

Phase relations in the binary Hg–S

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Abstract

Phase relations were determined by monitoring the bulk resistance of Hg_{1-x}S as a function of temperature, composition, and fugacity of sulfur, as well as by appearance-of-phase and DTA runs. Six invariant points involving vapor, cinnabar (cn), metacinnabar (mcn), and hypercinnabar (hcn) were found: (1) cn + mcn + Hg; (2) cn + mcn + S; (3) mcn + hcn + Hg; (4) mcn + hcn + S; (5) hcn + Hg + liquid; and (6) hcn + S + liquid, respectively at: (1) $345 \pm 2^\circ\text{C}$, $\text{Hg}_{1.00}\text{S}(\text{cn}-\text{mcn})$; (2) $315 \pm 3^\circ$, $\text{Hg}_{0.969}\text{S}(\text{cn})-\text{Hg}_{0.864}\text{S}(\text{mcn})$; (3) $481 \pm 2^\circ$, $\text{Hg}_{0.969}\text{S}(\text{mcn})-\text{Hg}_{0.967}\text{S}(\text{hcn})$; (4) $470 \pm 2^\circ$, $\text{Hg}_{0.946}\text{S}(\text{mcn})-\text{Hg}_{0.945}\text{S}(\text{hcn})$; (5) $804 \pm 3^\circ$, $\text{Hg}_{0.966}\text{S}(\text{hcn})$; and (6) $788 \pm 2^\circ$, $\text{Hg}_{0.969}\text{S}(\text{hcn})$. $\text{Hg}_{0.969}\text{S}(\text{hcn})$ melted congruently at $820 \pm 3^\circ\text{C}$.

The crystallographic properties, optical properties, and density vary as a function of composition. Density measurements show that nonstoichiometry is caused by mercury vacancies and interstitial sulfur.

For the reaction $2\text{Hg}(l) + \text{S}_2(\text{g}) = 2\text{HgS}(\text{s})$, the ΔG_R for stoichiometric cinnabar was found to equal $-54,000 + 43.28T \pm 500$ calories. $\Delta G_{f,298.15}^\circ$ was found to be 11.9 ± 0.05 kcal and 11.3 ± 0.8 kcal for cinnabar and metacinnabar, respectively.

Introduction

Some thermodynamic consequences of nonstoichiometry in "polymorphic" phase transitions were examined by Barnes and Scott (1966) and later evaluated experimentally for a cubic to hexagonal transition in the Zn–S system (Scott and Barnes, 1972). A system with an opposite change in symmetry of the "polymorphic" transition was chosen for further investigation of the implications of nonstoichiometry to phase transitions. To this end, the present study characterizes mercuric sulfides with respect to composition, stability, thermodynamic and physical properties, and, especially, polymorphic phase relations.

In the Hg–S binary, at least three mercuric sulfides have been reported: cinnabar, metacinnabar, and a third, as yet incompletely characterized, form. Phase relations involving stoichiometric cinnabar and metacinnabar were investigated most recently by Dickson and Tunell (1959) and by Kullerud (1965). However, they did not determine the extent of nonstoichiometry of mercuric sulfides nor its effect on the

phase transition between cinnabar and metacinnabar. The third, higher-temperature form was first mentioned by Mikolaechuk and Dutchak (1965) and designated gamma-mercuric sulfide (referred to hereafter as hypercinnabar), but their characterization included only its diffraction pattern. Subsequently, this same phase was also identified by X-ray techniques in an assemblage from Central Asia (USSR) that also appeared to contain a fourth form of mercuric sulfide (Protodyakonova *et al.*, 1971).

Experimental techniques

The mercuric sulfide used in this investigation was prepared from mercury and sulfur, both 99.999 percent pure. The starting material was taken from 40-gram lots of mercuric sulfide prepared by multiple sequences of syntheses, grindings, and annealings to assure homogeneous compositions. Components, weighed to ± 0.1 mg, were placed in 11–13 mm O.D. silica tubes which were then evacuated and sealed. These sealed tubes were sequentially heated, first to approximately 200°C for two to three hours, then slowly raised over several hours to $570\text{--}600^\circ\text{C}$, and finally held there for two to three days. The tubes were quenched in ice water, and the products were removed and ground. Usually the products at this

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stage included some minor amounts of sulfide-armored mercury. The walls of the silica tube invariably were thinly coated with both sulfur and mercuric sulfide quenched from the vapor. To compensate for the sulfur lost to the vapor, the tube was weighed and then washed with carbon disulfide to dissolve the sulfur and free the mercuric sulfide apparently included in the thin film of sulfur. The mercuric sulfide recovered from the walls and the silica tube was weighed, and the amount of sulfur lost (*i.e.*, dissolved by the carbon disulfide) was calculated by difference. An amount of sulfur equal to that lost, plus the recovered mercuric sulfide, was added to the other products and then mixed by grinding. For further heating, this mixture was sealed into a second evacuated silica tube having minimum vapor space.

In the second heating cycle, the charge was heated to 570–600°C for approximately 24–30 hours and then cooled slowly to 350–310°C and annealed for 6–10 days before being quenched. The product was removed and ground, and any sulfur lost to the vapor, usually 2 to 5 mg at this stage, was added by the above method. Finally, the products were sealed in a third silica tube and annealed at 350–310°C for two to four days to insure homogeneity. This tube was then quenched, and its composition corrected for the sulfur lost to the vapor during the annealing process. It is estimated that, by this procedure, all compositions are known to within ± 0.15 atomic percent mercury. This uncertainty is primarily due to the loss of material during grinding and regrinding of the products. The amount of material lost was determined by comparing the initial starting weight of the reactants

and the weight of the mercuric sulfide (corrected for sulfur lost to the vapor) recovered at the conclusion of the synthesis.

Most of the experimental data were gathered in this investigation by monitoring the relative resistance, R , of charges of mercuric sulfide while varying either temperature, T , at constant composition, X , T at constant fugacity of sulfur, fS_2 , or by varying both T and fS_2 . The R of a charge of mercuric sulfide, or, for that matter, any sulfide solid solution, is a function of T , X , fS_2 , and crystalline state. Varying any one of these parameters produces a concomitant change in R . The change may be very large where phase changes occur, as caused, for example, by the difference in resistivity of 10^{10} ohms between cinnabar and metacinnabar (Zallen and Slade, 1970). Each phase has not only a definitive R but also different values of $(dR/dT)_{X,fS_2}$ and $(dR/dfS_2)_{T,X}$. Any discontinuous change in these partial derivatives indicates a change in the phase assemblage present; consequently, the determination of phase boundaries is possible by measuring R at controlled T and fS_2 without having to resort to quenching.

To measure R as a function of the three variables, T , X , and fS_2 , two Ti electrodes were buried in powdered charges of mercuric sulfide, as illustrated in Figure 1. To conduct runs so that T and fS_2 could be varied, a 32-cm-long resistance cell, shown in Figure 1a, was used. The cell was placed in two abutting furnaces so that T could be controlled independently for each end of the cell. The cell used to measure R as a function of T and X was smaller, about 6 cm long, and simpler in design (Fig. 1b). A mercuric sulfide of known X was sealed in the single-tube cell and R was measured with increasing T as the whole cell was heated in a single furnace.

The bulk relative resistance is a function of the packing, volume, X , and T of the material between the electrodes. Electrode spacings were adjusted to maintain roughly the same R for each run. The titanium electrodes (99.9 percent) were sheathed in glass except for the small portion buried in the mercuric sulfide. The two factors controlling the life of a resistance cell were the migration of the charge to the cool end of the double-tube cell by vapor transport, and the reaction of the electrodes to form a sulfide or amalgam. Mercuric sulfide does not appear to dissolve significant amounts of titanium; however, in the presence of mercury vapor or liquid sulfur, the surface of the electrodes eventually tarnished. Surface films affected the resistance locally, causing minor random fluctuations in R as they formed or decomposed during the run. This effect was readily detect-

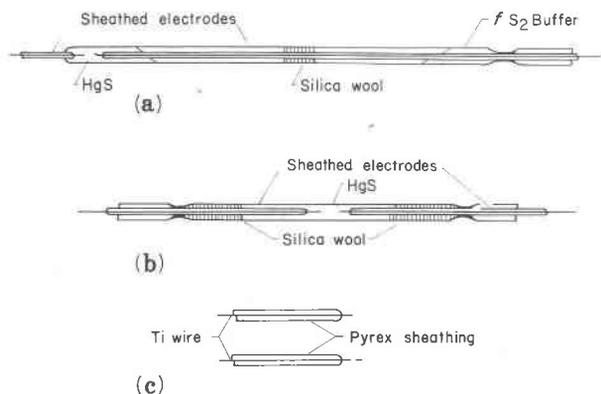


Fig. 1. Resistance cells and electrodes used in this study. (a) Double-tube resistance cell used to measure R as a function of T and fS_2 . Each end of the tube is enclosed in separate adjacent furnaces. (b) Single-tube resistance cell used to measure R as a function of T and X . (c) Design of sheathed electrodes used within tubes of types (a) and (b).

able and was found to occur after 500 to 600 hours of use. Apparently, mercury was the more effective agent in attacking the electrodes, as those used in determining the dissociation of mercuric sulfide were the shortest lived.

Temperatures were measured using chromel–alumel thermocouples, a Wolf potentiometer, and an electronic reference junction simulating 0°C. The thermocouples used in this study were calibrated against a platinum resistance thermometer, and temperatures corrected accordingly.

Liquid sulfur in the low-temperature end of the double-tube resistance cell (Fig. 1a) was used to buffer the fS_2 in the high-temperature end of the cell. At a total sulfur pressure fixed by the liquid sulfur at the cold end, the fS_2 is a function of temperature along the tube, because of changes in degree of polymerization of sulfur vapor. Based on this total sulfur pressure, the association constants for the vapor, and the temperature, the fS_2 at the high-temperature, mercuric sulfide end of the resistance cell may be calculated. The total sulfur pressure and equilibrium constants for the polymers of sulfur vapor as a function of temperature, derived from the measurements of Detry *et al.* (1964), were used for this calculation.

The quenched-tube experiments were prepared similarly to the "simple silica tube" experiments described by Kullerud (1971). In these experiments, charges were equilibrated at temperature for 1 to 30 days, quenched, and the contents examined by X-ray diffraction and transmitted and reflected-light microscopy.

DTA measurements were made on previously synthesized mercuric sulfide samples of known stoichiometry sealed in an evacuated silica tube with a thermocouple well in its base; measurements were also made on mixtures of HgS and Hg to evaluate effects of armoring.

Earlier experimental work on the inversion of stoichiometric mercuric sulfide was based on identifying cinnabar and metacinnabar by color (Dickson and Tunell, 1959). However, we found that composite grains of cinnabar and metacinnabar appeared black when viewed in reflected light, whereas in transmitted light they consisted of patches of red (cinnabar) and black (metacinnabar). Therefore, it was assumed that if a finely-powdered charge of mercuric sulfide appeared black in reflected light, it contained metacinnabar. Consequently, the color of charges was monitored as a function of temperature to determine the lower boundary of the cinnabar + metacinnabar two-phase field.

In order to observe the color at temperature, a

finely-powdered charge of mercuric sulfide was sealed in an evacuated tube having minimized vapor space, and that tube was sealed inside a second silica tube which in turn was sealed in a third silica tube. This procedure insulated the charge during observation of the hot sample. A series of nested tubes was placed in a split furnace, heated to the desired temperature, and held at the temperature for 6–24 hours, after which the furnace was opened and the color of the charge examined under strong overhead illumination from a high-intensity tungsten lamp.

Different compositions of cinnabar had colors varying from bright vermilion to a dull reddish-black for powders, or a dark purple in clear transparent crystals. This observation was quantified by reflectance spectra obtained on a Beckman 2A reflectance spectrometer with powdered MgO as a reference standard. Prior to measurement, mercuric sulfide samples were ground to a fine powder and pressed into the sample holders. The spectra were measured, and then the mercuric sulfide was removed, reground, and again mounted in the sample holder to repeat the spectral measurements. The effect of grain size on the spectra was minimized by this procedure.

Solid phases were identified at elevated temperature with an X-ray diffraction camera in which both T and fS_2 could be controlled. The basic features of the design of this unit are as follows: the sample holder, with an fS_2 buffer, was sealed in an evacuated silica tube with a 190° mica window for the X-ray beam. This assemblage had a chromel heating element cemented to its outer surface, which was further enclosed in insulation. The furnace unit was then mounted in an aluminum vacuum chamber with a nickel window that, in turn, was mounted on a Picker X-ray diffractometer for use with Cu radiation.

Experimental results

Figure 2 is a T - X condensed phase diagram of the system mercury–sulfur. Most of the experimental data on which the diagram is based were obtained on compositions between 50 and 46 atomic percent mercury at temperatures of 100 to 600°C. However, a series of experiments were conducted to check the configuration of the phase fields at other compositions shown as solid circles in Figure 2. These consisted of seven quench-tube runs, one DTA run, and a series of aqueous and dry experiments intended to synthesize any phase of the composition Hg_2S .

The contents of two quench-tube experiments in the two-liquid region on the sulfur-rich side of mercuric sulfide were analyzed by microprobe after quenching to determine the composition of the sulfur

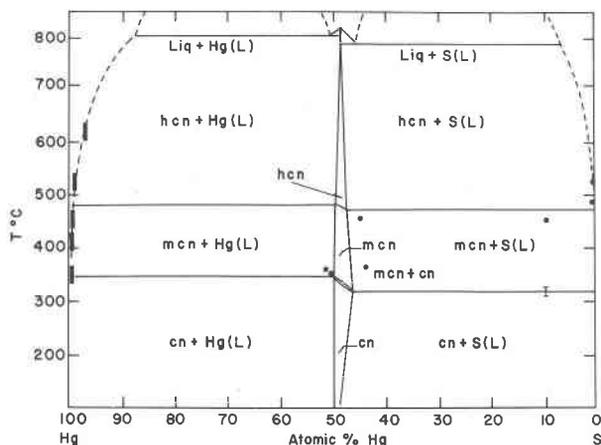


Fig. 2. Phase relations in the mercury-sulfur system. Vapor is present with all assemblages.

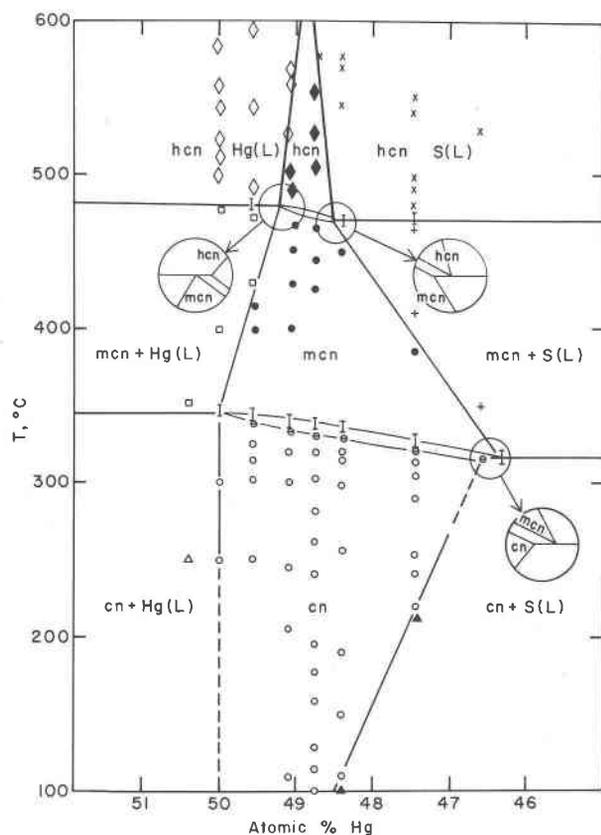


Fig. 3. An enlargement of the central part of Fig. 2. The symbols in order from top to bottom and left to right represent the following assemblages all of which include vapor: open diamonds, hypercinnabar + Hg; filled diamonds, hypercinnabar; X, hypercinnabar + S; open boxes, metacinnabar + Hg; filled circles, metacinnabar; +, metacinnabar + S; open triangles, cinnabar + Hg; open circles, cinnabar; and filled triangles, cinnabar + S. Phase boundaries, and their uncertainties, where determined by resistance measurements are shown by I-bars and where determined by quenched runs by a circled dash.

liquid. At 485°C the sulfur liquid contained 0.4 atomic percent mercury, whereas at 520°C the sulfur liquid had a composition of 0.5 atomic percent mercury.

The data on the composition of the mercury-rich liquid in Figure 2 (rectangles) are from Pajczkowska and Dzuiba (1971). However, they failed to correct for sulfur lost to the vapor, so these data points may be somewhat too high in sulfur content.

Figure 3 shows an expansion of that part of Figure 2 where most of the experiments were conducted, *i.e.*, 100–600°C and from 50–46 atomic percent Hg. Limiting conditions in the phase relations on Figures 2 and 3 are as follows. The maximum congruent melting temperature for mercuric sulfides was found for a composition of 48.90 atomic percent mercury at $820 \pm 3^\circ\text{C}$. Because a vapor phase is present, the composition of the melt and solid will not necessarily be the same at this melting point. Hypercinnabar is in equilibrium with melt down to $804 \pm 3^\circ\text{C}$ on the mercury-rich side, and down to $788 \pm 2^\circ\text{C}$ on the sulfur-rich side. Hypercinnabar in equilibrium with liquid mercury inverts to metacinnabar at $481 \pm 3^\circ\text{C}$, and at $470 \pm 3^\circ\text{C}$ in equilibrium with liquid sulfur. In equilibrium with liquid mercury, metacinnabar inverts to cinnabar at $345 \pm 2^\circ\text{C}$, and in equilibrium with liquid sulfur the inversion occurs at $315 \pm 3^\circ\text{C}$.

Evidence for a compound of the composition Hg_2S has been reported by Glistenko (1936), Zhuk (1954), and others. Glistenko (1936) claims to have synthesized it by precipitation from a mercurous chloride solution when reacted with a sodium sulfide solution. His procedure was followed, and the precipitate was examined by X-ray diffraction, but it consisted of finely crystalline metacinnabar. Because this procedure was similar to those used by the other authors, these results, along with the inability to synthesize it directly from the elements, suggest that Hg_2S is not a stable phase in the mercury-sulfur system.

In comparison to the quenched-tube experiments, the resistance experiments (Fig. 1a) used to determine phase boundaries at fS_2 and T equilibrated more rapidly because they involved solid-vapor reactions, which are not as readily plagued by armoring as solid-solid reactions. The results of these experiments are shown in Figure 4, together with the sulfur condensation curve taken from Barton and Skinner (1967). Each of these invariant points has a fourth phase curve, with vapor absent, originating from it and extending to higher total pressures; these curves cannot be shown in Figure 4.

The reflectance spectra for four compositions of

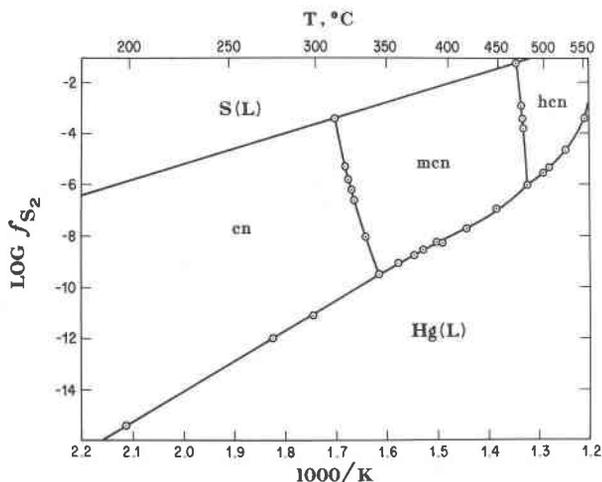


Fig. 4. T - f/S_2 projection of the system mercury-sulfur. The size of data points indicates the uncertainty of numerical values; see Fig. 7.

cinnabar are shown in Figure 5 for wavelengths between 500 and 800 nm. A plot of reflectance *vs.* Hg/S atomic ratio at two wavelengths, 600 and 700 nm, was constructed from the data of Figure 5 as a basis for analysis (Fig. 6). The scatter in the points in Figure 6 was the result of grain-size variation, which caused reflectance to change by a maximum of 5 percent; in confirmation, Hunt *et al.* (1971) show variations of 20 percent at the same wavelength with a wider range of grain size than was employed in our measurements. They show near the absorption edge, at approximately 600 nm, a minimum in the spread of their values owing to grain size. Our values taken near 600 nm (Fig. 6) yield a linear relation between reflectance and composition with a maximum uncertainty in values of reflectance of 2 percent. Applying this technique allows for the determination of composition to within ± 0.005 in mole fraction Hg. The major disadvantage of this technique is that it requires about 1 gram of material.

An IRD Guinier-Hägg camera and an X-ray diffractometer were used with an internal NaCl standard to measure the X-ray diffraction patterns of mercuric sulfides. The resulting cell dimensions of five different compositions of cinnabar are given in Table 1. Over the respective composition range of cinnabar, a changes 0.35 percent and c changes 0.39 percent. The variation of the unit cell of cinnabar with composition can be used to determine composition within ± 0.005 in Hg:S atomic ratio.

In the pure mercury-sulfur system, hypercinnabar is a nonquenchable phase; however, mercuric oxide (~ 2 percent) was found to stabilize hypercinnabar

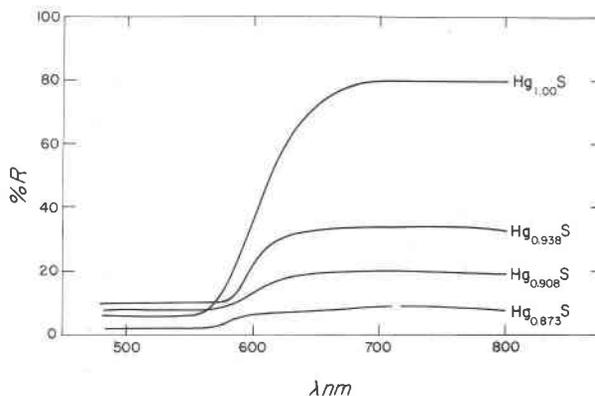


Fig. 5. Reflectance spectra of four different compositions of cinnabar using MgO as a reference standard.

just as iron and zinc stabilize metacinnabar, which allowed quenching to room conditions. The stabilized hypercinnabar has the same X-ray pattern as that listed for gamma-mercuric sulfide in the Powder Diffraction File. The high-temperature X-ray pattern accounts satisfactorily for the major reflections of hypercinnabar, thus confirming its identity as the high-temperature phase.

Discussion of results

Phase equilibria

Most of the phase equilibria were determined by monitoring R as a function of the variables T , X , and

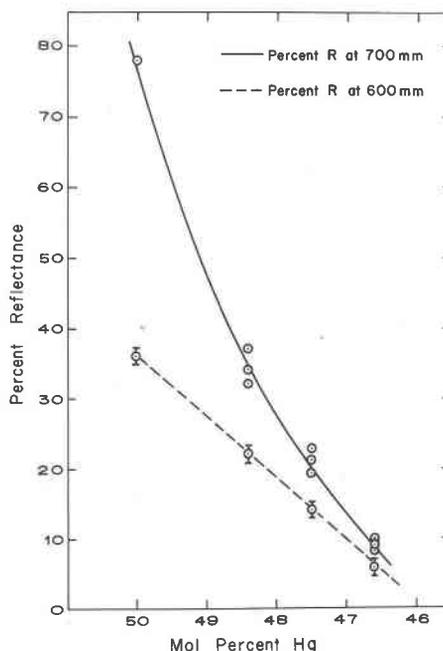


Fig. 6. Reflectance of powdered cinnabar for light of two wavelengths, 600 nm (dashed line) and 700 nm (solid line).

Table 1. Unit-cell dimensions for five cinnabars (hexagonal) of different compositions

Hg/S	a in Å ⁰	c in Å ⁰
1.000	4.1479 ± 0.0007	9.4960 ± 0.0015
0.951	4.1525 ± 0.0007	9.5075 ± 0.0016
0.938	4.1547 ± 0.0008	9.5127 ± 0.0018
0.908	4.1585 ± 0.0012	9.5218 ± 0.1128
0.873	4.1624 ± 0.0017	9.5327 ± 0.0038

fS_2 . The validity of this method for determining phase boundaries can be seen by comparing the results with those determined by DTA. Table 2 shows such a comparison for the cinnabar–metacinnabar transition for various compositions of mercuric sulfide. Both methods yield values for the transition that are in agreement within the estimated uncertainties.

There has been satisfactory agreement on the temperature of the cinnabar–metacinnabar transition for stoichiometric mercuric sulfide. Dickson and Tunell (1959) and Kullerud (1965) reported the cinnabar–metacinnabar transition to occur at $344 \pm 2^\circ$ and $345 \pm 2^\circ\text{C}$, respectively. Our results for stoichiometric mercuric sulfide (*i.e.*, mercury-saturated) are in agreement with the above values. Curtis (1962) reported the cinnabar–metacinnabar transition at 315°C in an H_2S atmosphere, a high fS_2 environment. This value is the same as we obtained for the cinnabar–metacinnabar transition in equilibrium with liquid sulfur.

In contrast to our results, mercuric sulfide is reported to be stoichiometric by Kullerud (1965). However, he used DTA runs with mixtures of initially stoichiometric mercuric sulfide plus either excess

Table 2. Comparison of the temperature of transformation for cinnabar with metacinnabar obtained by differential thermal analysis and resistance

Hg/S	Temperature, °C	
	By D.T.A.	By R
1.000	345 ± 2	345 ± 5
0.982	342 ± 2	342 ± 5
0.965	340 ± 2	340 ± 5
0.938	337 ± 2	336 ± 5
0.908	326 ± 2	328 ± 5
0.864	315 ± 3	316 ± 5

mercury or sulfur, which favored armoring (isolating the reactants from the system by a coating of mercuric sulfide) and inhomogeneous sulfides. In a test for the effects of armoring, our experiments showed no reaction between $\text{Hg}_{0.988}\text{S}$ and Hg during two DTA runs to 550°C .

A melting temperature of 883°C was determined by Pajaczkowska and Dzuiba (1971) for mercuric sulfide. It was based on extrapolating the solubility of mercuric sulfide in mercury on a plot of atomic fraction sulfur *vs.* $1000/T$ up to the composition of stoichiometric mercuric sulfide, which was then taken as the melting temperature. This approximation is in error because a two-liquid region exists between the mercury and the stoichiometric composition for mercuric sulfide. A lower melting temperature of 572°C , reported by Potter and Barnes (1971), resulted from a misinterpretation of a thermal effect, produced by lime glass rods used to reduce the vapor space in the DTA tube, as melting of the mercuric sulfide.

Thermodynamics

The basic thermodynamic parameters of the various forms of mercuric sulfide can be calculated if the aS_2 is known as a function of composition and temperature. An empirical equation for fS_2 as a function of T and mole fraction HgS (X) in the system $\text{HgS}-S_2$ was derived by fitting a trend surface by multiple linear least-squares regression to the T , X , and fS_2 data. The resulting equations have the general form:

$$\log fS_2 = \sum_i^m \alpha_i T^i + X \sum_i^m \beta_i T^i \quad (1)$$

where α_i and β_i are empirical constants (Table 3). This form of the equation is the lowest order that will describe the data within the uncertainties.

Table 3. Coefficients for the equations of $\log a\text{HgS}$ and $\log aS_2$ as a function of T and X for cinnabar and metacinnabar

	Cinnabar	Metacinnabar
α_0	1.92150×10^3	4.934710×10^2
α_1	-5.459073	-1.847293
α_2	4.004478×10^{-3}	1.949659×10^{-3}
β_0	-1.977729×10^3	29.685636×10^3
β_1	5.580053	-1.432580×10^2
β_2	-4.078241×10^{-3}	$2/301631 \times 10^{-1}$
β_3	--	-1.235560×10^{-4}

In the presence of liquid mercury, the formation of mercuric sulfide in the solid solution may be written



$$K = \frac{a_{\text{HgS}}}{a_{\text{Hg}} a_{\text{S}_2}^{1/2}} \quad (3)$$

Where the liquid mercury is pure and the solid solution is stoichiometric HgS, as for cinnabar + mercury, then equation (3) reduces to

$$K = a_{\text{S}_2}^{-1/2} \quad (4)$$

and

$$\Delta G_f = 1/2 RT \ln a_{\text{S}_2} \quad (5)$$

If the liquid mercury is pure but the solid solution is not stoichiometric HgS, as for metacinnabar + mercury, then equation (3) becomes

$$K = a_{\text{HgS}} a_{\text{S}_2}^{-1/2} \quad (6)$$

and

$$\Delta G_f = RT(1/2 \ln a_{\text{S}_2} - \ln a_{\text{HgS}}) \quad (7)$$

The standard states used to evaluate the equilibrium constants and free energies are as follows. The standard state for S₂ gas is the pure component at *T* with a fugacity of one atm and, thus, $a_{\text{S}_2} = f_{\text{S}_2}$ numerically, although not dimensionally. Hence, equation (1) can be used to calculate a_{S_2} as a function of *T* and *X*. The standard state for liquid mercury was taken as the pure liquid at each temperature. The assumption that a_{Hg} is unity for liquid mercury is a reasonable approximation up to 400°–450°C, due to the very limited solubility of HgS in this phase (Fig. 2). The standard state for mercuric sulfide was chosen

as the pure stoichiometric compound at *T* but a_{HgS} can be taken as unity only if the mercuric sulfide is stoichiometric.

The a_{HgS} of equation (6) can be calculated from the empirical equation (1) for f_{S_2} as a function of *T* and *X* using the Gibbs-Duhem equation:

$$\sum X_i d\mu_i = 0 \quad (T, P \text{ constant}) \quad (8)$$

where μ_i is the chemical potential of the *i*th component. Thus, for any phase in the HgS–S₂ system, we can write equation (8) as:

$$X d \log a_{\text{HgS}} + (1 - X) d \log a_{\text{S}_2} = 0 \quad (9)$$

Differentiating equation (1) and substituting into equation (9) and then integrating from the boundary condition that $a_{\text{HgS}} = 1$ at *X* = 1 yields the following relationship for log a_{HgS} :

$$\log a_{\text{HgS}} = X \sum_1^m \beta_1 T^1 - \ln X \sum_1^m \beta_1 T^1 - \sum_1^m \beta_1 T^1 \quad (10)$$

The values generated by these equations can be used to calculate ΔG_R using equation (7).

Free energies at temperatures greater than 400°–450°C are difficult to calculate for two reasons. The first is that a_{Hg} can no longer be assumed to be unity, due to the significant dissolution of HgS in liquid mercury at temperatures greater than 400°C. Secondly, at temperatures greater than 380°C significant amounts of HgS(g) are present (Goldfinger and Jeunehomme, 1963), which invalidates the assumption used to calculate the f_{S_2} , *i.e.*, that Hg(g) and S₂(g) were the dominant species in the gas. This effect is reflected in Figure 4 where, at temperatures greater

Table 4. Comparison of experimental thermodynamic parameters with the available data from the literature. Cn = cinnabar and mcnc = metacinnabar

Reference	$\Delta G_{f,298}^{\circ}$ cn kcal/mol	$\Delta H_{f,298}^{\circ}$ cn kcal	ΔH_{298}° of vaporization for cn kcal	$\Delta G_{f,298}^{\circ}$ mcnc kcal	$\Delta H_{f,298}^{\circ}$ mcnc kcal
This study	-11.9 ± 0.5	-13.7 ± 0.5	87.6 ± 1	-11.3 ± 0.8	-12.65 ± 0.8
Mitchell and Munir (1970)	-11.7 ± 1.5	-13.5 ± 1.5	87.4 ± 1.5	--	--
Goldfinger and Jeunehomme (1963)	-12.0 ± 0.5	-13.8 ± 0.5	87.7 ± 1.0	--	--
Treadwell and Schaufelberger (1946)	-12.2 ± 1.0	-14.0 ± 1.0	87.9 ± 2.0	-11.8 ± 1.0	-13.2 ± 1.0
Rinse (1928)	-12.2 ± 1.0	-14.0 ± 1.0	87.9 ± 2.0	-11.6 ± 1.0	-13.0 ± 1.0

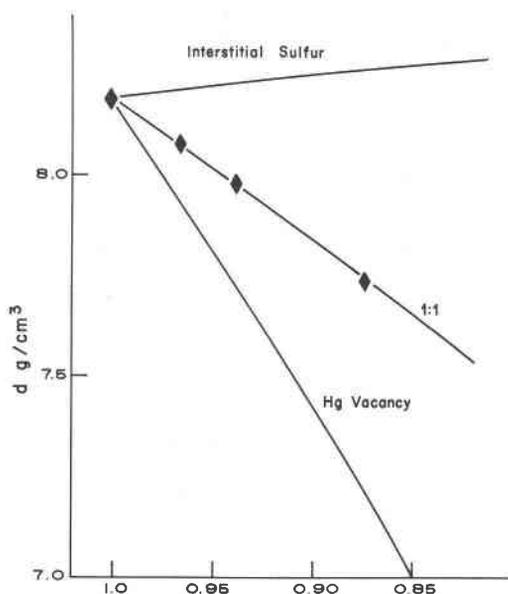


Fig. 7. Measured densities of cinnabar (diamonds) for various Hg:S ratios compared with three calculated defect models; all interstitial sulfur, 1:1 interstitial sulfur and mercury vacancies, and all mercury vacancies.

Table 5. Properties of hypercinnabar

Stability*	Table 1 and Figure 5
Cell constants* (hexagonal)	$a = 7.01 \pm 0.3$ $c = 14.13 \pm 0.7$
Density measured*	7.43
Density calculated*	7.54
Z*	12
Cleavage*,**	None observed
Fracture*,**	Subconchoidal to uneven
Color*,**	Black with purple cast
Luster*,**	Adamantine
Streak*,**	Dark black purple
Moh's hardness*,**	3
Color in reflected light in air**,**	Greyish white
Color in reflected light in oil**,**	Brownish grey
Reflectance at 540 nm**	25%
Bireflectance	Not present
Anisotropy*,**	Distinct in oil
VHN (25)**	51.5 ± 8.0
Polishing hardness**	< metacinnabar, > cinnabar
Quench properties	Not quenchable in pure system

* Measured on synthetic material

** Measured on natural material containing iron.

than 400°C, there is significant curvature to the univariant curve between HgS and Hg(l).

However, from the data on temperature and K , the $\Delta H^0(\text{transition})$ for cinnabar–metacinnabar and metacinnabar–hypercinnabar can be calculated. The general equation for the formation of a mercuric sulfide is:



where x varies from 0.000 to 0.136. The ΔH_R^0 for the above equation can be calculated from the following:

$$\Delta H_R^0 = -R(d \ln K/d(1/T))$$

If it is assumed that ΔH_R^0 is constant over the temperature range of the transition and for the small range of x indicated, the above equation yields:

$$\Delta H_R^0(\text{cal/mol}) = 4.5758[(\log K_{T_2} - \log K_{T_1}) / (1/T_1 - 1/T_2)]$$

ΔH_R^0 for each phase was calculated at the transition temperature from smoothed data over a limited temperature range (5°C) where composition of the solid and the vapor is essentially constant. Once ΔH_R^0 for each polymorph of the appropriate composition has been calculated, the $\Delta H^0(\text{transition})$ for each polymorphic transition can be calculated for each composition from the following relations:

$$\Delta H^0(\text{transition cn-mcn}) = \Delta H_R^0(\text{mcn}) - \Delta H_R^0(\text{cn})$$

$$\Delta H^0(\text{transition mcn-hcn}) = \Delta H_R^0(\text{hcn}) - \Delta H_R^0(\text{mcn})$$

$$\Delta H^0(\text{transition mcn-hcn}) = \Delta H_R^0(\text{hcn}) - \Delta H_R^0(\text{mcn})$$

The resulting $\Delta H^0(\text{transition})$ for cinnabar–metacinnabar and metacinnabar–hypercinnabar transitions (mercury-saturated, $x = 0$) are 1050 ± 400 and 500 ± 600 calories/mol, respectively.

The only $\Delta H^0(\text{transition})$ that had been previously determined directly was that of cinnabar–metacinnabar transition, and the value of 950 calories/mol (Kapustinskii and Chentsova, 1941) is in good agreement with the value, 1050 ± 400 calories/mol, determined in this study.

Using the calculated $\Delta H^0(\text{transition})$, the cinnabar data, and the entropy data from Mills (1974), the $\Delta G_f^0, 298$ and $\Delta H_f^0, 298$ were calculated. These calculated values are compared with other values from the literature in Table 4.

Defect models for mercuric sulfide

Three possible models, vacancies in mercury sites, interstitial sulfur, and a coupled substitution of one

vacancy for each interstitial sulfur, were evaluated for cinnabar using a density-composition diagram (Fig. 7). The experimentally-measured densities were found to correspond to a coupled model of one interstitial sulfur for each vacancy in a mercury site. The charge balance would then be satisfied either by S^{2+} in the Hg^{2+} site or by an interstitial S atom forming a disulfide group. Either mechanism is possible, although the very similar size of the S^{2+} and Hg^{2+} makes this mechanism attractive. Similar mechanisms are proposed for the other forms of mercuric sulfide, although density data are lacking to confirm this hypothesis.

*Hypercinnabar—a new mineral*²

Studies by reflected-light microscopy of metacinnabar from the Mount Diablo Mine, California, revealed within it a second mineral similar in color and texture but anisotropic. Subsequent X-ray studies demonstrated that this material was the high-temperature polymorph of mercuric sulfide, here named hypercinnabar. The properties (Table 5) of hypercinnabar were determined on both synthetic and natural specimens. Electron microprobe analyses of natural material (using synthetic mercuric sulfide standards) confirmed the hypercinnabar to be metal-deficient, in agreement with compositions determined by synthesis in the binary system. Iron was also present in the natural hypercinnabar ($Hg_{0.91}Fe_{0.07}S$) in solid solution. Pure hypercinnabar is not quenchable in the binary system, but can be quenched if doped with oxygen. The presence of trace quantities of oxygen in the natural material could not be confirmed with the electron microprobe.

Conclusions

Mercuric sulfide is a non-stoichiometric compound and deviation from stoichiometry significantly affects the transition temperatures between the various "polymorphs." The physical properties, as well as the thermodynamic parameters, are dependent on the composition of the mercuric sulfide. The term "polymorphism," as currently used by many, implies an isocompositional transition. Because the transitions cinnabar-metacinnabar-hypercinnabar generally require compositional changes, the question arises as to whether or not these should be called polymorphic transitions.

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² Approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association.

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