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Pressures of Hg and Selenium over HgSe(c) from Optical Density Measurements

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The optical density of the vapors at 860°C that are in equilibrium with Hg-saturated, Se-saturated, and congruently subliming HgSe(c) in the range 450° to 816°C has been measured between 2000 and 7000 Å. No indication of the species HgSe(g) is found. Assuming the optical density is the sum of those obtained with pure Se and pure Hg, the partial pressure of Hg(g), p_{Hg}, and the total selenium pressure, P_Σ, are determined along a substantial portion of the HgSe(c) three-phase lines. Hg-saturated HgSe(c) is in equilibrium with essentially pure Hg(l) up to 659°C and is at least 48.5 at. % Se. The total selenium pressure attains a maximum value of 0.62 atm for Se-saturated HgSe near 722°C. The value of p_{Hg} for congruently subliming HgSe(c) is close to that required by the value of P_Σ and the published thermodynamics of selenium vapor. Between about 450° and 600°C the standard Gibbs free energies of formation for both Se-saturated and congruently subliming HgSe(c) are obtained and are the same within experimental error. Taking an average, $\Delta G_f^\circ[\mathrm{Hg(g)}+\tfrac{1}{2}\mathrm{Se_2(g)}=\mathrm{HgSe(c)}]=-41.92+42.40(10^{-3})T$ kcal/mole. Extrapolating to 300°K, we obtain $\Delta H_f^\circ=-10.8$ kcal/mole and $\Delta S_f^\circ=-4.99$ eu/mole for the formation of HgSe(c) from Hg(l) and Se(c).

I. INTRODUCTION

A NUMBER of recent investigations have involved the optical and galvanomagnetic properties[1–3] of HgSe(c). The material is a semimetal[1] with the zincblende structure and a lattice constant[4] $a=6.08$ Å. Although complete studies have not been carried out, the concentration of electronic carriers is influenced by deviations from stoichiometry[2,5] and varies from about 4×10^{18} to 2×10^{17} electron/cm^3 as the compound is made as Hg-rich or as Se-rich as possible between about 200° and 600°C. The liquidus has been established by thermal analysis for atom percentages of Se greater than 50.[6] A single, equiatomic compound melting at 799°C, a monotectic at 686°C with the two-melt region extending between about 71 and 85 at. % Se, and a eutectic at 220°C and close to pure Se in composition were observed. Mass-spectrographic analysis[7] of the effusion products of a Knudsen cell containing HgSe(c) has yielded a value for the standard enthalpy of formation from Hg(g) and $\tfrac{1}{2}\mathrm{Se_2(g)}$ at 500°K of −45 kcal/mole. The standard enthalpy of formation[8] has also been determined near 298°K but no determination of the standard Gibbs free energy of formation has been made.

We have measured the optical density between 2000 and 7000 Å of the vapor at 860°C which originates from $\mathrm{Hg_{1-x}Se_x(c)}$ at known lower temperatures. The major vapor species are Hg(g) and molecular selenium species. In agreement with mass-spectrographic studies[7] no HgSe(g) is detected. Assuming the optical density is the sum of those obtained with the pure elements, the partial pressure of Hg(g), p_{Hg}, and the total selenium pressure, P_Σ, are determined along the three-phase lines of $\mathrm{Hg_{1-x}Se_x(c)}$. They are also determined for congruently subliming HgSe(c) between 450° and 600°C. The latter measurements allow a specification of the number density of selenium atoms in all molecular forms, $\sum_j jC_{\mathrm{Se}_j}$. This is in good agreement with values calculated from published thermodynamic descriptions of selenium vapor. Using the equilibrium constants of Illarionov and Lapina,[9] partial pressures of Se$_2$, p_2, are calculated from our measured values of total pressure, P_Σ, and the standard Gibbs free energies of formation of congruently subliming HgSe(c) and that of Se-saturated[10] HgSe(c) are obtained between about 450° and 600°C and found to agree within experimental error. No significant change results if p_2 is calculated using the data of Stull and Sinke on selenium vapor. It is shown that the variation in the standard free energy with composition is less than 0.3 kcal/mole if the limits of stability of HgSe do not lie outside the range, 49.5 to 50.5 at. % Se.

II. EXPERIMENTAL

The cylindrical, fused-silica optical cells were 22-mm o.d., ¼ to 2 in. long, with flat parallel windows and an 8.5-in.-long sidearm at right angles to the cylindrical axis. The end of the sidearm away from the cell was the sealoff point (2 to 6×10^{-6} Torr) and

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* Operated with support from the U.S. Air Force.

[1] T. C. Harman and A. J. Strauss, J. Appl. Phys. Suppl. **32**, 2265 (1961).

[2] M. D. Blue and P. W. Kruse, J. Phys. Chem. Solids **23**, 577 (1962).

[3] G. B. Wright, A. J. Strauss, and T. C. Harman, Phys. Rev. **125**, 1534 (1962).

[4] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958), p. 688.

[5] T. C. Harman and A. J. Strauss, Solid State Research Report, Lincoln Laboratory, MIT 15 October 1960 (unpublished).

[6] A. J. Strauss and L. B. Farrell, J. Inorg. Nucl. Chem. **24**, 1211 (1962).

[7] P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. **59**, 2851 (1963).

[8] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Joffe, Natl. Bur. Std. (U.S.) Circ. No. 500 (1952).

[9] V. V. Illarionov and L. M. Lapina, Dokl. Akad. Nauk. SSSR **114**, 1021 (1957).

[10] For simplicity of expression the terms Se-saturated HgSe(c) and Hg-saturated HgSe(c) are used to indicate HgSe(c), that is, respectively, as selenium rich or as mercury rich as possible at a given temperature.

during measurements contained the condensed phases providing the vapor. Temperatures were measured to ±1°C using Pt; Pt, 13% Rh thermocouples. A Cary Model 14–H spectrophotometer was used to measure optical densities between 0.01 and 2.8 and for wavelengths between 2000 and 7000 Å. The resolution (2 to 5 Å) and wavelength correction (1 Å or less) as a function of wavelength and the manner in which the spectrometer were used have been described.[11] A schematic of the furnace arrangement which kept the optical cell at $T_0=860°C$ (700°C for some runs) while that of the reservoir, T_R, was varied from room temperature upwards has also been published.[12] As usual the zero of optical density was measured with $T_0=860°C$ and T_R at or near room temperature, so that essentially no vapor was present in the cell. The manner in which the optical cells were cleaned and outgassed has been described in detail.[11]

The spectroscopically pure elements were weighed out to the nearest 0.1 mg, sealed off under vacuum in a 22-mm-o.d., 4-in.-long, outgassed silica tube and then annealed. The reacted mass was crushed so the largest pieces were about 1 mm in diameter and the amount of fine powder was a minimum. These particles were then sealed off in an optical cell under vacuum. For Se-saturated HgSe, 10 g of 51.0 at. % Se, Hg–Se annealed for 3 h at 755°C and then 60 h at 495°C were sealed in a 46.7-mm-optical-path cell and T_R varied between 390° and 620°C. For comparison 15 g of the previously unreacted elements, whose over-all composition was 51.0 at. % Se, were sealed in a 22.1-mm-path cell and measurements taken for $500 \leq T_R < 816°C$. For Hg-saturated HgSe 20 g of 48.5 at. % Se, Hg–Se reacted for 50 h at 580°C and then annealed for 72 h at 460°C were sealed in a 5.97-mm-path cell and measurements taken between 396° and 659°C. Congruently subliming HgSe was studied using a 22.1-mm-path cell containing 0.57 g of a crushed single crystal[13] grown by the Bridgman–Stockbarger method. After this cell was run at $T_0=860°C$ and $350 \leq T_R \leq 600°C$ the reservoir was quenched. About 75% of the material was removed and heated under vacuum in a 25.0-mm-path-length cell. When a visible sublimate was driven completely out of the cell, it was sealed off under vacuum. This second cell was run at both $T_0=860°$ and 700°C and for $353 \leq T_R \leq 600°C$. Except for the cell containing the previously unreacted elements for $T_R < 630°C$, steady optical densities were generally attained within 5 to 45 min after a steady temperature state was reached. This indicates that the somewhat arbitrary annealing times and temperatures used were adequate to insure complete reaction of the elements and that any subsequent changes necessary to maintain equilibrium were rapid. Cells containing pure Hg and pure Se were also investigated. The latter results are described in detail elsewhere.[14]

TABLE I. Optical absorption of Hg(g) at 860°C. Value of r_λ in $p_{Hg}=r_\lambda(D_\lambda/L)^{\frac{1}{2}}$.

(Å)	No. of data points	Pressure range (atm)	r_λ (atm·mm$^{\frac{1}{2}}$)	r_λ(755°C/r_λ(860°C)
2550	7	0.3 – 1.1	5.62	0.92
2560	12	0.3 – 2.6	8.54	0.99
2570	11	0.3 – 3.5	11.6	0.96
2600	9	0.54– 4.4	18.9	0.89
2700	11	0.81–11	39.0	0.86
2800	12	1.2 –16	60.4	0.86
2900	13	1.85–24.5	84.6	0.87
3000	11	4.7 –24.5	117	0.89
3100	8	5.1 –24.5	166	0.90
3200	7	7.7 –24.5	247	0.92
3300	4	14.0 –24.5	387	0.91
3405	3	16.0 –24.5	732	•••

III. RESULTS

Mercury

The absorption at $T_0=860°C$ is similar to that described[11] for 755°C. The initially sharp atomic line at 2537 Å is extensively broadened towards the red due primarily to perturbations of the energy level of the excited electronic state by neighboring atoms.[15] For wavelengths not too close to the peak absorption, the data are fit to within a few percent by parallel straight lines on a plot of $\log D_\lambda$ against $10^3/T_R$. Consistent with the predominant effect of pairwise interactions, the slope of these lines is twice that of the total vapor pressure. Between 600° and 930°K the vapor pressure of Hg is given to within better than 1% by the equation[16,17]

$$\log p_{Hg}(\text{atm}) = -3.08(10^3)/T + 4.891. \tag{1}$$

The data can be represented by

$$p_{Hg}(\text{atm}) = r_\lambda(D_\lambda/L)^{\frac{1}{2}}, \tag{2}$$

where L is the optical path length in millimeters and the values of r_λ are given in Table I. Also shown in this table are the number of data points taken and the low and high values of p_{Hg} covered at each wavelength. The last row gives the ratio of r_λ previously obtained[11] at $T_0=755°C$ to that obtained here for $T_0=860°C$. If the only effect of optical-cell temperature were to decrease the concentration of Hg atoms for a given

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[11] R. F. Brebrick and A. J. Strauss, J. Phys. Chem. Solids, **26**, 989 (1965).

[12] R. F. Brebrick and A. J. Strauss, J. Chem. Phys. **40**, 3230 (1964).

[13] The crystal of HgSe was kindly supplied by T. C. Harman.

[14] R. F. Brebrick, J. Chem. Phys. **43**, 3031 (1965).

[15] H. Kuhn and K. Freudenberg, Z. Physik **76**, 38 (1932).

[16] W. T. Hicks, J. Chem. Phys. **38**, 1873 (1963).

[17] S. Sugawara, T. Sato, and T. Minamiyama, Bull. JSME Japan Soc. Mech. Engrs. **5**, 711 (1962).

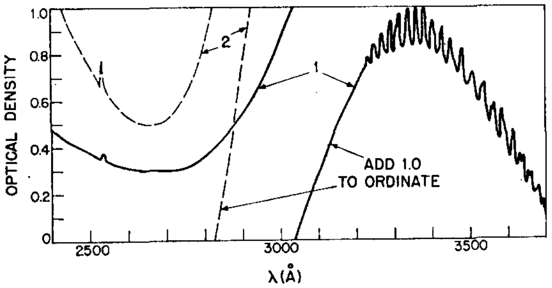

FIG. 1. Spectrum of the vapor over Se-saturated HgSe(c) for a 46.7-mm optical path at 860°C. For Curve 1, $p_{\mathrm{Hg}}=4.6(10^{-3})$ atm and the total selenium pressure, P_{Σ}, is $9.11(10^{-3})$ atm. For Curve 2, $p_{\mathrm{Hg}}=2.15(10^{-2})$ atm and $P_{\Sigma}=3.90(10^{-2})$ atm. The narrow peak at 2537 Å is due to Hg(g). The rest of the spectrum is that of $\mathrm{Se_2(g)}$.

value of p_{Hg}, the ideal-gas law would lead to

$$r_{\lambda}(755°\mathrm{C})/r_{\lambda}(860°\mathrm{C})=1.10.$$

In contrast the ratios observed are all near 0.9. The absorption decreases with increasing wavelength and is already weak at 3405 Å, where one of the strongly absorbing vibronic bands of $\mathrm{Se_2}$ is located. A slitwidth of 0.157 mm (nominal resolution of 3 Å) at

$$2500\leq\lambda\leq2600\ \text{Å}$$

was used in the above measurements. Measurements made up to $p_{\mathrm{Hg}}=1.5$ atm with a slitwidth of 0.08 mm showed no significant change in D_{λ} for the wavelengths listed.

In order to measure relatively low values of p_{Hg}, the optical density at the peak absorption, D_{2537}, was measured for $8.5(10^{-3})\leq p_{\mathrm{Hg}}\leq0.5$ atm with the usual slitwidth of 0.157 mm and for $8.5(10^{-3})\leq p_{\mathrm{Hg}}\leq3.8(10^{-2})$ atm with a slitwidth of 0.08 mm. As expected, $\log D_{2537}$ vs $10^3/T_R$ does not yield a straight line. The optical density is 1.75 times as large for a 0.08-mm as for a 0.157-mm slitwidth. For a 0.157-mm slitwidth D_{2537} is 25 and 5.7 times as large as D_{2550} for $p_{\mathrm{Hg}}=0.12$ and 0.52 atm, respectively.

The data taken for $T_0=700$°C are less extensive. For $0.12\leq p_{\mathrm{Hg}}\leq1.1$ atm, D_{λ} for 2550, 2560, 2570, and 2580 Å varies as the square of p_{Hg}. For $0.011\leq p_{\mathrm{Hg}}\leq0.33$ atm, $\log D_{2537}$ begins at low pressures as a straight line of slope -3.08 when plotted against $10^3/T_R$ but then increases more rapidly and finally less rapidly. At 0.1 atm, D_{2537} is 35 times as large as D_{2550} for a slitwidth of 0.157 mm, but at 0.48 atm it is only 8.0 times as large.

Hg-Saturated HgSe(c)

Between 396° and 659°C the spectrum of the vapor in the cell containing a 48.5-at. %-Se reservoir was that of pure Hg(g), the ratio of D_{λ} for various wavelengths being the same within experimental error as those observed with a pure Hg reservoir. Moreover at a given value of T_R the value of D_{λ}/L was the same as for a pure Hg reservoir indicating that (1) p_{Hg} over Hg-saturated HgSe is essentially the same as over pure Hg up to 659°C, and (2) the Hg-rich solidus of $\mathrm{Hg_{1-\mathit{x}}Se_{\mathit{x}}(c)}$ is at least 48.5 at. % Se up to 659°C. In analogy with results on $\mathrm{Hg_{1-\mathit{x}}Te_{\mathit{x}}(c)}$ and consistent with incomplete experiments on $\mathrm{Hg_{1-\mathit{x}}Se_{\mathit{x}}(c)}$ itself, one expects the homogeneity range of the selenide to be narrower than 1 at. % and to be located close to 50 at. %.[2,5] At 659°C, the mercury pressure was 37 atm and the optical cell failed. At this temperature the composition of the condensed phases was richer in Se than initially, due to preferential loss of Hg to the vapor phase, and was calculated to be 49.2±0.3 at. % Se. The Hg-rich solidus line of HgSe(c) at 659°C must contain more than this percentage of selenium.

Crystals of HgSe have been equilibrated with Hg between 255° and 600°C and quenched.[2,5] The room-temperature values for the difference in electron and hole concentrations, $n-p$, all fall in the range 3 to 6×10^{18} cm^3. The irregular variation of $n-p$ with equilibration temperature suggests this quantity is nearly independent of the equilibration temperature. Such behavior may of course be attributable to the quenching process, which was not investigated, but which may not have been fast enough. On the other hand, a nearly temperature-independent Hg-rich solidus line for HgSe(c) is consistent with, but not necessarily implied by, our finding that p_{Hg} is the same over pure Hg and HgSe that is as Hg-rich as possible.

Se-Saturated and Congruently Subliming HgSe(c)

The vapor absorption spectra for the 51.01 at. % Se reservoir appeared to be the sum of the spectra due to Hg(g) and selenium vapor as shown in Fig. 1. The Hg(g) absorption is relatively weak and shows up as a 3-to-18-Å-wide (at the base) peak, at 2537 Å, that occurs near a minimum in the selenium absorption. This minimum results from the overlap of a strong $\mathrm{Se_2}$ band system having its maximum near 3400 Å with a weaker band with maximum absorption near 2133 Å. The vibronic bands of $\mathrm{Se_2}$ are resolved and the ratio of the optical densities at five-band maxima between 3405 and 3978 Å are the same as for a pure Se reservoir. No evidence for a HgSe(g) species is seen.

The optical cell containing the unreacted elements whose over-all composition was 51.01 at. % Se gave a spectrum characteristic of pure Hg(g) when held for 1.5 h at each of the reservoir temperatures, $T_R=473$°, 517°, and 573°C. At higher temperatures the spectra of Hg(g) diminished and that of $\mathrm{Se_2(g)}$ grew. Finally after 1.5 h at 630°C the spectrum was steady, indicated a significant amount of $\mathrm{Se_2(g)}$, and was consistent with the optical densities obtained with the cell containing prereacted material. Measurements were then made up to 816°C. For $T_R\geq732$°C, the optical densities for this 22.1-mm optical path length were all greater than 2.0 for $2000\leq\lambda\leq4500$ Å. The optical densities at 5000, 6000, and 7000 Å went through maximum values near $T_R=727$°C and showed a sharp discontinuity in slope at about 799°C. Between 799° and 816°C they increased with increasing reservoir temperature.

The spectra obtained with the cell containing a crushed HgSe crystal are qualitatively similar to those shown in Fig. 1. However, they indicate a lower, total selenium pressure at a given reservoir temperature than obtained with Se-saturated HgSe(c). The values of D_λ were reproduced after part of the crushed HgSe was subject to sublimation under vacuum and sealed in a new cell. In view of the narrow homogeneity range of $Hg_{1-x}Se_x$(c) and the strong dependence of optical density upon the composition of the solid, we conclude that a stable, congruently subliming composition exists and was attained in these measurements.

The partial optical densities of Hg(g) at 2537 and 2550 Å were obtained[18] by making a linear interpolation between both tails of the 2537-Å peak and subtracting the optical densities given by this line from the total values measured. At a given reservoir temperature the partial optical densities of Hg(g) were larger for congruently subliming HgSe(c) than for Se-saturated HgSe(c), consistent with the fact that the total selenium pressure was lower. The ratio of the partial optical densities of Hg(g) obtained with 0.157- and 0.08-mm spectrometer slitwidths was close to that observed with a pure-Hg reservoir.

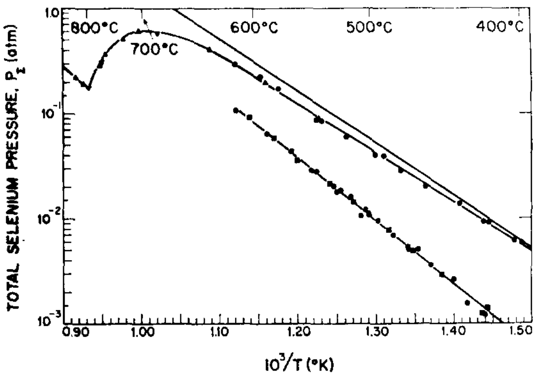

Fig. 2. Total selenium pressure on a log scale plotted against reciprocal absolute temperature. The uppermost line is for pure Se(l). Below 799°C the upper line through the data points is for Se-saturated HgSe(c) and the coexisting Se-rich liquid. Above 799°C it is for a 51.0 at. % Se liquid. ▼, indicates 16h at temperature. The lower line through data points is for congruently subliming HgSe(c). ■, $T_0=700$°C; ●, $T_0=860$°C.

Pressures

Extensive measurements using a pure Se(l) reservoir have been made and are discussed in detail elsewhere.[14] The values of P_Σ over HgSe were determined by first noting the temperature of a pure-Se(l) reservoir necessary to give the same value of D_λ/L as observed over HgSe and then calculating P_Σ from the vapor-pressure equation for Se(l) as given by Brooks[19]

$$\log P_\Sigma(\text{atm}) = -4.9895(10^3)/T+5.2078 \ (260°\text{–}670°\text{C}). \qquad (3)$$

(The vapor pressure equation of Illarionov and Lapina[9] gives values of P_Σ within 3% of those from Eq. (3) between 500° and 800°C.) The optical density used was the largest of those at 3405, 3792, 3978, 5000, and 6000 Å that was still small enough to be measured. However, all the measured optical densities generally led to closely agreeing values of P_Σ. The contribution of Hg(g) to the absorption at these wavelengths was negligible. To quantitatively illustrate the calibration results for selenium vapor, some of these are given below over limited pressure ranges where they take the simplest analytical form. For $T_0=860$°C and $10^{-4}\leq P_\Sigma \leq 0.2$ atm

$$P_\Sigma=0.236(D_{3405}/L) \qquad (4)$$

$$D_{3405}=2.35D_{3792}=4.88D_{3978}, \qquad (5)$$

where L is the optical path length in millimeters and the wavelengths are those at maxima of vibronic bands of Se_2. For $T_0=860$°C and $0.1\leq P_\Sigma\leq 1$ atm

$$(P_\Sigma)^{1.71}=9.43(D_{5000}/L). \qquad (6)$$

For $T_0=700$°C and $10^{-4}\leq P_\Sigma \leq 0.05$ atm

$$P_\Sigma=0.193(D_{3405}/L). \qquad (7)$$

The total selenium pressures were then calculated on the basis of the above assuming that P_Σ and p_{Hg} were individually constant throughout the optical cell and sidearm for each measurement. As is seen below, this assumption appears to be essentially valid, since the pressures derived from data for $T_0=860$°C and those derived from data for $T_0=700$°C are in close agreement.

The total selenium pressures are shown in Fig. 2. The top curve through the data points gives P_Σ along the three-phase line for Se-saturated HgSe(c). Along this curve the pressure reaches a maximum value of 0.62 atm between 717° and 727°C. At lower temperatures it asymptotically approaches the vapor pressure of pure Se. At higher temperatures it decreases to a value of 0.18 atm near 799°C, then increases again. The sharp discontinuity in slope corresponds to the liquidus point for 51.0 at. % Se. There are not sufficient data to establish the liquidus temperature precisely, but they do show the liquidus temperature is at, or somewhat below, 799°C. This is consistent with the reported[6] maximum melting point of 799°C for HgSe(c). There is no indication of the monotectic reported[6] at 686° ($10^3/T=1.043$) although the marked curvature of the three-phase line in this region and the scarcity

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[18] Only a few values at 2550 Å were large enough to be measured accurately.

[19] L. S. Brooks, J. Am. Chem. Soc. 74, 227 (1952).

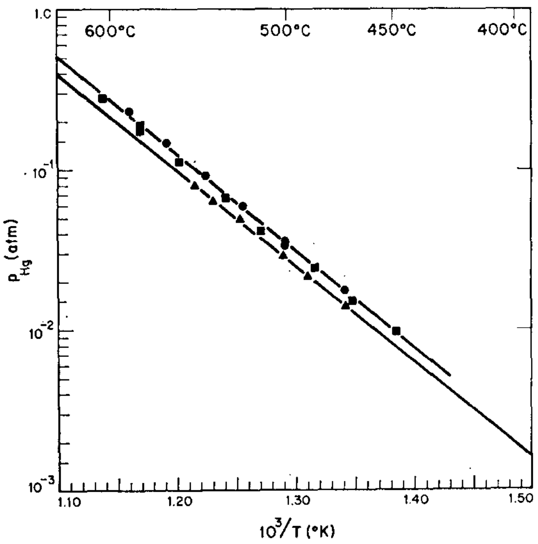

FIG. 3. Partial pressure of Hg(g) on a log scale plotted against reciprocal absolute temperature. The top line and data points are for congruently subliming HgSe(c). ●, $T_0=860$°C; ■, $T_0=700$°C. The bottom line and data points (▲) are for Se-saturated HgSe(c).

of experimental points could easily account for this. Up to 600°C the data are well represented by

$$\log P_\Sigma(\text{atm})=-4.71(10^3)/T+4.76. \tag{8}$$

The lower curve through the data points in Fig. 2 gives P_Σ over congruently subliming HgSe(c). The data obtained with the two cells at $T_0=860$°C agree closely and are not distinguished. The data obtained with the cell at 700°C are distinguished and their agreement with the 860°C data shows the absence of significant effects of thermal diffusion upon P_Σ. The data are well represented by

$$\log P_\Sigma(\text{atm})=-6.04(10^3)/T+5.82. \tag{9}$$

The value of P_Σ over Hg-saturated HgSe was too small to be measured up to $T_R=659$°C. An upper limit of $1.5(10^{-3})$ atm can be placed on P_Σ at 659°C.

The values of p_{Hg} for congruently subliming and for Se-saturated HgSe(c) are shown in Fig. 3 as the top and bottom lines, respectively.

For Se-saturated HgSe(c) between 473° and 550°C the data are well represented by

$$\log p_{Hg}(\text{atm})=-5.99(10^3)/T+6.17. \tag{10}$$

For congruently subliming HgSe(c) the values of p_{Hg} derived from 700° and 860°C optical-cell data agree at the lowest values where thermal diffusion effects should be largest. However, they diverge at higher pressures and ultimately differ by 14%. The two highest values of p_{Hg} derived from measurements with $T_0=700$°C were obtained from the partial optical densities of Hg(g) at 2550 Å which should be less sensitive to any pressure broadening by selenium species than the partial density at the 2537-Å peak. These two highest values fall close to the same straight line that best fits the lower values of p_{Hg} derived from data at $T_0=700$°C. The best straight line that fits all the values of p_{Hg} for congruently subliming HgSe(c) between 450° and 600°C is given by

$$\log p_{Hg}(\text{atm})=-5.90(10^3)/T+6.22. \tag{11}$$

In comparison, the transpiration of HgSe(c) in an argon stream has been measured[20] between 340° and 450°C. Quantitative chemical analysis and x-ray-diffraction patterns showed the sublimate to be HgSe. The data were analyzed assuming the predominant vapor species to be HgSe(g) and yielded

$$\log \bar{P}(\text{atm})=-7{,}521.92/T+8.183. \tag{12}$$

The data are reinterpreted here under the assumption that congruent sublimation was attained, that Hg(g) and selenium species are predominant, there being no species HgSe(g), and that

$$p_{Hg}=(FW/M_{Hg})(RT/V). \tag{13}$$

Here F is the weight fraction of Hg in HgSe,

$$F=M_{Hg}/M_{HgSe},$$

W is the weight transpired and the M's are formula weights. Then $\bar{P}$ of Eq. (12) is identical with p_{Hg} and can be compared with our result for congruently subliming HgSe given by Eq. (11). The agreement is not good, the value of p_{Hg} at 400°C given by Eq. (12) being about one-half that of our value given by Eq. (11).

IV. DISCUSSION

Results for Congruently Subliming HgSe(c) and the Thermodynamics of Selenium Vapor

Consistent with the existing data[2,5] the homogeneity range of $Hg_{1-x}Se_x$(c) is assumed to depart from 50 at. % by much less than 1 at. %. Then the compositions of the congruently subliming solid and its coexisting vapor are also essentially 50 at. % so that

$$p_{Hg}=\sum_j j p_{Se_j}, \tag{14}$$

where the sum is over all pure selenium vapor species. Thus for congruently subliming HgSe(c) the average number of atoms per molecular selenium species in the vapor is given by p_{Hg}/P_Σ, which from Figs. 2 and 3 lies between 3 and 3.5. Figure 4 shows the extent to which our measured values of p_{Hg}, shown as points, agree with values calculated using Eq. (14). The upper line gives p_{Hg} calculated from Eq. (14) using Eq. (9) for P_Σ and the equilibrium constants (given by Illarionov and Lapina[9]) for the dissociation of Se_8, Se_6, and Se_4 into Se_2. This line is about 15% high at the lowest pressures near 450°C. At the highest pressures it agrees

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[20] R. A. Isakova, V. N. Nesterov, and V. S. Yesiutin, Tr. Inst. Met. i Obogashch. Adad. Nauk. Kaz. SSR **8**, 6 (1963).

with the values of p_{Hg} obtained from measurements with an 860°C optical cell but is about 10% higher than the best line through all the measured data given by Eq. (11) (and shown in Fig. 3). The lower line gives p_{Hg} calculated again from Eq. (14) using Eq. (9) for P_Σ but now using the Se_2–Se_6 equilibrium constant given by Stull and Sinke.[21] This line agrees closely with our measured values of p_{Hg} except near the highest pressures where it is about 14% below the best experimental line given by Eq. (11). Thus our measured values of p_{Hg} and P_Σ for congruently subliming HgSe(c) are generally consistent with both sets of thermodynamic data for selenium vapor, although at not too high pressures the agreement with the data of Stull and Sinke is best. This is in contrast to measurements[14] of the optical density of pure selenium vapor which yielded values for the partial pressure of Se_2, p_2, between 400° and 860°C, in close agreement with those calculated from Illarionov and Lapina and significantly different from those calculated from Stull and Sinke. Since these latter measurements were more direct and the conclusions less dependent on small experimental errors, we assume below that the data of Illarionov and Lapina yield correct values for p_2.

Standard Gibbs Free Energy of Formation of HgSe(c)

Using the equilibrium constants of Illarionov and Lapina,[9] values of p_2 were calculated from the measured values of P_Σ for Se-saturated and congruently subliming HgSe(c) as given by Eqs. (8) and (9), respectively. These were combined with the corresponding measured values of p_{Hg} given by Eqs. (10) and (11) to obtain standard Gibbs free energies of formation using the equation

$$\Delta G^\circ_f[\text{Hg(g)}+\tfrac{1}{2}\text{Se}_2\text{(g)}=\text{HgSe(c)}]=RT\ln p_{\text{Hg}}p_2^{\frac{1}{2}}. \tag{15}$$

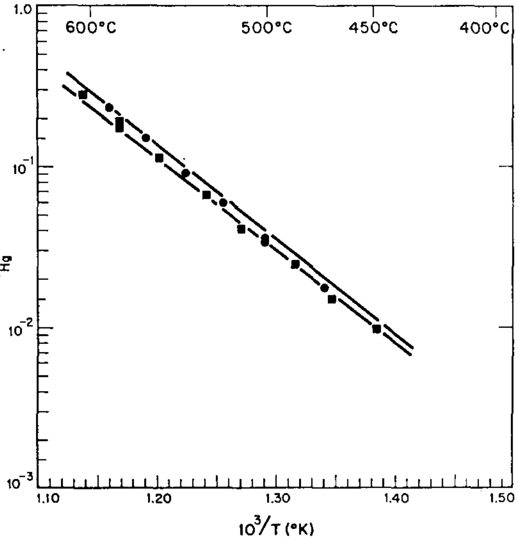

FIG. 4. Partial pressure of Hg(g) on a log scale plotted against reciprocal absolute temperature for congruently subliming HgSe(c). Experimental points shown. Upper line is calculated from measured value of P_Σ and data of Illarionov and Lapina[9] on selenium vapor. Lower line is calculated from measured value of P_Σ and data of Stull and Sinke[21] on selenium vapor. Circles obtained with $T_0=860$°C, squares with $T_0=700$°C.

TABLE II. Extrapolated thermodynamic functions for Hg(l)+Se(l, c)=HgSe(c).

T (°K)	$-\Delta H_f^\circ$ (kcal/mole)	$-\Delta S_f^\circ$ (eu/mole)	$-\Delta G_f^\circ$ (kcal/mole)
800	13.66	6.19	8.71
700	13.28	6.36	8.83
600	12.90	6.59	8.95
500	12.51	6.79	9.11
400	10.96	4.73	9.07
300	10.77	4.99	9.27

For Se-saturated HgSe between 470° and 550°C,

$$\Delta G^\circ_f=-41.12+41.50(10^{-3})T\ \text{kcal/mole}. \tag{16}$$

For congruently subliming HgSe between 450° and 590°C,

$$\Delta G^\circ_f=-42.72+43.29(10^{-3})T\ \text{kcal/mole}. \tag{17}$$

The free energies given by Eqs. (16) and (17) differ by 3% or less between 400° and 600°C. The standard enthalpy and entropy of formation are almost identical to those found[11] for the formation of HgTe(c) from Hg(g) and Te_2(g).

If the free energies of formation are calculated as before, but using the data of Stull and Sinke to obtain p_2 from the measured P_Σ, results essentially identical to those given by Eqs. (16) and (17) are obtained. The standard enthalpies agree within 0.2 kcal/mole and the standard entropies within 0.2 eu/mole.

In comparison with our average value for the enthalpy of formation of HgSe(c) at 800°K, −41.9 kcal/mole, Goldfinger and Jeunehomme[7] have given a value of −45 kcal/mole at 500°K. These authors subjected the effusion products of a Knudsen cell containing HgSe(c) in the effusion steady state[22] to mass spectrographic analysis and measured only the Se_6^+/Se_2^+ ion ratio. As a consequence, their calculated value for the enthalpy of formation of HgSe(c) is dependent upon the accuracy of the published values for a large number of quantities.

The use of Eq. (15) assumes exactly stoichiometric HgSe(c). The error introduced thereby is less than 0.04 kcal/mole if the compositions of Se-saturated and congruently subliming HgSe do not lie outside the range 49.5 and 50.5 at. % Se. [See Eq. (10) of Ref. 11.] Assuming the same limits of stability and knowing the values of p_{Hg} over Hg-saturated HgSe, the value of

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[21] D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements* (Am. Chem. Soc., Washington, D.C., 1956).

[22] R. F. Brebrick and A. J. Strauss, J. Phys. Chem. Solids **25**, 1441 (1964).

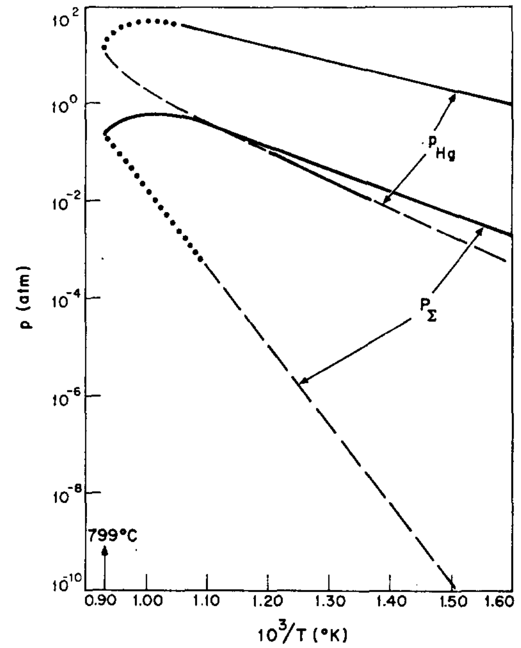

FIG. 5. Values of p_{Hg} and P_Σ along the three-phase lines of HgSe(c) as a function of reciprocal absolute temperature. Solid portions of curves are from measurements, dashed portions are calculated, dotted portions are best estimates.

p_2 over the latter can be bracketed [Eq. (12) of Ref. 11]. For Hg-saturated HgSe, $-8.11 \leq \log p_2 \leq -7.89$ at 450°C and $-5.28 \leq \log p_2 \leq -5.12$ at 600°C. Consequently, the standard Gibbs free energy of formation for Hg-saturated HgSe(c) can be calculated and lies within 0.3 kcal/mole of those given by Eqs. (16) and (17) for Se-saturated and congruently subliming HgSe(c), respectively.

The enthalpy and entropy of formation of HgSe(c) from Hg(l) and Se(l) at 800°K were calculated from average values of the enthalpies and entropies given by Eqs. (16) and (17); the heat and entropy of vaporization of Hg(l) to Hg(g) deduced from Eq. (1); and the heat and entropy of vaporization of Se(l) to Se_2(g) deduced from the results of Illarionov and Lapina.[9] These latter quantities are 28.34 kcal/mole of Se_2(g) and 27.66 eu/mole, respectively, and differ from the values of Stull and Sinke[21] by about 3%. The changes in the enthalpy and entropy of HgSe(c) between 800° and 300°K were then calculated using $C_P[\text{HgSe(c)}] = 10.89 + 3.37(10^{-3})T$ cal/mole. This heat capacity is based on a measured value[23] at 300°K of 11.90 cal/mole and the approximation[24] that $C_P = 14.5$ cal/mole at the melting point. Combining these changes with the corresponding changes for Hg(l)[16] and Se(l, c)[21] in the literature, the standard enthalpy and entropy of formation of HgSe(c) from Hg(l) and Se(l, c) was calculated between 800° and 300°K. The results are shown in Table II. The value for $\Delta H^\circ_{f,300}$ of -10.8 kcal/mole is almost twice as large as older values[8,23] of -5.1 kcal/mole. It is significantly lower than the recent value of -14.0 kcal/mole obtained by Goldfinger and Jeunehomme.[7] We believe our result ought to be somewhat more reliable in view of the more direct determination of the enthalpy at 800°K from which it is derived.

Complete Three-Phase Lines

The complete three-phase lines for HgSe(c) are shown in Fig. 5 for both p_{Hg} and P_Σ. The solid portions are measured values. The dashed portions are calculated, that for P_Σ over Hg-saturated HgSe as indicated in the last section. The value of p_{Hg} over Se-saturated HgSe(c) above 600°C was calculated from the measured value of P_Σ and Eq. (15). Equation (16) was used for ΔG°_f and the equilibrium constants of Illarionov and Lapina[9] were used to obtain p_2 from P_Σ. The dotted portions of the three-phase lines were sketched in to be consistent with the calculated and measured portions and a maximum melting point of 799°C.[6]

ACKNOWLEDGMENT

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[23] P. V. Gul'tyaev and A. V. Petrov, Sov. Phys. — Solid State **1**, 330 (1959); [Fiz. Tver. Tela **1**, 368 (1959)].

[24] O. Kubaschewski and E. Evans, *Metallurgical Thermochemistry* (John Wiley & Sons, Inc., New York, 1956), p. 183.