

The Hg-Sr (Mercury-Strontium) System

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Equilibrium Diagram

The assessed Hg-Sr phase diagram (Fig. 1) is a slightly modified form of the diagram of [1974Bru], who studied the system by thermal analysis, metallography, and x-ray diffraction (XRD). The modifications include the deletion of $Hg_{-13}Sr$, the existence of $Hg_{5-8}Sr$, the shifting of stoichiometry Hg_9Sr_2 to $Hg_{58}Sr_{13}$, and the correction of temperature of the $\alpha \leftrightarrow \beta$ transformation of Sr. Special points of the diagram are presented in Table 1. The Hg-Sr system consists of the following phases: (1) the (Hg) phase with a low solid solubility of strontium; (2) the liquid (L) with boiling denoted by dashed line; (3) the gas (G); (4) nine (or more) intermetallic compounds $Hg_{11}Sr$, $Hg_{5-8}Sr$, $Hg_{58}Sr_{13}$, $Hg_{51}Sr_{14}$, Hg_3Sr , Hg_2Sr , $HgSr$, Hg_2Sr_3 , and $HgSr_3$; Hg_2Sr and $HgSr$ melt congruently while the rest of the compounds decompose by peritectic reactions; and (5) (αSr) and (βSr) with very low solubilities of Hg.

Boiling

[1930Dev] observed that the Sr amalgam containing 14.75 at.% Sr boiled at 390 °C: pressure was not specified,

but presumably was the normal ambient pressure. The further addition of Sr up to 20.5 at.% Sr elevated the boiling temperatures of the amalgam by only several degrees Celsius.

Liquidus

All experimental liquidus results are collected in Table 2. [1974Bru] determined the liquidus points over the whole composition range with the use of the thermal analysis of many Hg-Sr alloys. The alloys were prepared in closed Armco iron capsules that were sealed in an Ar atmosphere. Free volumes over the samples were not reported, and some quantities of Ar were always present inside the capsules. During the performance of the thermal analyses, the pressures were certainly elevated to keep Hg in the liquid state. Due to the strong interaction between Hg and Sr, the partial Hg vapor pressures over the Sr amalgams were significantly lower than those over pure Hg [1974Bru] claimed that the temperatures in their measurements were accurate to ± 2 °C. It seems more likely that the experimental precision and accuracy were in fact ± 5 °C; there is only rough agreement between their results and those of other investigators in the low-temperature range.

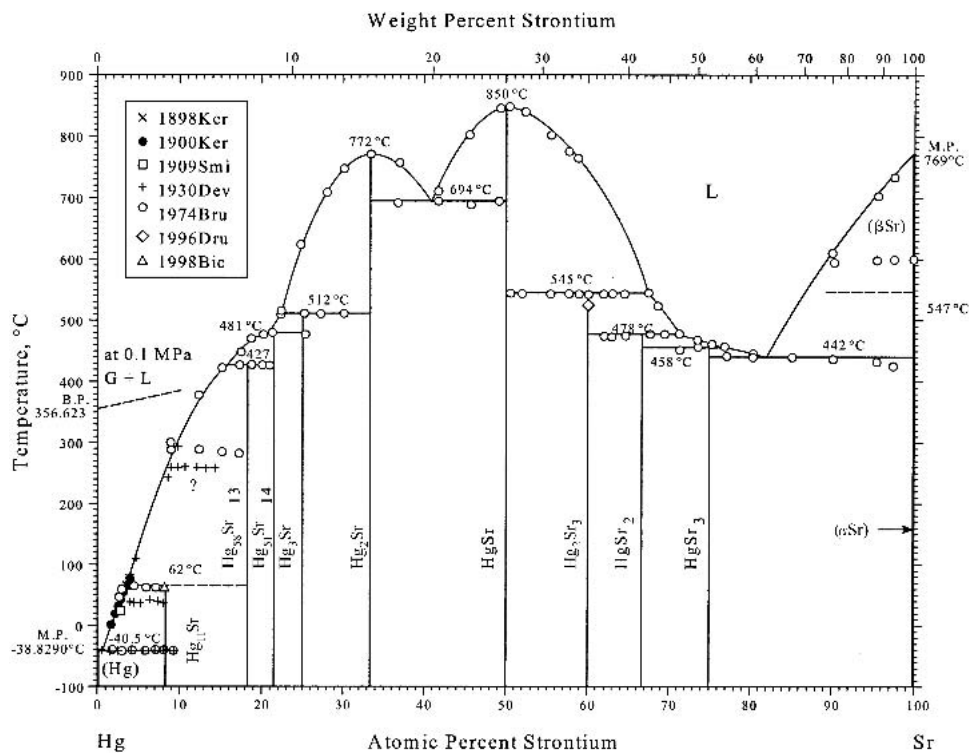


Fig. 1 Assessed Hg-Sr phase diagram at constrained pressure

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Table 1 Special points of the assessed Hg-Sr phase diagram

Reaction	Composition of the respective phases, at.% Sr			Temperature, °C	Reaction type
L ↔ Hg		0		-38.8290	Melting point
L ↔ (Hg) + Hg ₁₁ Sr	~0.8	<0.1	8.3	~ -40.5	Eutectic
L + Hg ₅₋₈ Sr ↔ Hg ₁₁ Sr	3.5	11-17	8.3	62	Peritectic
L + Hg ₅₈ Sr ₁₃ ↔ Hg ₅₋₈ Sr	8	18.2	11-17	-285	Peritectic
L + Hg ₅₁ Sr ₁₄ ↔ Hg ₅₈ Sr ₁₃	16	21.5	18.2	427	Peritectic
L + Hg ₃ Sr ↔ Hg ₅₁ Sr ₁₄	21	25.0	21.5	481	Peritectic
L + Hg ₂ Sr ↔ Hg ₃ Sr	22	33.3	25.0	512	Peritectic
L ↔ Hg ₂ Sr	...	33.3	...	772	Congruent
L ↔ Hg ₂ Sr + HgSr	40.5	33.3	50.0	694	Eutectic
L ↔ HgSr	...	50.0	...	850	Congruent
L + Hg ₂ Sr ₃ ↔ HgSr	68	60.0	50.0	545	Peritectic
L + HgSr ₂ ↔ Hg ₂ Sr ₃	72	66.7	60.0	478	Peritectic
L + HgSr ₃ ↔ HgSr ₂	77	75.0	66.7	458	Peritectic
L ↔ HgSr ₃ + (αSr)	82	75.0	>99.9	442	Eutectic
αSr ↔ βSr	...	100	...	547	Allotropic
L ↔ βSr	...	100	...	769	Melting point

Note: all temperatures above the boiling point of Hg are at constrained pressure; temperatures are given as reported.

Table 2 Liquidus data of the Hg-Sr system

Reference	Composition, at.% Sr	Temperature, °C	Reference	Composition, at.%Sr	Temperature, °C
[1898Ker]	3.4	64.7	[1974Bru](a)	22.1	518
	3.6	81		24.8	621
[1900Ker]	1.65	0.0		27.0	708
	2.35	20		30.0	748
	2.85	30		33.3	772
	3.05	46		36.6	757
	3.45	56		41.3	716
	4.00	64.5		45.2	803
	3.7-4.4	81		49.0	846
[1909Smi]	2.5	23		50.3	850
[1930Dev]	1.1	-42.8		52.0	840
	2.5(a)	39		55.2	803
	4.73	110		57.5	777
	8.55	244		58.7	767
	9.8	296		60.0	739
[1974Bru](a)	2.0	43		67.5	544
	3.0	57		68.5	526
	8.7	302		71.2	478
	12.0	377		73.5	470
	15.0	423		75.3	460
	16.8	450		77.0	458
	18.4	472		80.3	448
	20.0	480		90.0	609
	21.0	483		95.2	702
				97.5	735

Note: temperatures are given as reported. (a) Read out from enlarged figures by the evaluator

Earlier, [1930Dev] had also used thermal analysis to investigate the Hg-rich alloys at many compositions between 0.164 and 14.75 at.% Sr. Only five thermal arrests reflecting the liquidus were recorded; they were in accordance with the solubility determinations carried out previously by

[1898Ker], [1900Ker], [1909Smi], and [1910Smi]. Two peritectics at ~39 and ~262 °C, and a eutectic at -42.8 °C were well defined in the experiments of [1930Dev], but all of these temperatures are in disagreement with [1974Bru]. The thermocouple outputs reported in [1930Dev] were re-

ferred correctly to the melting and boiling points of Hg, but, unfortunately, these authors used Sr containing up to 2% of impurities. Only the amalgams that were more diluted than 2 at.% Sr were prepared by electrolysis, and these were certainly more pure.

[1898Ker], [1900Ker], [1909Smi], and [1910Smi] measured the solubility of Sr in liquid Hg by means of chemical analysis of the saturated amalgam filtrate. Precise determinations were best achieved near room temperature. Distinct breaks on the liquidus line at ~ 40 and 62 °C were observed by [1900Ker], thus corroborating the peritectic temperatures found later by [1930Dev] and [1974Bru] respectively.

A predicted hypoeutectic line that was evaluated through the use of the Van't Hoff relation intersects with the extrapolated hypereutectic liquidus data: that of [1974Bru] at ~ 0.1 at.% Sr and -39.0 °C; that of [1900Ker] at ~ 0.8 at.% Sr and -40.4 °C; and that of [1930Dev] at ~ 1.0 at.% Sr and -40.7 °C. Because the data of [1900Ker] seem to be the most reliable in the low-temperature range, the authors adopted a eutectic point in this evaluation of ~ 0.8 at.% Sr and approximately -40.5 °C.

Solid Solubilities

With the use of XRD, [1974Bru] analyzed the powder patterns of the Sr alloys containing up to 5 at.% Hg. Besides some weak reflections of the Sr_3Hg compound, the main reflections corresponded to αSr with the same lattice constant as for the pure metal αSr . This means that the solubility of Hg in solid αSr is negligible. X-ray diffraction (XRD) and metallographic methods showed the absence of solid solubility for the well-defined Hg-Sr intermediate phases.

[1971Ale] analyzed the dependence of the solubility of metals in solid Hg on their position in the periodic table of elements and came to the conclusion that the Sr content in Hg at -40 °C should be not higher than 0.1 at.% Sr. This estimation is in agreement with the assessed phase diagram.

Intermetallic Compounds

Compositions of the intermetallic compounds formed in this binary system have been convincingly established by the following methods: XRD of the alloy powders and single crystals [1954Fer, 1955Duw, 1964Ian, 1970Bru, 1974Bru, 1995Dru, 1996Dru, 1998Bie, 1999Bie], chemical analysis of isolated crystals [1897Gun, 1898Ker, 1900Ker, 1900Lan, 1906Gun, 1930Dev, 1954Fer, 1964Ian, 1970Bru], metallographic analysis [1970Bru, 1974Bru], and thermal analysis of the alloy samples [1930Dev, 1974Bru, 1995Dru, 1996Dru, 1998Bie, 1999Bie]. On this basis, the existence of the following intermetallic compounds was demonstrated: HgSr_3 [1974Bru], HgSr_2 [1974Bru], Hg_2Sr_3 [1974Bru, 1995Dru, 1996Dru], HgSr [1900Lan, 1954Fer, 1974Bru], Hg_2Sr [1970Bru, 1974Bru], Hg_3Sr [1964Ian, 1974Bru], $\text{Hg}_{51}\text{Sr}_{14}$ [1974Bru], $\text{Hg}_{58}\text{Sr}_{13}$ [1974Bru], and Hg_{11}Sr [1897Gun, 1898Ker, 1900Lan, 1906Gun, 1955Duw, 1974Bru, 1998Bie, 1999Bie].

[1995Dru] did not detect Hg_3Sr_5 compound formation in XRD and differential thermal analysis experiments. The

peritectic decomposition temperature of Hg_2Sr_3 measured in this laboratory was 20 °C lower than the one observed by [1974Bru], which is probably connected with the fact that Hg_2Sr_3 samples of [1995Dru] and [1996Dru] were sealed under vacuum, whereas the samples of [1974Bru] were sealed under an Ar atmosphere.

There have been several attempts to estimate the composition of the most Hg-rich solid phase that exists in equilibrium with the saturated liquid in the vicinity of room temperature. [1897Gun] already have observed that the crystals directly separated from the heterogeneous amalgam by filtration had the composition Hg_{-14}Sr ; however, after the appearance of a Hg excess from the amalgam during its centrifugation, the formula for the solid phase changed to Hg_{-11}Sr . The latter composition was confirmed in the subsequent studies of [1898Ker], [1900Lan], and [1906Gun]. The investigations of [1900Ker] and [1910Smi] pointed rather to the crystal formula Hg_{-12}Sr . [1974Bru] reported, in addition to Hg_{11}Sr , the existence of Hg_{-13}Sr , but the authors were not able to obtain either its pure crystal form or the proper XRD patterns for evidence. [1998Bie] and [1999Bie] repeated thermal analyses and XRD experiments in the Hg-rich composition range and found irrefutably that Hg_{11}Sr peritectically decomposes at 63 ± 3 °C. These authors also claimed that Hg_{11}Sr is the most Hg-rich and thermodynamically stable compound in the system.

The statements of [1998Bie] and [1999Bie] are in partial agreement with the earlier observations of [1900Ker] that a solid in equilibrium with the saturated liquid at 46 to 81 °C had a composition of Hg_{7-8}Sr . [1906Gun] obtained an Hg_6Sr phase by the vacuum distillation of Hg excess from Hg_{11}Sr . A possible formation of Hg_{-5}Sr was reported by [1900Lan] and [1964Ian]. [1930Dev], with the use of thermal analysis, established that the Hg_8Sr compound is stable up to its peritectic decomposition at ~ 262 °C. If one looks carefully at the phase diagram figure of [1974Bru], one observes the actual decomposition of Hg_{11}Sr at 62 °C (misinterpreted by the authors) and additional thermal arrests spread between 279 and 289 °C, which should belong to a peritectic decomposition of a Hg-poorer, unidentified phase. Thus, one may infer from the existence of an Hg_{5-8}Sr solid phase that according to the studies of [1930Dev] and [1974Bru] should be stable up to 262 to 289 °C.

Precise compositions of $\text{Hg}_{58}\text{Sr}_{13}$ and $\text{Hg}_{51}\text{Sr}_{14}$, denoted earlier as $\text{Hg}_{4,5}\text{Sr}$ and $\text{Hg}_{3,6}$, respectively, were established by means of crystallographic data and the general classification of alloy structures.

Crystal Structures and Lattice Parameters

The crystallographic structures and lattice constants of the Hg-Sr phases are summarized in Tables 3 and 4; respectively. All mentioned intermetallic compounds were prepared and investigated by [1974Bru], who used 99.8% pure Sr and 99.99% pure Hg. The melting points and crystallographic data for the elements were in good agreement with the accepted values of [Massalski2], but the $\alpha\text{Sr} \leftrightarrow \beta\text{Sr}$ transformation in the article by [1974Bru] was observed at higher temperature than in [Massalski2]. Therefore, one

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Table 3 Hg-Sr crystal structures

Phase	Composition, at.% Sr	Pearson's symbol	Space group	Strukturbericht designation	Prototype
Hg	0	<i>hR1</i>	$R\bar{3}m$	A10	α Hg
Hg ₁₁ Sr	8.3	<i>cP36</i>	$Pm\bar{3}m$	D2e	BaHg ₁₁
Hg ₅₋₈ Sr	11-17	Unknown
Hg ₅₈ Sr ₁₃	18.2	<i>hP142</i>	$P6_3/mmc$...	Gd ₁₃ Zn ₅₈
Hg ₅₁ Sr ₁₄	21.5	<i>hP65</i>	$P6/m$...	Ag ₅₁ Gd ₁₄
Hg ₃ Sr	25	<i>hP8</i>	$P6_3/mmc$	D0 ₁₉	Ni ₃ Sn
Hg ₂ Sr	33.3	<i>oI12</i>	<i>Imma</i>	...	CeCu ₂
HgSr	50.0	<i>cP2</i>	$Pm\bar{3}m$	B2	CsCl
Hg ₂ Sr ₃	60.0	<i>tP10</i>	$P4/mbm$	D5 _a	Si ₂ U ₃
HgSr ₂	66.7	Unknown
HgSr ₃	75.0	<i>oP16</i>	<i>Pnma</i>	D0 ₁₁	CFe ₃
α Sr	100	<i>cF4</i>	$Fm\bar{3}m$	A1	Cu
β Sr	100	<i>cI2</i>	$Im\bar{3}m$	A2	W

Table 4 Hg-Sr lattice parameter data at room temperature

Phase	Composition, at.% Sr	Lattice parameters, nm			Comment	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
Hg	0	0.3005	...	$\alpha = 70.53^\circ$	at -48 °C	[Massalski2]
Hg ₁₁ Sr	8.3	0.95099(8)	[1955Druw]
		0.9510	[1974Bru]
		0.9510(2)	[1998Bie, 1999Bie]
Hg ₅₈ Sr ₁₃	18.2	1.594	...	1.579	...	[1974Bru]
Hg ₅₁ Sr ₁₄	21.5	1.378	...	0.9880	...	[1974Bru]
Hg ₃ Sr	25.0	0.6878	...	0.5097	...	[1964Ian]
		0.6906	...	0.5106	...	[1974Bru]
Hg ₂ Sr	33.3	0.4934	0.7697	0.8472	...	[1970Bru]
		0.4985	0.7754	0.8550	...	[1974Bru]
HgSr	50.0	0.3930	[1954Fer]
		0.3955	[1974Bru]
Hg ₂ Sr ₃	60.0	0.8877	...	0.4556	...	[1974Bru]
		0.8883(2)	...	0.4553(1)	...	[1995Dru, 1996Dru]
HgSr ₃	75.0	0.8523	1.108	0.7405	...	[1974Bru]
α Sr	100	0.6084	[Massalski2]
		0.6084	[1974Bru]
β Sr	100	0.487	at >547 °C	[Massalski2]

should consider the indicative contamination of Sr used by [1974Bru]. The purity of the elements used in other studies were: in [1998Bie]: Hg, 99.999%; Sr, 99.95%; in [1995Dru] and [1996Dru]: Hg, 99.99%; Sr, 99%; and in [1954Fer] and [1964Ian]: Hg, 99.9+%; Sr, 99.9+%. The crystal structures of all compounds were determined by the XRD powder method. In all cases, good accord between the observed and calculated intensities of reflections was achieved. The structures of Hg₋₁₃Sr and HgSr₂ were not established because their XRD photographs were too poor for a structural interpretation.

In the case of Hg₁₁Sr, a perfect agreement of “a” parameter from [1955Druw], [1974Bru], [1998Bie], and [1999Bie] was observed. The crystallographic constants for Hg₃Sr, Hg₂Sr, and HgSr in the older articles [1954Fer], [1964Ian], and [1970Bru] were 0.2 to 1% smaller than in [1974Bru].

Because these data were obtained in the same laboratory using materials of similar purity, it seems that the apparatus and procedure used for the determination of lattice constants in [1974Bru] was improved. Hg₂Sr, which was initially assigned to the AlB₂ prototype by [1964Ian], was later found to be of the CeCu₂ prototype [1970Bru, 1974Bru].

The structural analysis of Hg₂Sr₃ from a powder sample was confirmed in single-crystal investigations by [1974Bru], [1995Dru], and [1996Dru]. Both results agreed within the experimental errors.

Thermodynamics

Thermodynamic functions for the formation of the infinitely diluted liquid strontium amalgam were derived from the electromotive force measurements of [1974Kor],

Table 5 Partial thermodynamic functions of formation of infinitely diluted Sr amalgams at 25 °C

$\Delta\hat{G}_{\text{Sr}}^{\text{ex}}$ kJ/mol Sr	$\Delta\hat{H}_{\text{Sr}}$ kJ/mol Sr	$\Delta\hat{S}_{\text{Sr}}^{\text{ex}}$ J/K · mol Sr	Reference
...	-249	...	[1949Bri]
-195.1	-217.6	75.3	[1956Fri]
-192.9	[1974Kor]
-190.5 ± 0.04	-221.8 ± 0.04	105.1 ± 0.04	[1975Lon]
-190.6 ± 1.5	[1989Gum]
-203.5	[1990Kor]

Note: the values are referred to mol of Sr atoms.

[1975Lon], and [1990Kor], as well as from the determinations of equilibrium constant of the reaction $2\text{Na}^+ + \text{Sr}(\text{Hg}) \leftrightarrow 2\text{Na}(\text{Hg}) + \text{Sr}^{2+}$ by [1949Bri] and [1956Fri], who took into account the known thermodynamic functions of formation of Na^+ , $\text{Na}(\text{Hg})$, and Sr^{2+} . [1989Gum] calculated the $\Delta\hat{G}_{\text{Sr}}^{\text{ex}}$ from the difference of the selected standard potentials of Sr/Sr^{2+} and $\text{Sr}(\text{Hg})/\text{Sr}^{2+}$. The results are collected in Table 5.

Because only rough values of the component enthalpies were known in the estimation by [1949Bri], the uncertainty in $\Delta\hat{H}_{\text{Sr}}$ may be even higher than ±10%. The precision of the values reported by [1975Lon], especially for $\Delta\hat{H}_{\text{Sr}}$ and $\Delta\hat{S}_{\text{Sr}}^{\text{ex}}$, are too optimistic because the standard potential of Sr/Sr^{2+} is still not known very precisely [1985Tos]. Nevertheless, agreement of the data for $\Delta\hat{G}_{\text{Sr}}^{\text{ex}}$ from [1974Kor], [1975Lon], and [1989Gum] is acceptable.

[1983Hil] predicted that the integral enthalpy of formation of solid HgSr from solid Sr and liquid Hg would be -61.6 kJ/mol atoms. The estimation was based on the Pauling model using the electronegativity scale of Gordy and Thomas. The procedure seems to be accurate within ±10%. BaHg , HgSr , CaHg , and HgMg form a homologous series of compounds with the same crystal structure and a predominantly ionic character for the bonding.

Suggestions for Future Experimental Research

The following features of the Hg-Sr phase diagram need further investigation to confirm some predictions made in this evaluation:

- Position of the eutectic point on the Hg-rich side
- Peritectic decomposition temperature and precise composition range of the Hg_{5-8}Sr phase
- Estimation of structures of the intermediate phases Hg_{5-8}Sr and HgSr_2
- Determination of the integral thermodynamic data of formation of the Hg-Sr compounds

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Indicates the presence of a phase diagram.

* Indicates a key paper.

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