77.7 | 0.39543 |
| | | 80.2 | 0.39595 |
| | | 90.1 | 0.39389 |

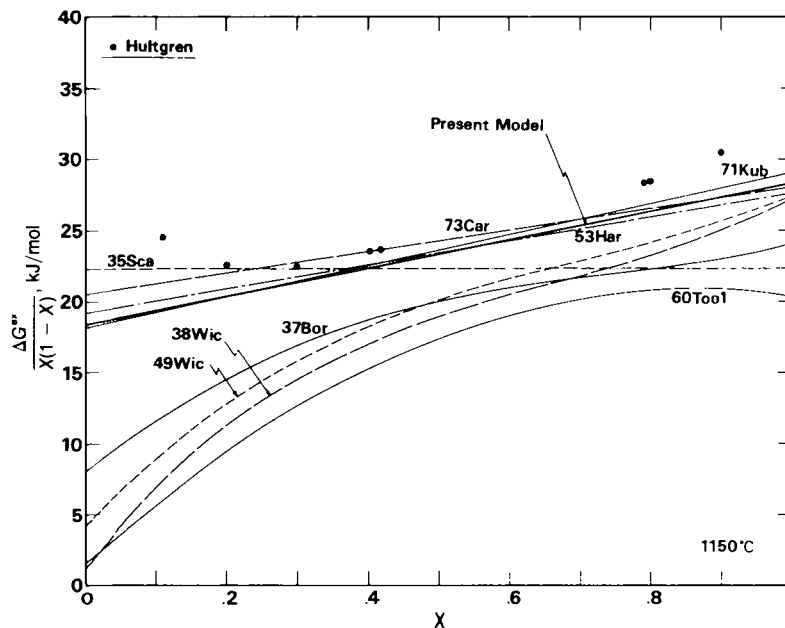
(a) Although the original data are given in 10⁻⁸ cm, it is likely to be in kX units. A factor of 0.100202 was used to convert to nanometers.

Table 6 Au-Pt Crystal Structure and Lattice Parameter Data

| Phase | Composition range(a), at.% Pt | Prototype | Lattice parameters, nm | | Comment | Reference |
|--------------------------|-------------------------------|-------------------------|--------------------------------------|--------|---|-----------|
| | | | a | c | | |
| Metastable phases | | | | | | |
| Au ₃ Pt | 5 to 40 | AuCu ₃ -type | 0.3880 0.3901 0.3926 0.3928 | ... | 5 at.% Pt 15 at.% Pt 25 at.% Pt 35 at.% Pt | [51Gru] |
| AuPt | 50 | ... | 0.3920 | 0.3900 | (b) | [61San] |
| AuPt ₃ | 75 | ... | 0.3920 | ... | ... | [61San] |

(a) From the phase diagram. (b) Tetragonal.

Fig. 4 Comparison of Composition Dependence of $\Delta G^{ex}/X(1 - X)$ at 1150 °C



X is the atomic fraction of Pt.

H. Okamoto and T. B. Massalski, 1985.

the binary Au-Pt section should follow the relationship $\Delta H = X(1 - X)(23\,860 - 11\,930X)$ J/mol. This form is rather difficult to accept (see Fig. 5). The ΔH value deduced from short-range order coefficients by [76Mac] is also shown in Fig. 5.

No data are available for the liquid phase.

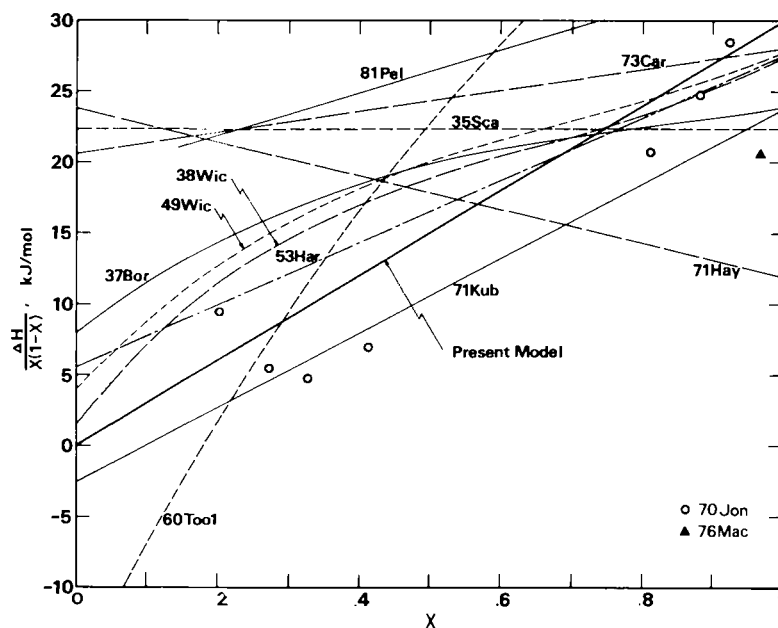
Earlier Thermodynamic Evaluations. Because the Au-Pt system is associated with a typical phase diagram involving both a continuous solubility in the solid phase and a miscibility gap in the same phase at lower temperatures, many models have been proposed in the process of developing suitable thermodynamic approaches to phase diagram calculations [34Sel, 35Sca, 35Sel, 37Bor, 38Wic, 49Wic, 52Har, 53Har, 58Wei, 60Too1, 71Kub, 73Car, 79Mul, 79Sch, 80Mie, 80Ovc, 81Pel]. The proposed thermodynamic functions for both liquid and solid phases are summarized in Table 7 in terms of the enthalpy and excess entropy of mixing. Most of the modeled functions were derived from experimental phase boundaries. [58Wei] attempted to explain the asymmetry of the miscibility gap on the basis of electronic and lattice specific heats. However, [61Mei] noted that the model by [58Wei] is incorrect. Although the Gibbs energy function of [60Too1] gives reasonable forms of phase boundaries and spinodal curves, [65Def] found a calculation error in the original paper. A seemingly correct set of coefficients resulted in an unacceptable form of the Gibbs energy curve. A model for the solid phase by [71Kub] was derived from the thermodynamic data of [70Jon]. The Gibbs energy function calculated by [79Mul] from a nearest-neighbor interaction model failed to reproduce the miscibility gap. [79Sch] estimated the contributions to the excess Gibbs energy of the solid phase by separating them into an electronic part and a lattice distortion part and obtained the following expression:

$$\begin{aligned} \Delta G_{Au}^{ex} - \Delta G_{Pt}^{ex} = & -6w + 12RT \\ & \ln \{2X/(1 - 2(1 - X)T\beta)\} \\ & + K_1(1 - X) \\ & + K_2(1 - X)^2 + K_3(1 - X)^3 \end{aligned}$$

where $w = -5.53$ kJ/mol, $\beta = [1 - 4X(1 - X)(1 - \exp(-w/RT))]^{1/2}$, $K_1 = 4.0$ kJ/mol, $K_2 = -9.3$ kJ/mol, $K_3 = 22.7$ kJ/mol. [80Ovc] introduced the effect of short-range order into a model Gibbs energy function. However, the resulting phase diagram is of a peritectic form. The semiempirical model for the liquid phase proposed by [80Mie] suggests that the deviation from the regular solution is not significant. [81Pel] also suggested that the liquid phase is approximately regular. Modeled ΔG^{ex} functions for the solid phase at 1150 °C by [35Sca], [37Bor], [38Wic], [49Wic], [53Har], [60Too1], [71Kub], [71Hay], [73Car], and [81Pel] (from graph) together with the experimentally determined values by [70Jon] and the estimated value of [76Mac] from short-range order coefficients are shown in Fig. 5.

Present Thermodynamic Evaluation of the Phase Diagram. The lattice stability parameters given in Table 7 for pure Au and Pt were derived from the heats of transformation [83Cha] at the melting point ($\Delta H(Au) = 13\,000$ J/mol, $\Delta H(Pt) = 19\,650$ J/mol) and by assuming $\Delta C_p = 0$ for both components. Because of the lack of experimental basis for the thermodynamic modeling, only simple expressions for the excess Gibbs energy function

Fig. 5 Comparison of Composition Dependence of $\Delta H/X(1 - X)$



X is the atomic fraction of Pt.

H. Okamoto and T. B. Massalski, 1985.

Table 7 Thermodynamic Functions for the Liquid and Solid Phases

| Reference | Enthalpy of mixing, $\left(\frac{\Delta H}{X(1-X)}\right), \text{J/mol}$ | Excess entropy of mixing, $\left(\frac{\Delta S^{ex}}{X(1-X)}\right), \text{J/mol}\cdot\text{K}$ |
|-----------------------|---|--|
| Liquid phase | | |
| [35Sca]..... | 22 096 | 0 |
| [73Car]..... | 24 560 - 368 X | 0 |
| [80Mie]..... | 17 000 + 1 000 X | ... |
| [80Pel]..... | 5 200 | ~0 |
| Present model..... | 23 500 + 4 000 X | 0 |
| Solid phase | | |
| [35Sca]..... | 22 270 | 0 |
| [37Bol]..... | 7 900 + 40 320 X - 40 320 X ² + 16 210 X ³ | 0 |
| [38Wic]..... | 1 372 + 62 560 X - 71 870 X ² + 35 290 X ³ | 0 |
| [49Wic]..... | 3 949 + 55 040 X - 60 650 X ² + 29 510 X ³ | 0 |
| [53Har]..... | 5 523 + 22 092 X | - 9.73 + 9.73 X |
| [60Too1]..... | -16 608 + 98 296 X - 39 296 X ² | -12.739 + 37.626 X - 9.4331 X ² |
| [71Hay]..... | 28 360 - 11 930 X | ... |
| [71Kub]..... | -2 653 + 26 464 X | -14.64 + 10.88 X |
| [73Car]..... | 20 640 + 7 372 X | 0 |
| Present model..... | 30 000 X | -13.00 + 14.183 X |

Note: X is atomic fraction of Pt. ΔH and ΔS^{ex} were assumed to have no temperature dependence.

Lattice stability parameters, J/mol

$$G_1^0(\text{Au}) = 0$$

$$G_1^0(\text{Pt}) = 0$$

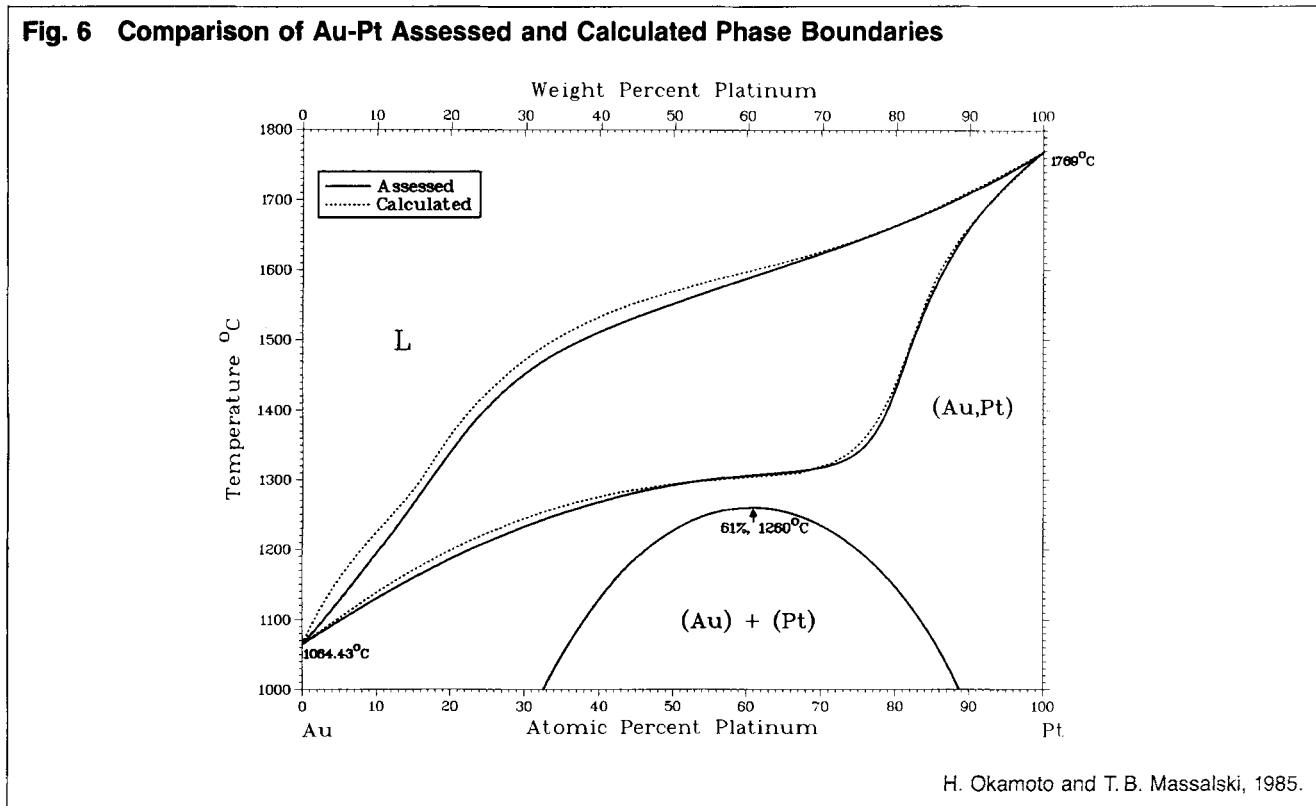
$$G_2^0(\text{Au}) = -13\,000 + 9.7190 T$$

$$G_2^0(\text{Pt}) = -19\,650 + 9.6224 T$$

have been assumed here in the form $\Delta G_s^{ex} = X(1 - X) \cdot (A + BX - (C + DX)/T)$ for the solid phase and $\Delta G_L^{ex} = X(1 - X)(E + FX)$ for the liquid phase.

It appears that the Au-rich side of the miscibility gap boundary goes through $X = 0$, or intersects the composition axis at a slightly positive side when the temperature, T , is extended to 0 K. Therefore, the $\Delta H/X(1 - X)$ function is likely to be zero or negative at $X = 0$. Only the models by [60Too1] and [71Kub] satisfy this condition. The model by [71Kub] shows a narrow miscibility gap and the critical point at a temperature that is too high. The ΔH function by [60Too1] (Fig. 5) appears to be changing too rapidly with composition. It was assumed in the present model that $\Delta H/X(1 - X)$ is 0 at $X = 0$. The term linear with the composition in the $\Delta H/X(1 - X)$ function was taken to be $30X$ kJ/mol for the best fitting by trial and error. The excess entropy term can be calculated from the critical point of the miscibility gap. The expressions derived in the present model are given in Table 7, and Fig. 4 and 5. The parameters for the liquid phase assumed in the present model are also given in Table 7.

The calculated phase boundaries (Fig. 6) are within the experimental uncertainty limits except for a part of the liquidus near 10 at.% Pt. The calculated liquidus shows an unusual depression at about 15 at.% Pt (Fig. 6). This reflects the existence of the miscibility gap that nearly touches the solidus. (The presently assessed critical temperature is only 40 °C below the solidus.) If the solidus and the miscibility boundary actually touched to involve a peritectic reaction, the depression at 15 at.% Pt would develop into two separate branches of the liquidus having different slopes above and below the peritectic temperature. The experimental data show no clear sign of the calculated depression, but it is considered that this effect



is real. Very careful work in this composition range should be able to demonstrate this.

Suggestions for Future Experimental Research

In the opinion of the present evaluators, the following features of the Au-Pt phase diagram may be considered to be tentative, or in need of future research:

- Both liquidus and solidus curves need reexamination because of substantial scatter (Fig. 1). No two reports in the literature are alike in detail.
- The possibility that a stable Au₃Pt phase exists should be explored further experimentally.
- Thermodynamic data for this system are scarce. More information would be beneficial as an aid in accurate calculation of phase boundaries.

The Au-Pt system, as contributed in a short version by S. P. Singhal, was published in provisional form in the *Bulletin* [81Sin]. The present evaluation reviews all bibliography and data on the Au-Pt system available in the literature through 1982 and includes information pertaining to the crystal structures, metastable phases, and thermodynamics. The present authors have also performed a thermodynamic assessment of certain phase boundaries. The present evaluation may be considered as superseding the earlier work.

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*Indicates key paper.

#Indicates presence of a phase diagram.

Au-Pt evaluation contributed by H. Okamoto and T.B. Massalski, Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213, USA. Work was supported by the International Gold Corporation Limited (InterGold) and American Society for Metals (ASM). Literature searched through 1983. Part of the bibliographic search was provided by ASM. Professor Massalski is the ASM/NBS Data Program Editor-in-Chief for the Binary Alloys, and also Category Editor for binary gold alloys, jointly with Dr. Okamoto.

The Mg-Pb (Magnesium-Lead) System

24.305

207.2

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Equilibrium Diagram

The equilibrium phase diagram of the Mg-Pb system was determined by several investigators [05Gru, 05Kur, 65Dob, 65Eld]. The general characteristics of the Mg-Pb equilibrium diagram as given in [Hansen] are well established and agreed upon. The equilibrium diagram of the Mg-Pb system modified by the work of [65Eld], which also has appeared in compilations of [Shunk], [Metals Handbook], and [Hultgren, Binary], has not been unequivocally confirmed. (See "Liquidus".)

The assessed equilibrium Mg-Pb phase diagram shown in Fig. 1 includes: (1) L, the liquid; (2) (Mg), the terminal

Mg solid solution with a maximum solid solubility of 7.75 at.% Pb (41.73 wt.% Pb); (3) Mg₂Pb, the stoichiometric intermetallic compound with a cubic antiferrofluoride structure; (4) (Pb), the terminal Pb solid solution with a maximum solid solubility of 6 at.% Mg (94 at.% Pb); and (5) two eutectic reactions, one at 19.1 at.% Pb and one at 83 at.% Pb. (See Table 1.)

Figure 2 shows the data for the liquidus, solidus, and the solvus boundaries taken from the ten principal studies of the system, along with the calculated boundaries.

Liquidus. The first thermal analysis of Mg-Pb alloys was done by measuring the effect of Mg on the freezing point of

