obtained, the plot gives calculated values (dashed lines), determined for one component from the measured values for the other, or estimated values (dotted lines). Analysis of the data shows that Hg-saturated HgSe(c) is in equilibrium with essentially pure Hg(ℓ) up to 659°C and contains at least 48.5 atomic-percent selenium. The maximum value of p_{Hg} over HgSe(c) is estimated to be about 50 atm. The maximum value of p_{Σ} is 0.62 atm, the pressure over Se-saturated HgSe(c) near 722°C.

Values of p_{Hg} and p_{Σ} in equilibrium with congruently subliming HgSe(c) were measured between about 450° and 600°C. The data are well represented by the expressions $\log p_{Hg}(atm) = -5.90(10^3)/T + 6.22$ and $\log p_{\Sigma}(atm) = -6.04(10^3)/T + 5.82$. The experimental values of p_{Hg} agree closely with those calculated from the measured values of p_{Σ} by applying the condition that the atom fractions of mercury and selenium in the congruently subliming vapor are essentially equal and using the published[7] equilibrium constants for the dissociation of $Se_4(g)$, $Se_6(g)$, and $Se_8(g)$ into $Se_2(g)$.

Since both p_{Hg} and p_{Σ} were measured for congruently subliming and Se-saturated HgSe(c), these data could be used to calculate the standard Gibbs free energy of formation of HgSe(c) according to the expression $\Delta G_f^{\circ}[Hg(g) + 1/2\ Se_2(g) = HgSe(c)] = RT \ln p_{Hg} p_2^{1/2}$. The values of p_2, the partial pressure of $Se_2(g)$, were calculated from the measured values of p_{Σ} by using the published[7] equilibrium constants for Se vapor. The values of ΔG_f° obtained for congruently subliming and Se-saturated HgSe(c) are the same within the limits of experimental error. Taking the average gives $\Delta G_f^{\circ} = -41.92 + 42.40(10^{-3})\ T$ kcal/mole between about 450° and 600°C. These are the first values which have been reported for the free energy of formation of HgSe(c). Values of $\Delta H_f^{\circ} = -10.8$ kcal/mole and $\Delta S_f^{\circ} = -4.99$ eu/mole are obtained for the formation of HgSe(c) from Hg(ℓ) and Se(c), all at 300°K, by extrapolating the free energy expression and using published thermodynamic data for HgSe(c), Hg(g, ℓ), and Se(g, ℓ, c).

R.F. Brebrick

C. THERMODYNAMIC STUDIES OF InTe PRESSURE-TEMPERATURE DIAGRAM

The pressure-temperature diagram for InTe has been reported previously.[8] The pressure at which the low-pressure phase, InTe (I), is transformed into the high-pressure phase, InTe (II), decreases with increasing temperature. The melting point of InTe (II) increases with increasing pressure. The melting curve of InTe (I) and the precise location of the InTe (I)-InTe (II)-InTe (liquid) triple point could not be determined. It was found that at sufficiently low temperatures InTe (II) can be retained at atmospheric pressure as a metastable phase.

As an extension of the pressure-temperature studies, two properties of InTe have been measured at atmospheric pressure: ΔV_f, the change in volume of InTe (I) on melting, and ΔH_t, the heat of transformation of metastable InTe (II) into InTe (I). These quantities are related to the slopes of the melting curve of InTe (I) and of the phase boundary between InTe (I) and InTe (II), respectively, by the Clausius-Clapeyron equation: $dT/dP = T\Delta V/\Delta H$, where T is the absolute temperature of the phase transition, P is the pressure, ΔV is the change in volume, and ΔH is the heat of transition.

The value of ΔV_f for InTe (I) at 696°C and 1 atm was determined by the method of fed and unfed castings, as modified by Ball.[9] The densities found by this method for solid and liquid InTe at the melting point are, respectively, 5.845 ± 0.081 g/cm^3 (average of six determinations)

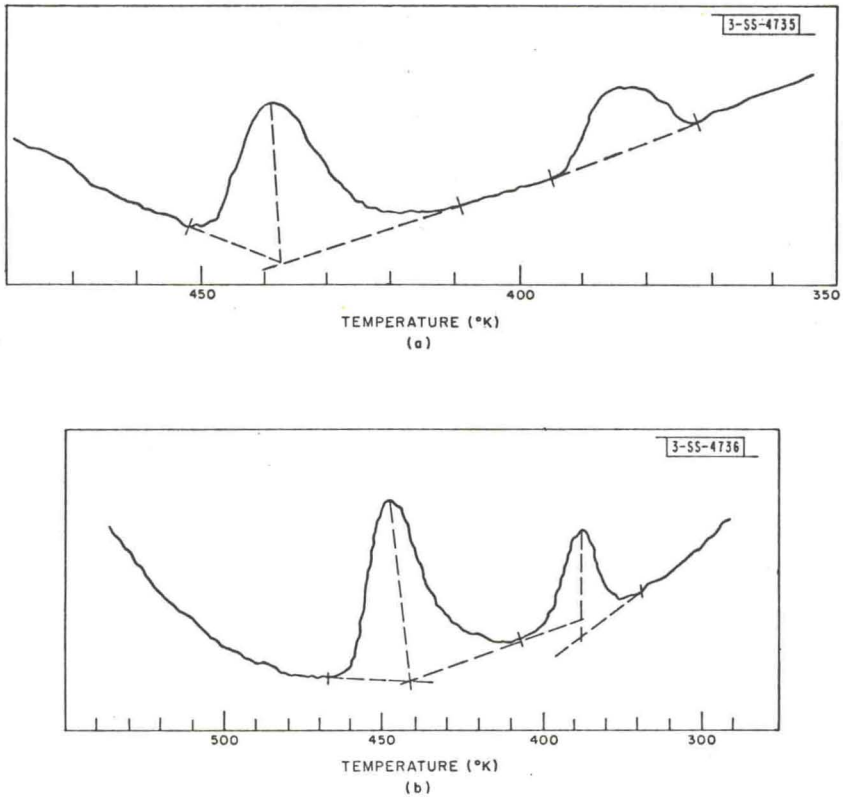

Fig. III-3. Recorder traces obtained during two differential-scanning calorimeter runs in which high-pressure form of InTe, InTe (II), was transformed into low-pressure form, InTe (I). Abscissa and ordinate give temperature in degrees Kelvin and power in arbitrary units, respectively. Dashed lines are estimated base lines used in determining areas under power peaks. (a) Heating rate: 20 deg/minute. (b) Heating rate: 40 deg/minute.

and 5.733 ± 0.033 g/cm^3 (average of seven determinations). The corresponding molar volumes are 41.48 ± 0.44 and 42.28 ± 0.27 cm^3/mole, respectively, and the value of ΔV_f is therefore 0.80 ± 0.72 cm^3/mole. Substituting this value for ΔV_f and the measured[10] value of 4.29 kcal/g-atom for ΔH_f into the Clausius-Clapeyron equation gives dT_f/dP = 2.16 deg/kbar as the initial slope of the melting curve for InTe (I). If this slope does not change with pressure up to the triple point, the InTe (I) melting curve intersects the InTe (I)-InTe (II) phase boundary at 11 kbar and 718°C. This location for the triple point is close to the one estimated previously.[8]

Values of ΔH_t for the InTe (II) → InTe (I) transition at atmospheric pressure were obtained by both metal-solution and differential-scanning calorimetry. The first method was used to determine ΔH_t at 0°C by comparing the temperature changes which occurred when samples of InTe (I) and InTe (II) initially at 0°C were separately dissolved in molten bismuth initially at 350°C. The final concentrations of indium and tellurium in the bismuth bath were kept below 2 atomic-percent so that the calculations could be made for the case of infinite dilution. The calorimeter was calibrated by adding bismuth initially at 0°C to the bismuth bath. Details of the experimental technique and calculation procedure are given elsewhere.[11] The value of ΔH_t found by this method is 0.44 ± 0.01 kcal/g-atom.

The value of ΔH_t was also determined with a differential-scanning calorimeter (Perkin-Elmer Model DSC-1). In this apparatus the sample and an inert standard, which are sealed into separate aluminum-foil capsules, are heated at a constant rate by independent resistance heaters. The differences in heater power required to keep the sample and standard temperatures equal throughout the run are recorded as a function of temperature. When one stable phase is transformed into another, a peak appears on the recorder chart at the transformation temperature, and the area under the peak is proportional to ΔH_t. Although there is no thermodynamically defined temperature for the transformation of a metastable to a stable phase, ΔH_t for such a transition can also be measured by scanning calorimetry if the rate of transformation is strongly temperature dependent. In that event, for sufficiently rapid heating rates the transformation occurs predominantly within a narrow temperature range and produces a well-defined exothermic peak. In the present experiments, two such peaks were observed in each run, as seen in the typical recorder traces shown in Figs. III-3 (a-b). These traces were obtained for heating rates of 20 and 40 deg/minute, respectively.

The existence of two exothermic peaks indicates that the InTe (II) → InTe (I) transformation takes place in two steps, and therefore confirms the finding of Sclar, Carrison, and Schwartz[12] that at atmospheric pressure an intermediate phase, InTe (II)', is formed during the transformation. In eight runs, the temperatures at which the evolution of heat was first detected were 94 ± 6°C for the first peak and 134 ± 6°C for the second peak. These values are consistent with the results which Sclar, et al.,[12] obtained in their x-ray and metallographic studies. The relative quantities of heat liberated during the two steps differed considerably from run to run. The percentage of the total evolved during the first step ranged from 14 to 39 percent. However, the total heat liberated during the two steps was quite reproducible. The average value obtained for ΔH_t is 0.42 ± 0.03 kcal/g-atom, in excellent agreement with the result found by metal-solution calorimetry.

The value of ΔH_t for the InTe (II) → InTe (I) transformation at room temperature and 30 kbar can be calculated according to the Clausius-Clapeyron equation from the measured[8] slope of the

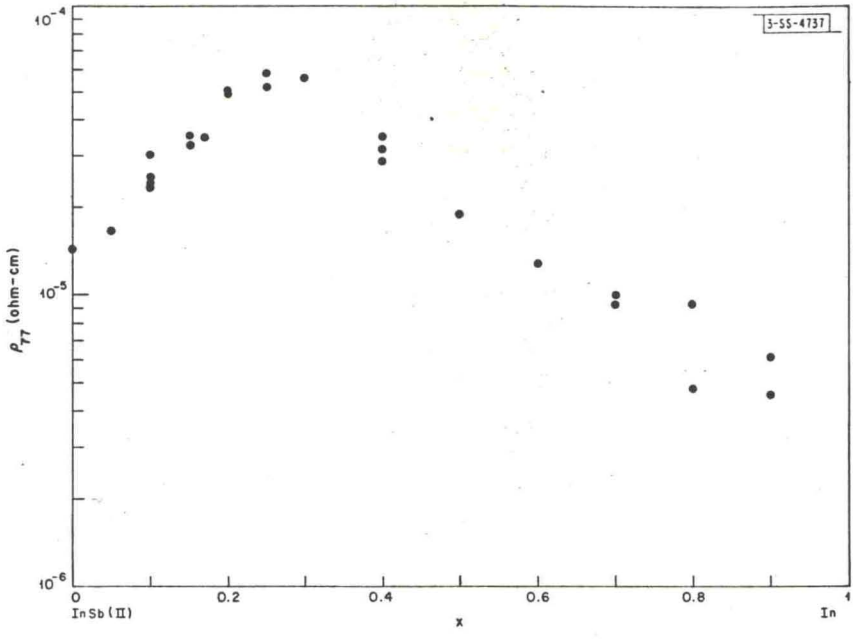

Fig. III-4. Resistivity at 77°K (ρ_{77}) vs composition for the high-pressure InSb-In system. Composition parameter is x in formula $InSb(II)_{1-x}(2\ In)_x$.

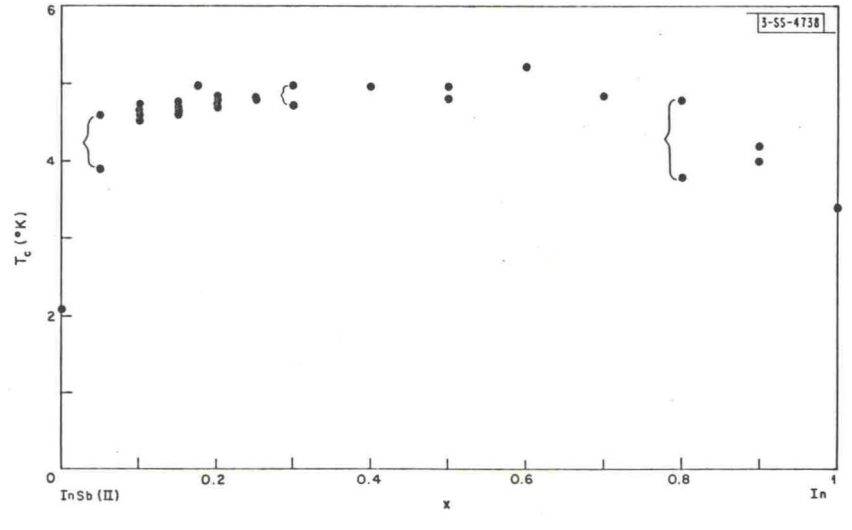

Fig. III-5. Superconducting transition temperature (T_c) vs composition for high-pressure InSb-In system. Where there are two bracketed points, two discrete transitions were observed.

InTe (I)-InTe (II) phase boundary and the value of ΔV_t obtained from the x-ray densities of the two phases at atmospheric pressure and their compressibilities[13] between 1 atm and 30 kbar. The calculated value of ΔH_t is 0.21 kcal/g-atom, only about half the calorimetric value for 1 atm. The difference indicates that the average pressure coefficient of heat content is greater for InTe (I) than for InTe (II) by about 8×10^{-6} kcal/(g-atom)-atm between 1 atm and 30 kbar.

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