

The Ca-Pb (Calcium-Lead) System

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Equilibrium Diagram

The assessed Ca-Pb phase diagram (Fig. 1) consists of: (1) the liquid, L; (2) the fcc solid solution, (Pb), with a solid solubility of ~ 0.36 at.% Ca at the eutectic temperature; (3) the solid solutions, (α Ca) and (β Ca), with negligibly small solubility of Pb; (4) two intermediate compounds, Ca₂Pb and CaPb₃, which melt congruently; and (5) two compounds, CaPb and Ca₅Pb₃, which are formed by peritectic reactions. Table 1 lists the invariant reactions.

Liquidus

The first complete Ca-Pb phase diagram was based on investigations by [08Don] and [11Baa] that were made by thermal and microscopic analysis. The experimental points are shown in Fig. 1. [08Don] studied nine alloys with 58.8 to 100 at.% Pb and found a congruently melting CaPb₃ compound and two eutectics—one between Pb and CaPb₃ at ~ 331 °C and one between CaPb₃ and an unknown compound at 625 °C and 65 at.% Pb. [11Baa] investigated 12 alloys containing less than 57.6 at.% Pb and found two more compounds—Ca₂Pb, which melts congruently, and CaPb, which is formed by a peritectic reaction. Two eutectic reactions were found between Ca and Ca₂Pb at 700 °C and 77 at.% Pb, and between CaPb and CaPb₃ at 634 °C and 64 at.% Pb. However, the materials used by [08Don] and [11Baa] were impure. The melting point of Ca was determined in [11Baa] as 808 °C, whereas the assessed melting temperature of β Ca is 842 °C [Melt]. Also, methods of alloy preparation were poor; for example, [11Baa] used a hydrogen atmosphere to prevent Ca from oxidizing, but this atmosphere can convert Ca into a hydride.

A number of liquidus points were added later to the Pb-rich side. [21Cow] contributed two points at 93 and 90.5 at.% Pb, [30Sch] reported seven points for alloys with more than 95 at.% Pb, [62Fed] gave one point at 0.82 at.% Ca, and [63Lan] determined seven points for alloys with > 77 at.% Pb (Fig. 1). [31Syr] found the position of the CaPb-CaPb₃ eutectic at 630 °C and 65.6 at.% Pb.

[76Bru] investigated the total system by X-ray, metallographic, and thermal analyses. The samples of alloys were prepared under an argon atmosphere in iron or pythagoras crucibles from 99.9 wt.% Ca and 99.999 wt.% Pb. The results of the thermal analyses made in [76Bru] are shown in Fig. 1. Four intermetallic compounds were described in [76Bru]—CaPb₃, Ca₂Pb, CaPb, and Ca₅Pb₃. Two eutectics were confirmed by [76Bru], one between (β Ca) and Ca₂Pb at

750 °C and 9.5 at.% Pb and one between CaPb and CaPb₃ at 638 °C and 63.5 at.% Pb.

[84Bou] and [89Not] measured the enthalpy of mixing of alloys > 50 at.% Pb in a Calvet calorimeter at 637 to 767 °C. The calorimeter was also used for thermal analysis. The alloys were prepared from 99.97 wt.% Pb and 99.5 wt.% Ca in iron crucibles. An attempt to analyze the alloys by X-ray powder diffraction could not be completed because an unknown phase was shown to be present in most photographs [84Bou]. This phase was described in [89Not] as an oxide phase that was formed during X-ray measurements.

According to the enthalpy measurements made at 637 °C, the Ca partial enthalpy, H_{Ca} , deviated from a constant value between 69.7 ± 0.2 and 79.7 ± 2 at.% Pb; these deviations were suggested as indicative of the liquidus. Similarly, liquidus points were found at 77.8 ± 2 at.% Pb at 646 °C and at 767 ± 0.2 at.% Pb. Thermal analyses were used to determine the melting point of CaPb₃, the temperature of the CaPb + CaPb₃ eutectic at 625 °C, and the existence of an ambiguous reaction on the Pb-rich side (see below).

L \leftrightarrow (Pb) + CaPb₃ Eutectic Reaction

Pb-rich alloys with > 95 at.% Pb were investigated by [30Sch] with thermal and microscopic analyses and with measurements of electrical conductivity and mechanical properties after different treatments. [30Sch] found a peritectic reaction with formation of (Pb) at ~ 328 °C. At this temperature, the solubility of Ca was 0.36 at.% in liquid alloy and 0.51 at.% in solid (Pb). This solid solubility decreased gradually to ~ 0.05 at.% Ca at 25 °C (Fig. 2).

[59Vig] investigated Pb-rich alloys by thermal and microscopic analysis and microhardness measurements. After zone recrystallization of a sample containing 99.59 at.% Pb, the microhardness and Ca content decreased in the leading sections and increased in the tailing regions of the specimen. This fact was interpreted by [59Vig] as evidence of a eutectic reaction rather than a peritectic reaction. The DTA cooling curves of alloys with 93.1, 94.1, and 99.54 at.% Pb showed that the invariant transformation occurred 1.3 °C below the melting point of Pb. The eutectic position was suggested at 99.59 at.% Pb. The solubility of Ca in (Pb) was measured in [59Vig] at 50, 150, 200, 250, and 300 °C. The results, shown in Fig. 2, agree satisfactorily with the data of [30Sch]. At 326.2 °C, the maximum solubility at ~ 0.36 at.% Ca was estimated by an extrapolation [59Vig].

The methods used in [76Bru] were not sufficiently accurate to resolve the disagreement between [30Sch] and [59Vig]

with regard to the eutectic coordinates. The eutectic reaction was confirmed in [84Bou], where its temperature was given as 327 °C. [89Not] attempted to clarify the discussed reaction. A 99.31 at.% Pb specimen was prepared from pure components: 99.999 wt.% Pb and 99.97 wt.% Ca. The difference between the thermograms of pure Pb and the alloy was interpreted in [89Not] as evidence of a peritectic reaction in the

system. However such an explanation is not the only possible one; the same illustration in [89Not] can be interpreted to show the melting of a hypereutectic alloy. Therefore the results of [89Not] did not solve the problem.

In the present assessment, preference is given to results of [59Vig]. The nature of the reaction (eutectic), its temperature

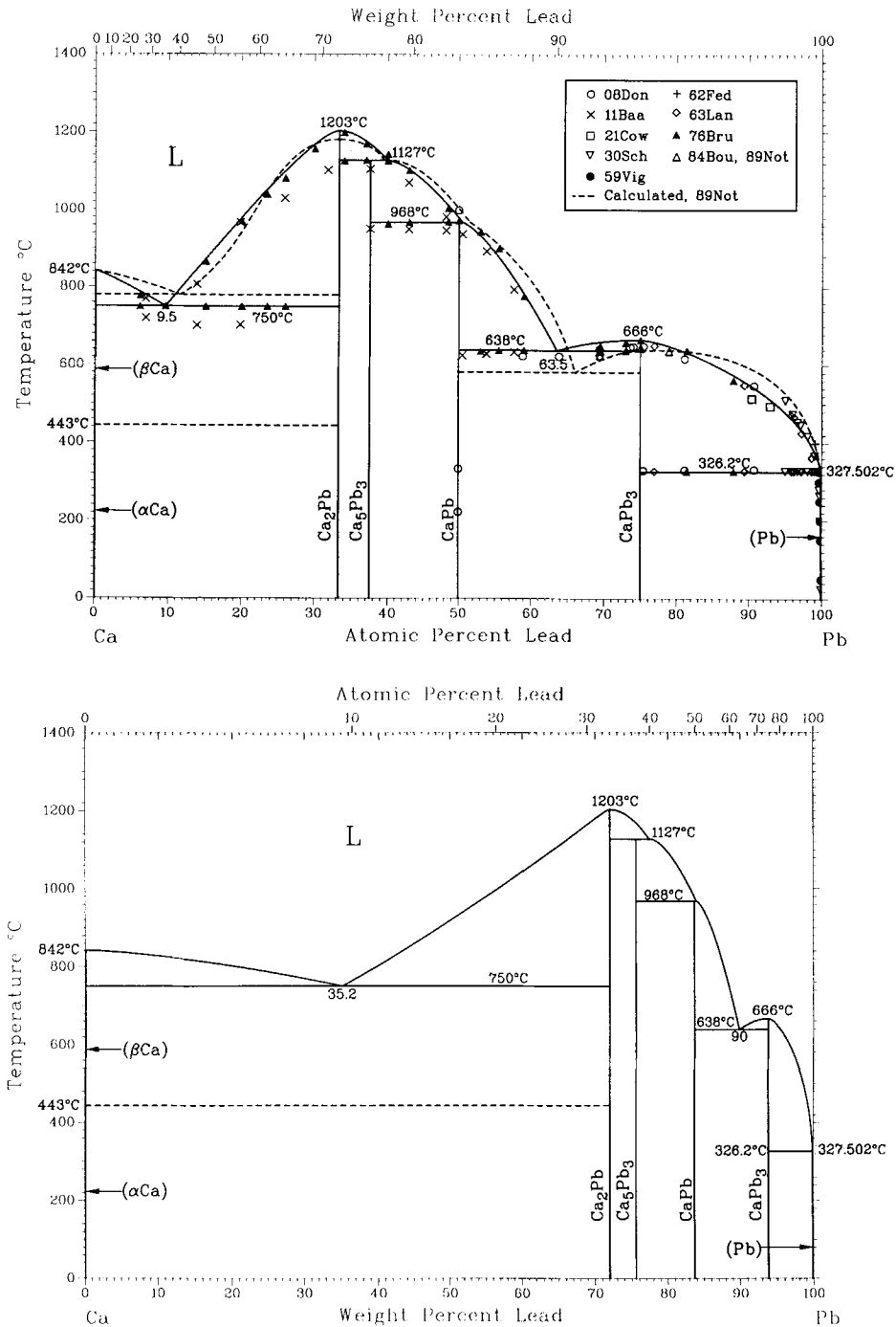


Fig. 1 Assessed Ca-Pb phase diagram.

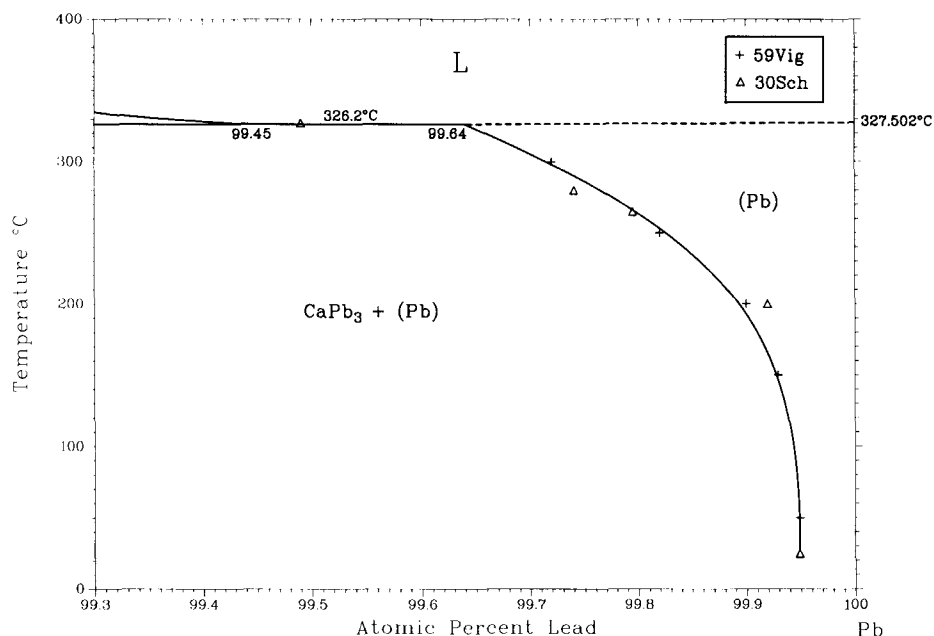


Fig. 2 Pb-rich region of the Ca-Pb phase diagram.

(326.2 °C), and maximum solubility of Ca in (Pb) are accepted from [59Vig]. However, the eutectic composition suggested by [59Vig] is probably not accurate. The present authors estimate 99.45 at.% Pb, assuming ideal dilute solutions of Ca in (Pb) and using 4770 J/mol for the enthalpy of fusion of Pb [85Cha]. This value is lower than that given in [59Vig] and [30Sch]. [63Lan] suggested this point at 99.23 at.% Pb. Therefore, the eutectic reaction shown in Fig. 3 needs further investigation.

[52Fal] measured the lattice parameter of (Pb) after rapid cooling of melts at different compositions. The parameter decreased from 0.49500 nm for pure Pb to 0.49485 nm for an alloy with 99 at.% Pb. The experiment showed that supersaturated (Pb) solid solutions can be obtained in which the Ca concentration is nearly triple the equilibrium value.

The solubilities of Pb in the terminal solid Ca solutions, (α Ca) and (β Ca), are assumed to be very small, because the lattice parameter of Ca does not change for Ca-rich specimens [76Bru].

Intermetallic Compounds

Several intermediate compounds were reported in the system— Ca_3Pb [63Hel], Ca_2Pb [11Baa, 61Eck, 76Bru], Ca_5Pb_3 [63Hel, 76Bru], CaPb [11Baa, 31Syr, 76Bru], Ca_2Pb_3 [06Hac, 25Kra], and CaPb_3 [08Don, 31Syr, 33Zin1, 76Bru].

Ca_3Pb , a compound with a cubic AuCu_3 -type structure and $a = 0.4853$ nm (powder method) was extracted from an alloy with 20 at.% Pb by [63Hel]. However, [76Bru] disputed its existence. Samples of the composition corresponding to Ca_3Pb were prepared by [76Bru] by sintering at low temperatures and by melting and annealing at different temperatures. All the specimens contained more than one phase. To achieve equilibrium composition, the Ca-rich alloys need a prolonged annealing at high temperatures. If this condition is not satisfied, a thermal arrest near 670 °C is observed on the cooling curves in [76Bru]. This corresponds to the melting point of the CaPb_3 phase and implies a high degree of inhomogeneity in the sample. The finding of [76Bru] suggests that single crystals of Ca_3Pb isolated by [63Hel] were actually of the CaPb_3 phase.

The compound Ca_2Pb melts congruently at 1105 °C, according to [11Baa], who also reported its homogeneity range at 700 °C to extend from 22.5 to 33.3 at.% Pb. [67Mur] deduced from vapor pressure measurements that this compound dissolves at least 4 at.% Pb at 650 to 850 °C. [76Bru] did not find any evidence of a solubility range for Ca_2Pb and determined its melting point as 1203 °C. This result was accepted as the most reliable.

[63Hel] determined the structure of Ca_5Pb_3 . Its existence was confirmed by the thermal and structural analyses of [76Bru], who determined the compound to form by a peritectic reaction at 1127 °C. CaPb is also formed by a peritectic re-

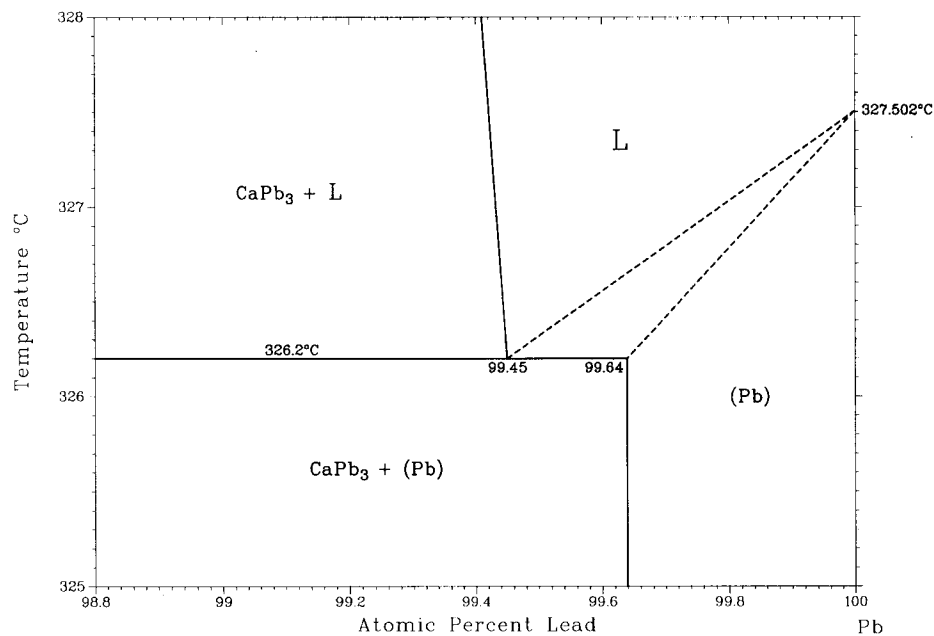


Fig. 3 Detail of the Pb-rich Ca-Pb eutectic.

Table 1 Special Points of the Assessed Ca-Pb Phase Diagram

Reaction	Composition of the respective phases, at. % Pb			Temperature, °C	Reaction type	Reference
L ↔ βCa.....	0			842	Melting	[Melt]
βCa ↔ αCa.....	0			443	Allotropic	[85Cha]
L ↔ (βCa) + Ca ₂ Pb.....	9.5	0	33.3	750	Eutectic	[76Bru]
L ↔ Ca ₂ Pb.....	33.3			1203	Congruent	[76Bru]
L + Ca ₂ Pb ↔ Ca ₅ Pb ₃	~ 40	33.3	37.5	1127	Peritectic	[76Bru]
L + Ca ₅ Pb ₃ ↔ CaPb.....	~ 50.5	37.5	50	968	Peritectic	[76Bru]
L ↔ CaPb + CaPb ₃	63.5	50	75	638	Eutectic	[76Bru]
L ↔ CaPb ₃	75			666	Melting	[76Bru]
L ↔ CaPb ₃ + (Pb).....	~ 99.45(a)	75	~ 99.66	326.2	Eutectic	[59Vig]
L ↔ Pb.....	0			327.502	Melting	[Melt]

(a) Estimated concentration.

Table 2 Ca-Pb Crystal Structure Data

Phase	Composition, at. % Pb	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
βCa (a).....	0	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W	[King2]
αCa (b).....	0	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	[Massalski2]
Ca ₂ Pb.....	33.3	<i>oP12</i>	<i>Pnma</i>	C23	Co ₂ Si	[61Eck]
Ca ₅ Pb ₃	37.5	<i>hP48</i>	<i>P6</i> ₃ <i>mc</i>	...	Ca ₅ Pb ₃	[63Hel]
CaPb.....	50	<i>tP4</i>	<i>P4/mmm</i>	L1 ₀	AuCu	[76Bru]
CaPb ₃	75	<i>cP4</i>	<i>Pm</i> $\bar{3}m$	L1 ₂	AuCu ₃	[33Zin1]
(Pb).....	99.66 to 100	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	[Massalski2]

(a) From 842 to 443 °C. (b) Below 443 °C.

Table 3 Ca-Pb Lattice Parameter Data

Phase	Composition, at.% Pb	Lattice parameters, nm			Comment	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
βCa	0	0.4480	Pure Ca	[King2]
αCa	0	0.55884	Pure Ca	[King1]
Ca ₂ Pb	33.3	0.8072	0.5100	0.9647	...	[61Eck]
Ca ₅ Pb ₃	37.5	1.623	...	0.704	...	[63Hel]
CaPb	50	0.5118	...	0.4491	...	[76Bru]
CaPb ₃	75	0.4897	[76Bru]
Pb	100	0.49502	Pure Pb	[King1]

action at 950 °C, according to [11Baa]. [76Bru] quoted a higher temperature, 968 °C, which is adopted in this assessment. The compound Ca₂Pb₃ assumed by [06Hac] and [25Kra] was not confirmed in subsequent publications.

According to [08Don], CaPb₃ melts congruently at ~ 650 °C and has a homogeneity range from 72.5 to 75 at.% Pb. In [31Syr], the melting point was given as 670 °C. No evidence of this homogeneity range was observed in [76Bru]. The melting point was determined as 666 °C by [76Bru].

[84Bou] and [89Not] determined the melting point of CaPb₃ (647 ± 2 °C) and the positions of the liquidus and the CaPb + CaPb₃ eutectic in the vicinity of the melting point of CaPb₃. These values may be better than [76Bru]; however, the almost twenty-degree difference between the melting point of CaPb₃ given in [31Syr] and [76Bru] suggests that an additional independent investigation should be made. The present authors selected for CaPb₃ the results of [76Bru] mostly because this study determined the liquidus for the total system.

[84Bou] and [89Not] also measured the enthalpy of fusion of CaPb₃ as 11.6 kJ/mol of atoms. [73Dam] measured the critical temperature of superconductivity in CaPb₃, which was ~ 0.8 K.

The assessed phase diagram (Fig. 1) is based mainly on the results of [76Bru]. Two fields in this diagram disagree with recent studies [84Bou, 89Not]—a region near the melting point of CaPb₃ and the eutectic reaction at the Pb-rich side. The position of the liquidus in these two areas require further investigation.

Crystal Structures and Lattice Parameters

Ca-Pb crystal structures and lattice parameters data are given in Tables 2 and 3, respectively.

Ca₂Pb

[61Eck] showed that Ca₂Pb has an orthorhombic structure of the PbCl₂ type, similar to Ca₂Si and Ca₂Ge. The compound has parameters $a = 0.8072 \pm 0.0004$, $b = 0.5100 \pm 0.0003$, and $c = 0.9647 \pm 0.0004$ nm. The lattice parameters given in [76Bru] $a = 0.8035$, $b = 0.5067$, and $c = 0.9617$ nm, agree with [61Eck]. However, [76Bru] (powder data) chose a different prototype, Co₂Si, for Ca₂Pb.

Ca₅Pb₃

Single crystals containing 38.6 at.% Pb were extracted from an alloy with 38.5 at.% Pb [63Hel]. Powder photographs of the crystals showed a basic cell with hexagonal structure and parameters $a = 0.937 \pm 0.001$ and $c = 0.704 \pm 0.006$ nm. The Weissenberg method was used to determine the space group $P6_3/mcm$ of the Mn₅Si₃ type; the *R* value was calculated as 0.14. [63Hel] observed weak superstructure reflections in Weissenberg photographs. These reflections were indexed by assuming a more complex unit cell of the space group $P6_3/mc$ constructed from three basic cells in combination with small atom displacement; lattice parameters of the supercell were determined as $a = 1.623 \pm 0.002$ and $c = 0.704 \pm 0.006$ nm. The *R* value for this cell as calculated as 0.18. The structure of subcell with parameters $a = 0.9355$ and $c = 0.7004$ nm was confirmed in [76Bru] by the powder method. In this assessment, a special structure was attributed to Ca₅Pb₃ in agreement with [63Hel]. [Pearson3] included two Ca₅Pb₃ records: for the cell [63Hel] and for the subcell [76Bru], [82Bru] quoted from [63Hel].

CaPb

Earlier attempts to identify the structure of CaPb were not successful [33Zin2, 49Ian]. [76Bru] interpreted powder photographs of CaPb as indicating a AuCu-type structure.

CaPb₃

[33Zin1] investigated the structure of CaPb₃ by a powder method. This compound has the cubic structure of the AuCu₃ type and a lattice parameter of 0.4901 nm. A parameter of 0.4897 nm, obtained by [76Bru], agrees well with [33Zin1] and was selected for Table 3.

Thermodynamics

Enthalpy Measurements

[39Kub] measured the enthalpies of formation of solid Ca-Pb alloys from solid components by direct reaction calorimetry at ~600 °C. The maximum value, -68.2 kJ/mol of atoms, was observed at the composition Ca₂Pb. The dependence of the enthalpy of formation as a function of concentration undergoes a change of slope near the composition of CaPb that corresponds to the value of -52.3 kJ/mol of atoms. Two more values can be obtained from [39Kub] -26.8 kJ/mol of atoms for CaPb₃ and -61.5 kJ/mol of atoms for Ca₅Pb₃. In a later compilation, [48Kub] reported corrected values for Ca₂Pb

and CaPb -72.0 ± 4.2 and -59.8 ± 4.2 kJ/mol of atoms, respectively.

[62Shc] obtained the value of -135 ± 1.5 kJ/mol of atoms for the enthalpy of formation of Ca₂Pb. This result cannot be very accurate because it represents a small difference between two large values for heats of dissolution of the compound and components in HCl. The value of [62Shc] exceeds that of [48Kub] by a factor of almost two.

[84Bou] and [89Not] measured the enthalpy of mixing by two methods. Direct calorimetry was carried out by gradual addition of small amounts of solid Ca to a liquid-lead bath. The Ca concentration of the bath, therefore, increases with each succeeding experiment. The measured heat effects could be interpreted as the Ca partial enthalpy of solution in liquid alloys, H_{Ca} . According to [89Not] at 637 °C, H_{Ca} was constant, -100 kJ/mol, from 80 to 100 at.% Pb. Between ~ 70 and 80 at.% Pb, deviations were observed due to precipita-

tion and dissolution of CaPb₃. The values obtained in this concentration range yielded the enthalpies of formation of CaPb₃ from β Ca and liquid Pb, -35 ± 0.3 kJ/mol of atoms. Similar experiments at 763 °C gave the enthalpy of formation of CaPb, $\Delta_f H = -57 \pm 2$ kJ/mol of atoms. This value is in fair agreement with [48Kub].

Figure 1 shows that, at 637 °C, alloys with < 64 at.% Pb consist of two phases, L and CaPb. In the range 64 to 50 at.% Pb, the H_{Ca} values should remain constant or even decrease due to the exothermal precipitation of CaPb. However an H_{Ca} vs composition graph, given in [89Not], shows at 637 °C an increase in H_{Ca} from -100 to -30 kJ/mol when the Pb content falls from 70 to 57 at.% Pb. This observation contradicts both Fig. 1 and statement by [89Not] that H_{Ca} is constant between 60 and 100 at.% Pb. This discrepancy makes studies by [84Bou and 89Not] less reliable and indicates the necessity of further investigation of the enthalpy of mixing.

Indirect calorimetry was performed by dissolving alloys and corresponding components separate in pure liquid Pb; the difference yields the integral enthalpy of formation of the alloy. The enthalpies of formation of compounds determined by indirect calorimetry are less accurate than the results from direct calorimetry. For CaPb₃, CaPb, Ca₅Pb₃, and Ca₂Pb the rounded values of $\Delta_f H$ at 300 K were recommended in [89Not] as -34.0 ± 0.5 , -52 ± 5 , -56 ± 5 , and -59 ± 5 kJ/mol of atoms, respectively.

Activity Measurements

[67Mur] determined the vapor pressures of components over five alloys with 10.7 to 54.4 at.% Pb in the temperature range from 465 to 890 °C by an effusion method with an analysis of the condensates. Below 750 °C, the composition 29.2 at.% Pb is within the two-phase region, (β Ca) + Ca₂Pb, and the Ca vapor pressure above such a specimen must be close to that of pure Ca. However, the experiment of [67Mur] gave smaller pressure values by almost three orders of magnitude. Using the vapor pressure measurements, [67Mur] found a substantial homogeneity range of > 4 at.% for Ca₂Pb. This result was not confirmed in [76Bru]. There are other discrepancies (for example, improbable values of Pb activities calculated from the data for an alloy with 54.4 at.% Pb) that caused the present authors to conclude that [67Mur] is an inaccurate study and its results cannot be recommended for thermodynamic calculations.

[79Del] measured Ca activities at 800 °C in liquid alloys containing > 60 at.% Pb by an emf method using a solid CaF₂ electrolyte and coulometric titration. Table 4 gives the results of measurements. The activities of Ca measured in [79Del] were used to obtain an expression for the excess Gibbs energy of mixing of liquid alloys from liquid components by regression analysis:

$$\Delta_{\text{mix}} G^{\text{ex}} = X_{\text{Ca}} X_{\text{Pb}} \left[-174\,540 - 90\,870 (X_{\text{Ca}} - X_{\text{Pb}}) - 33\,020 (X_{\text{Ca}} - X_{\text{Pb}})^2 - 7370 (X_{\text{Ca}} - X_{\text{Pb}})^3 \right] \text{ J/mol of atoms}$$

The above equation is valid at 800 °C from 60 to 100 at.% Pb. The Pb activities calculated from Eq 1 are given in Table 4.

Table 4 Ca and Pb Activities in Liquid Ca-Pb Alloys at 800 °C

Composition, at.% Pb	Ca activity (measured)	Pb activity (calculated)
60.....	5.3×10^{-5}	0.192
65.....	2.6×10^{-5}	0.304
70.....	1.3×10^{-5}	0.431
75.....	5.9×10^{-6}	0.560
80.....	3.1×10^{-6}	0.681
85.....	1.6×10^{-6}	0.786
90.....	7.8×10^{-7}	0.874
95.....	3.0×10^{-7}	0.944
98.....	9.9×10^{-8}	0.979

Note: Standard states, liquid Ca and Pb. From [79Del].

Table 5 Thermodynamic Quantities for the Ca-Pb System

Gibbs energies of the components

$$G^0(\text{Ca, L}) = + 8540 - 7.659T$$

$$G^0(\text{Pb, L}) = 0$$

$$G^0(\text{Ca, bcc}) = 0$$

$$G^0(\text{Ca, fcc}) = -840 + 1.173T$$

$$G^0(\text{Pb, s}) = -4800 + 7.991T$$

Properties of the compounds and liquid solution

$$G^0(\text{Ca}_2\text{Pb}) = -61\,700 + 10.5T$$

$$G^0(\text{Ca}_5\text{Pb}_3) = -59\,700 + 9.3T$$

$$G^0(\text{CaPb}) = -56\,600 + 10.6T$$

$$G^0(\text{CaPb}_3) = -35\,000 + 9.8T$$

$$\Delta_{\text{mix}} H(\text{L}) = X_{\text{Ca}} X_{\text{Pb}} [-189\,477 - 7443 (X_{\text{Ca}} - X_{\text{Pb}}) + 254\,823 (X_{\text{Ca}} - X_{\text{Pb}})^2 + 164\,113 (X_{\text{Ca}} - X_{\text{Pb}})^3]$$

$$\Delta_{\text{mix}} S^{\text{ex}}(\text{L}) = X_{\text{Ca}} X_{\text{Pb}} [-37.00 + 52.00 (X_{\text{Ca}} - X_{\text{Pb}}) + 197.63 (X_{\text{Ca}} - X_{\text{Pb}})^2 + 104.48 (X_{\text{Ca}} - X_{\text{Pb}})^3]$$

Note: From [89Not]. Values are in J/mol of atoms for the Gibbs energies and enthalpies and in J/K · mol of atoms for the entropies. T is in K. X_{Ca} and X_{Pb} are mole fractions. The reference state are liquid Pb and bcc Sr.

Section II: Phase Diagram Evaluations

[85Nou] measured the Ca activities in $\text{CaPb}_3 + \text{L}$ mixtures by an emf method. The measured activities represent liquid alloys on the liquidus line. As measurements were performed from 430 to 610 °C, the composition covers from 85 to 97 at.% Pb. (Fig. 1), and the activity values change from 1.22×10^{-6} to 1.26×10^{-9} , respectively. The activity values obtained by [85Nou] are subject to the simultaneous influence of temperature and composition. It is difficult to accurately separate these factors. It can only be assumed that the influence of concentration variations must be much stronger than that of temperature. In such an instance, the increase in activities by almost three orders of magnitude over a concentration range of <15 at.% contradicts the data of [79Del] where the increase slightly exceeded one order, and of [84Bou] and [89Not], who found the Ca partial enthalpy of mixing to have a constant value within the same concentration range. Therefore, the data of [89Nou] and the Gibbs energy of CaPb_3 , calculated from these data, were ignored in this assessment.

Thermodynamic Model

[89Not] proposed a thermodynamic model of the Ca-Pb system on the basis of their measurements and available thermodynamic [79Del] and phase diagram [76Bru] information. An analytical description of the different phases was obtained by an optimization technique. The expressions for the excess enthalpy and entropy of liquid alloys represent the values very crudely because the measurements were made only between 60 and 100 at.% Pb, while the equations cover the entire composition range. The proposed equations give a reasonable description of the assessed phase diagram (Fig. 1). The thermodynamic equations of [89Not] are reproduced in Table 5 in a different format, and they should only be used for rough estimations. The data for the components are taken from [85Cha].

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Ca-Pb evaluation contributed by V.P. Itkin and C.B. Alcock, Department of Metallurgy and Materials Science, University of Toronto, Toronto, Ontario M5S 1A4, Canada, and C.B. Alcock, Center for Sensor Materials, University of Notre Dame, 114 Cushing Hall, Notre Dame, IN 46556. This work was supported by a grant from ASM International. Literature searched through 1990. Part of the bibliographic search was provided by ASM International. Professor Alcock and Dr. Itkin are the Alloy Phase Diagram Program Category Editors for binary alkaline earth alloys.

The Cd-Cr System (Cadmium-Chromium)

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Equilibrium Diagram

No phase diagram is available for the Cd-Cr system. However, as discussed under "Thermodynamics," the lack of a tendency for compound formation in the Cd-Cr system permits presentation of a semi-quantitative phase diagram (Fig. 1) of the eutectic type, with the eutectic temperature indistinguishable from the melting point of pure Cd and with a eutectic liquid composition of 1.02×10^{-4} at.% Cr calculated from

Eq 1 at 321.108 °C. Special points of the Cd-Cr system are given in Table 1.

An initial attempt [08Hin] to dissolve Cr contaminated with 1.2 at.% Fe and 0.3 at.% Si equilibrated for 6 h in liquid Cd

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Table 1 Special Points of the Assessed Cd-Cr Phase Diagram

Reaction	Composition of the respective phases, at.% Cr	Temperature, °C	Reaction type
L ↔ Cd	0	321.108	Melting
L ↔ (Cd) + Cr	1.02×10^{-4} 0 100	321.108	Eutectic
L ↔ Cr	100	1863	Melting