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Vapor Pressure of Indium Chloride and Some Implications for the In-Se System

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The optical absorbance of the vapor over InCl in the ultraviolet spectrum was measured. Comparison with the published vapor pressure yields a Beer's law constant of 0.00143 atm-cm for the 267.6 nm peak, and a 1273 K optical path. The spectrum is found to match unidentified peaks found in a recent study of the In-Se system. The amount of InCl in the In-Se samples of the recent study was calculated and was found to be by weight and of negligible influence on the partial pressures obtained there. However, on the basis of the results obtained here and on those from the recent study of the In-Se system, it appears likely that the published partial pressure of the subselenide over 33.3 at.%Se (In-Se) is in error and is actually that of an InCl impurity.

1. Introduction

The current study yields information on the In-Cl system and enables the resolution of some ambiguities in a recent extensive study (Ref 1) of the In-Se system. The spectrum of InCl(g) in the ultraviolet range was obtained, and, using the published vapor pressure of InCl(s), the Beer's law constants for the InCl(g) peaks were established. These include the strong 266.6 and 267.6 nm peaks. A comparison of the InCl(g) spectrum with unidentified peaks observed in the In-Se study (Ref 1) shows that the latter are due to InCl(g). (See the 266.6 and 267.6 nm peaks in Fig. 4 of Ref 1.) Although the InCl(g) peaks were easily observed in the In-Se study, one can now conclude the total weight of InCl(g) present was most likely to be too low to affect the partial pressures of Se_2(g) and In_2Se(g) that were measured. Moreover, measurements on one of the two pure In sources used in the In-Se study also showed the presence of InCl(g) and so established the In as the source of the impurity. Finally, the discrepancy between the results of Ref 1 and a determination of the total pressure over 33.3 at.%Se (In-Se system) now seems likely to be due to the erroneous identification of InCl(g) as In_2Se in the total pressure study.

2. Experimental

$InCl_3$ was synthesized by dissolving In in HCl, evaporating it to dryness, then subliming the material at 660 K in a vacuum of about 10^{-6} atm. Then 0.126 g of the white trichloride flakes and 0.139 g of In were sealed in a T-shaped optical cell of fused silica at about 10^{-9} atm. These weights correspond to slightly more than 2 mol of In per mole of the trichloride, enough to give InCl + In on complete reaction. The optical cell, furnace, and general procedure were the same as those used in the previous study (Ref 1). A 15.2 cm long evacuated cell was placed against either side of the T-shaped optical cell to displace hot air from the optical path. The path of the optical cell containing the sample was 2.51 cm long. The sample in the end of the sidearm was held at 710 K with the cell proper at about 843 K for about 15 min, while an absorption spectrum was measured. The furnaces were cooled, and the furnace was opened to examine the sample in the sidearm. The optical cell was then heated to 1273 K, and the optical absorbance was measured with a 0.2 nm band-pass for a number of sample temperatures between 330 and 554 K.

A second optical cell containing In from one of the two sources used in the In-Se study was prepared, and the optical density measurements were made.

3. Results and Analysis

The first heating of the sample was above the 485 K melting point (Ref 2) of InCl(s), and prominent peaks starting at 266.6 and 267.6 nm had already appeared. Although the first two peaks overlap, on either side of them the absorbance is near zero, making them stand out. In contrast, the peaks of Se_2 overlap strongly so that the absorbance at the minima between peaks is about 90% that of the peaks themselves. The peak positions matched the positions of the band heads (Ref 3, 4) of InCl(g) to within about 0.4 nm. In view of this and the fact that InCl(g) is the predominant vapor species above InCl(s,l) (Ref 5, 6), it appears that the reaction between In and its trichloride was rapid. On cooling, the sample consisted of yellow flakes, which is characteristic of one allotropic form of InCl, along with some orange hemispheres, which presumably were a mixture of the yellow and red forms.

The same six peaks were observed with the 1273 K optical path and were at 266.6, 267.6, 270.0, 272.2, 273.4, and 275.0 nm. Again to within 0.4 nm, these matched band heads attributed to InCl and obtained at higher resolution (Ref 3, 4). Moreover, they also matched the unexplained

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peak positions seen in the In-Se study (Ref 1), and those can now be attributed to InCl. On a plot of the logarithm of the absorbance, D_λ, against reciprocal temperature the peaks fall on parallel straight lines. The absorbances at 276.6, 266.6, 270.0, 272.2, and 273.4 nm are in the ratio 1.0 to 0.8 to 0.20 to 0.06 to 0.032. The absorbance at 275.0 nm is lower and is too small to be measured accurately. For six values between 0.08 and 0.8, the strongest absorbance at 267.6 nm is given by:

$$\log_{10} D_{267.6}(2.51\ \text{cm}\ 1273\ \text{K}) = -4608/T + 8.1106;\ 495\text{–}559\ \text{K} \qquad \text{(Eq 1)}$$

Of the four published determinations of the vapor pressure (Ref 6-9), the slopes on a log pressure-reciprocal temperature plot obtained by Kuniga et al. (Ref 7) and by Robert (Ref 9) were −4580 and −4632, respectively, and were closest to that in Eq 1.

Taking a value of $5.74(10^{-5})$ atm at 500 K from Kuniga et al. (Ref 7), one obtains a Beers law constant of α = 0.00143 atm-cm for the 267.6 nm peak and a 1273 K optical path, where α is defined by:

$$P(\text{InCl, atm}) = \alpha D_{267.6}/L\ (\text{cm}) \qquad \text{(Eq 2)}$$

The Beer's law constants for the other wavelengths can be calculated from the ratios given just before Eq 1. Karlicek et al. (Ref 10) measured the absorption of InCl for a 973 K optical path. They used a 2 nm band-pass, which was ten times larger than the authors', and so did not resolve all the peaks. For 267 nm, they obtained an absorption coefficient of 51,000 ± 500 L/mol. From this, one calculates a Beer's law constant for a 1273 K path of 0.00421 atm-cm, which is about three times larger than our value for the 267.6 nm peak. With the 1273 K optical path and for sample temperatures as high as 528 K, the authors did not see the six peaks that are centered at about 350 nm that were reported by Kuniya and Hosada (Ref 11) for optical paths of 873 K and lower. For a 1273 K optical path, these are at least 50 times weaker than the 267.6 nm peak.

As mentioned above, the absorbance peaks observed here for InCl also matched those seen in the In-Se study (Ref 1), in which the absorbance peaks increased with increasing In content. With the use of the Beer's law constant obtained here, the partial pressure of InCl was calculated. It was found to vary weakly with the sample temperature from 1.63×10^{-5} atm at 584 K to 6.40×10^{-5} atm at 1080 K. At 1080 K, the partial pressure of In_2Se was 3×10^{-4} atm. Assuming the partial pressure of InCl was constant throughout the optical cell, then at 1083 K the total weight of InCl in the vapor phase was 4×10^{-6} g. Making the further, quite plausible assumption that essentially all of the InCl was in the vapor phase, the weight of InCl was about one-millionth that of the total sample weight. This most likely is too low to have significantly affected the partial pressures of Se_2 and In_2Se.

The cell containing the pure In also showed the InCl(g) peaks, identifying the 30-year-old In as the source of the InCl impurity.

Finally, the Beer's law constants for In_2Se(g) in Ref 1 were obtained by combining measured optical densities with published total pressure measurements made with a silica Bourdon gage (Ref 12) on a 50 at.% Se sample at 1000 K and above. Thus, there is a forced consistency between the optical density and the Bourdon gage measurements for this composition. However, the partial pressure of In_2Se over the 33.3 at.% Se sample obtained in Ref 1 is much lower than that obtained in another silica Bourdon gage measurement by the same authors (Ref 13). (J.H. Greenberg is the anglicized version of the first author's name in Ref 12). In Ref 1, the partial pressure of the subselenide reaches 10^{-4} atm only at 1000 K, which is consistent with the vapor pressures of other subchalcogenides (Fig. 5 of Ref 1). In the Bourdon gage measurements, the partial pressure of the subselenide was reported as 7×10^{-4} atm at 555 K and with a low enthalpy of vaporization of 12 kJ/mol. The Bourdon gage result is similar to the behavior of InCl(g) in the In-Se study described above. It is speculative, but the authors believe that it is likely that the samples in the Bourdon gage study also contained an InCl impurity the partial pressure of which was identified as that of the subselenide. The InCl impurity would tend to dominate the vapor phase for In-rich compositions and for temperatures below ~900 K.

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