Mercury Selenide Stoichiometry and Phase Relations in the Mercury–Selenium System

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The phase relations in the 0–65 at% Hg portion of the condensed mercury–selenium system were determined from liquidus temperatures to 250°C by evacuated silica tube experiments in which vapor is always a phase. Stoichiometric HgSe melts at 795 ± 2°C whereas $Hg_{0.51}Se_{0.49}$ melts at 797 ± 2°C and $Hg_{0.49}Se_{0.51}$ melts at 793 ± 2°C. In the HgSe–Se portion of the system a monotectic exists at 683 ± 3°C and 71.5 at% Se and a liquid immiscibility field at this temperature extends from 71.5 to 85.5 at% Se. The presence of HgSe depresses the melting temperature of Se by about 8°C. An eutectic exists between HgSe and Se at 208°C and a composition of more than 99.95 at% Se. In the Hg–HgSe portion of the system a monotectic exists at 708 ± 3°C and about 25 at% Se. The solubility of Hg in HgSe was found to exceed stoichiometry by 1.11 ± 0.25 at% at 650°C whereas the solubility of Se in HgSe exceeds stoichiometry by 0.75 ± 0.25 at% Se at the same temperature. All synthetic mercury selenides show the sphalerite type structure. The unit cell dimension of stoichiometric HgSe is $a_0 = 6.080 \pm 0.001$ Å. Mercury selenide synthesized in equilibrium with liquid Se gives $a_0 = 6.082 \pm 0.001$ Å and mercury selenide synthesized in equilibrium with Hg gives $a_0 = 6.078 \pm 0.001$ Å. © 1986 Academic Press, Inc.

Introduction

The system Hg–Se contains one binary phase, HgSe, which is known in nature as the mineral tiemannite that occurs in many ore deposits from different geologic environments (16). Although physicists and physical chemists have studied the properties of synthetic single crystals of mercury selenides and the composition of the vapor phase in equilibrium with this compound at different temperatures (2, 11, 7, 9, 10, 4, 1, 5, 13), the phase relations in the system

Hg–Se are not well known. The phase relations in the Se-rich portion of the Hg–Se system between 50 and 100 at% Se were investigated by Strauss and Farrell (17) by differential thermal analysis. No attempts were made to determine the solubility of Se or Hg in HgSe and the liquidus between 92–100 at% Se was indicated schematically in the phase diagram presented by Strauss and Farrell (17). In the present study the phase relations in the condensed Hg–Se system were investigated by differential thermal analysis, the appearance of phase method, and by determining, with the electron microprobe, the compositions of the phases coexisting in equilibrium.

A Russian translation of an early version

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of this manuscript was published in a special symposium issued by the Academy of Sciences of the USSR in honor of academician D. S. Korzhinsky (3). As no English translation of the proceedings of the symposium is available, and because the newly determined phase relations and the deviation in stoichiometry in mercury selenide are of interest to solid-state chemists and physicists, this more complete manuscript is now being published in English.

Experimental Approach

Experiments were conducted in evacuated silica tubes using the technique described by Kullerud (12). In all experiments a tightly fitting silica glass rod was placed in each silica tube to fill the free space over the charge, thus minimizing the loss of Hg and Se to the vapor phase. Bethlehem Apparatus triple-distilled mercury (nonvolatile residue by weight less than 0.1 part per million) and American Smelting and Refining Company sulfur (99.999 + wt%). Selenium pellets grade A-58 (As < 1 ppm; Te, Cu and Si < 1 ppm, halogen and S total < 0.0005%) were used as reactants. At high temperatures particularly in Hg-rich compositions transparent capillary quartz tubes with internal diameters between 2 and 5 mm and wall thickness between 8 and 10 mm were used and were capable of withstanding the high vapor pressure over the changes at temperatures up to 800°C and compositions containing up to 65 wt% Hg. To check the melting and monotectic temperatures as well as the liquidus relations, DTA experiments were conducted on appropriate compositions synthesized previously in evacuated silica tubes. In each DTA experiment, a small amount of tightly packed, fine grained, high purity quartz was placed over the charge to minimize the loss of Hg and Se to the vapor phase. Quartz also served as an internal standard by virtue of its α–β inversion at 573.1°C. Heating and cooling

rates of 3–5°C/minute were used in all experiments. Each DTA result represents the average of 2–3 heating and cooling cycles performed on the same composition.

To determine the compositional range of mercury selenide, appropriate compositions in the unvariant fields between HgSe and Se and between HgSe and Hg were annealed at various temperatures between 250 and 700°C for 108 days and the compositions of the mercury selenide in the quenched products were determined with the electron microprobe. The compositions of the quenched Se-rich liquids in equilibrium with the mercury selenide were also determined to delineate the liquidus in the Se-rich portion of the system. A Material Research Company Model 500 electron microprobe was used to determine the compositions of the phases in most of the quench products. The instrument has been modified by automation of the spectrometers to allow chemical analyses of several elements to be made at one and the same point. A quantitative analysis program (8) which performs matrix corrections using the method of Zeibold and Ogilvie (18) was used in analyzing the mercury selenides and the quenched liquids. About 15 grains of each phase were analyzed. For mercury selenide, the standard deviations for Hg
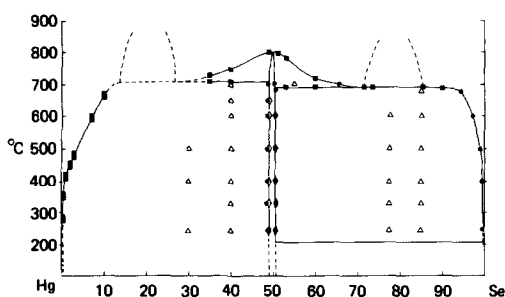

FIG. 1. Phase relations in the condensed Hg–Se system:(■) DTA experiments, this work; (◇) compositions determined by appearance of phase method; (△) bulk compositions; (●) compositions of phases determined by the microprobe; (▮) data from Pajaczkowska and Dzinba (14).

<table>
<tr><td colspan="4">TABLE I</td></tr>
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TABLE I

DTA EXPERIMENTS IN Hg–Se SYSTEM

Composition at% Se	Liquidus °C	Monotectic °C	Eutectic °C
35	732	708	—
40	747	708	—
49	797	—	—
50	795	—	—
51	793	—	—
53	786	683	—
60	715	685	—
71.5	—	685	—
73.5	—	682	208
85.5	—	686	208
90.0	673	—	206

Note. Temperature ±2–3°C.

TABLE II

COMPOSITIONS OF MERCURY SELENIDE IN EQUILIBRIUM WITH LIQUID Hg IN THE TEMPERATURE RANGE BETWEEN 250 AND 700°C DETERMINED BY ELECTRON MICROPROBE ANALYSES

Bulk composition	Temp. °C	wt% Se	wt% Hg	at% Se	at% Hg
$Hg_{0.60}Se_{0.40}$	250	27.19	72.63	48.75	51.25
$Hg_{0.70}Se_{0.30}$	250	27.20	72.69	48.69	51.31
$Hg_{0.60}Se_{0.40}$	328	26.86	73.30	48.21	51.79
$Hg_{0.60}Se_{0.40}$	400	26.87	72.59	48.46	51.54
$Hg_{0.70}Se_{0.30}$	400	27.18	72.61	48.74	51.26
$Hg_{0.60}Se_{0.40}$	500	27.07	72.71	48.61	51.39
$Hg_{0.70}Se_{0.30}$	500	27.20	72.80	48.70	51.30
$Hg_{0.60}Se_{0.40}$	600	27.20	72.49	48.80	51.20
$Hg_{0.60}Se_{0.40}$	650	27.28	72.45	48.89	51.11
$Hg_{0.60}Se_{0.40}$	700	27.08	72.73	48.61	51.39

analyses ranged from 0.17 to 0.74 with the majority below 0.50 wt% and those for Se ranged from 0.14 to 0.82 with the majority below 0.30 wt%. For quenched Se-rich liquids the standard deviations for Hg analyses were in the range 0.06–0.26 with the majority below 0.15 wt%; and those for Se analyses ranged from 0.8 to 1.9 with the majority below 1.0 wt%. The solubilities of Hg and Se in mercury selenide were also

determined by the appearance of phase method involving polished section investigations of all quenched products.

Phase Relations

The phase relations in the condensed Hg–Se system are shown in Fig. 1 and the results of the experimental investigations are given in Tables I–IV. "Stoichiometric"

TABLE III

COMPOSITIONS OF MERCURY SELENIDE IN EQUILIBRIUM WITH LIQUID Se IN THE TEMPERATURE RANGE 250 TO 700°C DETERMINED BY ELECTRON MICROPROBE ANALYSES

Bulk composition	Temp. °C	wt% Se	wt% Hg	at% Se	at% Hg	Liquid wt% Se	Liquid wt% Hg	Liquid at% Se	Liquid at% Hg
$Hg_{0.15}Se_{0.85}$	250	28.76	70.82	50.79	49.22	99.04	0.67	99.73	0.27
$Hg_{0.225}Se_{0.775}$[a]	250	28.92	71.15	50.80	49.20	—	—	—	—
$Hg_{0.15}Se_{0.85}$[a]	328	28.75	71.27	50.61	49.39	—	—	—	—
$Hg_{0.225}Se_{0.775}$[a]	328	29.00	70.96	50.94	49.06	—	—	—	—
$Hg_{0.15}Se_{0.85}$[a]	400	28.89	70.82	50.89	49.11	98.46	1.50	99.40	0.60
$Hg_{0.225}Se_{0.775}$	400	28.59	71.37	50.44	49.56	—	—	—	—
$Hg_{0.15}Se_{0.85}$	500	28.93	71.00	50.86	49.44	97.74	1.93	99.23	0.77
$Hg_{0.225}Se_{0.775}$	500	28.68	71.38	50.51	49.49	97.48	2.43	99.03	0.97
$Hg_{0.15}Se_{0.85}$	600	28.30	71.38	50.18	49.82	93.60	6.31	97.40	2.59
$Hg_{0.225}Se_{0.775}$	600	28.76	71.13	50.67	49.33	92.63	7.58	96.88	3.12
$Hg_{0.15}Se_{0.85}$	680	28.76	71.13	50.67	49.33	87.18	6.31	94.36	5.64
$Hg_{0.45}Se_{0.65}$	700	28.50	71.71	50.24	49.76	42.77	56.94	65.61	34.39

[a] Liquid not analyzed.

TABLE IV

COMPOSITIONAL LIMITS OF MERCURY SELENIDE
DETERMINED BY APPEARANCE OF PHASE METHOD

Composition at%		Temperature °C	Annealing time days	Products
Hg	Se			
51.5	48.5	650	8	Hg Se + Hg
51.5	48.5	600	11	Hg Se + Hg
51.5	48.5	500	21	Hg Se + Hg
51.5	48.5	400	45	Hg Se + Hg
51.5	48.5	300	45	Hg Se + Hg
51.5	48.5	250	45	Hg Se + Hg
51.0	49.0	650	8	Hg Se
51.0	49.0	600	11	Hg Se
51.0	49.0	500	21	Hg Se
51.0	49.0	400	45	Hg Se
51.0	49.0	300	45	Hg Se
51.0	49.0	250	45	Hg Se
48.9	51.1	550	7	Hg Se + L[a]
48.9	51.1	500	11	Hg Se + L
48.9	51.1	400	25	Hg Se + L
48.9	51.1	300	25	Hg Se + L
48.9	51.1	250	25	Hg Se + L
49.5	50.5	650	8	Hg Se + L
49.5	50.5	600	8	Hg Se
49.5	50.5	500	11	Hg Se
49.5	50.5	400	25	Hg Se
49.5	50.5	300	25	Hg Se
49.5	50.5	250	25	Hg Se

[a] "L" is liquid.

HgSe melts at 795 ± 2°C and a monotectic appears at 683 ± 3°C on the Se side of the system in agreement with the results of Strauss and Farrell (17). A composition of $Hg_{0.51}Se_{0.49}$ was found to melt at 797 ± 2°C whereas a composition of $Hg_{0.49}Se_{0.51}$ has a melting temperature of 793 ± 2°C (Table 1). Because the vapor volume was kept at a minimum in the DTA experiments corrections due to loss of Hg or Se to the vapor phase at melting are negligible.

On the Se-rich side of the system, the solubility of Hg in Se reaches 5.64 at% Hg at 680°C. The eutectic between HgSe and Se lies at a composition containing ≥99.95 at% Se at a temperature of 208 ± 2°C. The eutectic temperature is about 8°C below the melting temperature of pure Se. The approximate extent of the two-liquid field is from 71.5 to 85.5 at% Se at 683°C. Compositions annealed within this field and quenched to room temperature show two

immiscible liquids when examined optically (Figs. 2c and d). Attempts to analyze quenched products of the immiscible liquids were unsuccessful because they were intimately intergrown (see Fig. 2d).

The investigation of the phase relations was extended to 65 at% Hg. The monotectic in the Hg-rich portion of the system appears at 708 ± 3°C which is about 25°C higher than the monotectic temperature in the Se-rich part of the system. It was not possible to extend the DTA investigation about 700°C to compositions containing more than 65 at% Hg. The thermocouple well tubes used in the DTA experiments for these compositions tended to explode during the heating cycle even when an external confining pressure was applied to counterbalance the high vapor pressure over the charges. The data on the solubility of Se in Hg are after Pajaczkowska and Dzinba (15). These data are not corrected for loss of Se to the vapor phase.

Compositional limits of mercury selenide. Microprobe analyses of mercury selenide coexisting with liquid Hg shows that it contains a slight excess of mercury over stoichiometric proportions that ranges between 1.1 and 1.8 at% Hg (Table II). The solubility of Hg in mercury selenide, as determined by the appearance of phase method, was ≥1 at% but always less than 1.5% in the temperature range between 250 and 650°C (Table IV).

Microprobe analyses of mercury selenide coexisting with liquid Se (Figs. 2a and b) also showed a slight excess of Se, beyond stoichiometric proportions, ranging between 0.2 and 0.9 at% Se in the temperature range between 250 and 650°C (Table III). The results of appearance of phase experiments, however, indicate smaller solubilities than those obtained by microprobe analyses, amounting to ≥0.5 at% but always less than 1 at% Se (Table IV). Because of the limitations imposed by the accuracy of the microprobe analyses (±2%

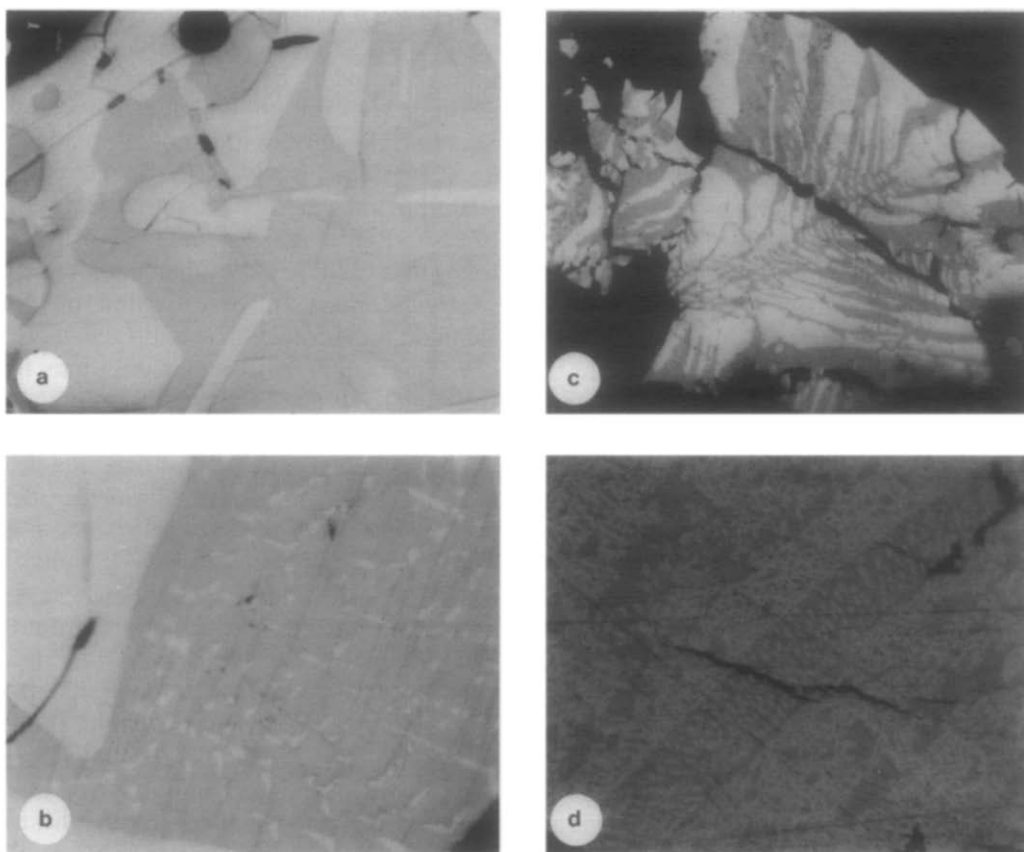FIG. 2. Textures displayed by a composition of $Hg_{22.5}Se_{77.5}$ heated at different temperatures and quenched to room temperature: (a) mercury selenide crystals in Se liquid, temperature 500°C, reflected light, 440×; (b) mercury selenide as large crystals and as skeletal crystals in Se liquid, temperature 650°C, reflected light, 440×; (c) mercury selenide and Se as two immiscible liquids, temperature, 687°C, reflected light, 720×; (d) intimate intergrowth of quenched HgSe and Se immiscible liquids, temperature 820°C, reflected light, 720×.

of the reported concentrations) and because of difficulties involved in detecting trace amounts of Hg or Se in polished sections of the quenched products it was not possible to refine the solubility limits of Se or Hg in mercury selenide beyond the data given above. It is interesting to note however that Brebrick (1965) found that the electrical properties of HgSe are controlled by deviation from stoichiometry and vary continually over the composition range from maximum Hg to maximum Se content. He also estimated from optical density measurements that Hg-saturated mercury selenide in equilibrium with essentially pure Hg up to a temperature of 659°C contains at least 49.2 ± 0.3 at% Se after correcting for preferential loss of Hg to the vapor phase. Mercury selenide in equilibrium with liquid mercury at 650°C in our experiments contained 48.89 at% Se which is close to the value given by Brebrick (4) considering that two different techniques were used in determining the composition of the mercury selenide. Brebrick (4) also observed that the total Se vapor pressure in

equilibrium with congruently sublimating HgSe was always lower at any given temperature than that of Se-saturated mercury selenide.

Brebrick and Strauss (5) saturated samples of HgSe with either Hg or Se at 75 to 600°C. Equilibrated samples of HgSe were found always to be extrinsic n-type and the electron concentration was determined by Hall measurement. Assuming the predominant donor was either a doubly ionized Se vacancy or interstitial mercury and that the concentration of neutral Hg or Se defects were negligible, a composition of 50.01 at% Hg for Se-saturated HgSe at 600°C can be calculated from the measured electron concentration of 4×10^{18}/cm^3. By similar calculation, it can be shown that Hg-saturated HgSe contains 50.02 at% Hg at 350°C (measured electron concentration 8×10^{18}/cm^3). These results are different from those reported in the present investigation. There are significant differences in the techniques used in the two investigations. Brebrick and Strauss (5) equilibrated HgSe with 1 g of mixtures of Hg + Se with an average composition of either 45 or 55 at% Se for 15 min at 600°C, 1 hr at 250°C, and 100–200 hr at 75°C. These short equilibration times which they found sufficient to Se-saturate an initially Hg-saturated sample and vice versa, led them to conclude that the interdiffusion rates are unusually high which suggests that the principle diffusing species is interstitial mercury. In our experiments two different bulk compositions of Hg + Se in each of the univariant fields between HgSe and Se, and Hg and HgSe were annealed isothermally for 108 days. The compositions of the nucleating HgSe were determined directly by electron microprobe analysis and verified by the appearance of phase method. The composition of HgSe determined for each pair of bulk compositions annealed isothermally are in good agreement, and the deviation from stoichiometry exceeds the limits of analytical uncertainty. In none of our experiments could equilibrium be achieved in the short durations reported by Brebrick and Strauss. For example we were not able to achieve Hg or Se saturation or compositional homogeneity of HgSe in 4 weeks at 250°C whereas the duration time at this temperature in Brebrick and Strauss' experiments is 1 hr. It is likely that in these experiments, a thin layer of Hg-saturated or Se-saturated mercury selenide was formed on the surface of HgSe crystals in such short annealing times thus isolating the bulk of the crystal from further reaction with Hg or Se. This suggestion may also explain the lack of agreement between the electrical measurements made above 350°C on HgSe in experiments where it was separated from the Hg + Se mixture by a silica shelf and on HgSe in experiments where it was not separated from the mixture in He-filled tubes.

In order to confirm the deviation from stoichiometry in mercury selenide, the lattice parameters of HgSe coexisting in equilibrium with a slight excess of Se, or Hg respectively, and that of HgSe synthesized from equiatomic proportions of Hg and Se were determined and refined using the lattice constants least-square refinement program of Burnham (6). X-Ray powder diffraction charts made of all the mercury selenide products always displayed sphalerite type structure. The lattice constants varied between 6.082 Å for mercury selenide in equilibrium with liquid Se and 6.078 Å for mercury selenide in equilibrium with Hg. For HgSe synthesized from equiatomic ratios of Hg and Se, a_0 was equal to 6.080 Å. The error in the lattice constants determination was <0.001 Å.

Discussion

The mercury–selenium system was studied as a part of an investigation of the ternary mercury–selenium–sulfur system. The only compound in the system, HgSe,

or more accurately $Hg_{1\pm x}Se$, occurs in nature as the mineral tiemannite which is isostructural with metacinnabar, a polymorph of mercury sulfide. Tiemannite and stoichiometric metacinnabar form complete solid solution with each other above 345°C. At this temperature pure metacinnabar inverts to the low-temperature polymorph, cinnabar.

In the condensed Hg–Se system tiemannite does not show any polymorphic transitions under the vapor pressure of the system. Kafalas *et al.* (*10*) reported the occurrence of a phase transition in mercury selenide at 7.5 kbars at room temperature. The high-pressure polymorph is hexagonal and is quenchable at temperatures below 170°K. This high-pressure phase transition represents also a transition from the semi-metallic to semiconducting state in HgSe. At higher pressures ($\simeq 155$ Kbar) HgSe undergoes another transition to a metallic phase with very low resistivity which is stable up to 200 Kbars (*14*). These high-pressure polymorphs are not expected to occur in nature because the pressure required for their stabilization is not achieved in the geologic environments where mercury selenides occur.

Acknowledgments

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