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## ABSTRACT

The indium sesquisulfide phase is shown by x-ray diffraction and mass spectrometer measurements to have a wide solution range at 600 to 800°C. The existence of InS and $In_5S_6$ (here identified as $InS_{1.12}$) is confirmed and the existence of $In_3S_4$ is disproved.

Mass spectrometer intensities vs time for $In_2S^+$ and $S_2^+$ are used to obtain values of the partial pressures of $In_2S$(g) and $S_2$(g) as functions of composition in the range from InS(s) to $InS_{1.5}$(s).

At 600 to 800°C the heat of formation of the indium sesquisulfide phase from liquid indium and $S_2$ gas is 0.37y - 44.3 kcal/g at., where y is the at.% In, and the corresponding heat of formation of $InS_{1.12}$ is -27.7 kcal/g at. and of InS is -26.5 kcal/g at.

For determination of the partial pressures of vapor species in multicomponent systems by a dynamic method (such as the Knudsen-effusion method), a choice of conditions that yield pressures which do not change with time at constant temperature is usually necessary. Time-independent pressures for a two-component system can be obtained by bringing two condensed phases to equilibrium with the vapor. Some, but not all, two-component systems have compositions of congruent vaporization that can also be studied by dynamic-pressure-measurement techniques. The pressures that characterize single-phase compositions of incongruent vaporization are not readily studied.

If, however, the variations in both composition and pressure can be determined as functions of time at constant temperature, a dynamic method for pressure measurement can be used to obtain pressure-vs-composition data in single-phase regions of arbitrary compositions. The mass spectrometer should be especially suitable for obtaining such data, because with a mass spectrometer continual records of the partial pressures of all species in a complex vapor can be obtained. But apparently no experimental evaluation of this use of the mass spectrometer has been made. The principal purpose of this paper is to report the results of such an evaluation.

The indium sesquisulfide phase was chosen for study (a) because the partial pressures of the two major vapor species at the composition of congruent sublimation were accurately known as a function of temperature,[3] (b) because the vapor pressure range is a convenient one for study with a high temperature mass spectrometer, and (c) because our preliminary investigations revealed the indium sesquisulfide phase to have a relatively wide solid solution range at high temperatures. As a preliminary to the mass spectrometer investigations, x-ray-vs-composition studies were made to establish the stable phases to be expected at 600 to 800°C.

## X-RAY DIFFRACTION PATTERN-VS-COMPOSITION STUDIES

Previous investigators identified the phases $In_2S_3$, $In_5S_6$, and InS by x-ray diffraction examination of room temperature samples.[4] A phase of approximate composition $In_3S_4$ ($InS_{1.33}$) was inferred from cooling curves and differential thermal analysis to be stable above 370°C.

In the present study, room-temperature diffraction patterns of indium sesquisulfide which had been heated at about 600° with excess sulfur were found to be identical to the diffraction patterns of $\beta$-$In_2S_3$. Samples of composition between 42.0 and 42.5 at.% indium, prepared by heating elemental indium with $In_2S_3$, showed a single phase with the 40% ($\beta$-$In_2S_3$) structure, but with contractions in the unit-cell volume. Samples whose compositions were 43 to 45% indium yielded x-ray patterns of the contracted $In_2S_3$ phase and of a second phase. The second phase was obtained pure by quenching a sample in the mass spectrometer at a composition for which the ion intensities were rapidly changing with time.

The diffraction pattern of the second phase agreed in spacing and approximate intensities with the pattern of a phase previously reported to have the approximate formula $In_5S_6$,[5] but the present study indicates a composition somewhat richer in indium. We will call the phase $InS_{1.12}$ in this paper.

The x-ray diffraction pattern of the 50 at.% In sample appeared to be that of a third single phase, identified thus as InS, and patterns of samples ranging from 47 to 50 at.% In contained lines of both InS and $InS_{1.12}$. The

InS pattern,[6] however, differed from the one reported by Schuffle.[7] Perhaps there are two crystallographic modifications of InS. A sample of overall composition $In_2S$ yielded the diffraction patterns of indium and of InS.

Since the mass spectrometer studies yielded further information on the composition of stable indium sulfide phases, a final evaluation of the x-ray data is deferred to the discussion section.

## MASS SPECTROMETER STUDIES

Experimental.---Samples of overall compositions 42 to 50 at.% indium were prepared by heating indium sesquisulfide with excess indium in sealed, evacuated fused-silica tubes. Indium sesquisulfide samples, which were slightly enriched in sulfur, were prepared by adding sulfur to congruently subliming indium sesquisulfide and heating in a fused-silica tube in vacuo.

Samples were introduced into a cylindrical, fused-silica Knudsen cell 1.5 cm high and 1.2 cm in diam. The fused-silica lids had cylindrical orifices that were 1.6 mm long and had one of three different diameters: 0.86, 1.22, or 1.80 mm. The cell was placed inside a tantalum crucible fitted with a tantalum lid. The bottom of the cell was ground flat and a 2-mil strip of tantalum was placed between the walls of the cell and crucible in order to effect better heat transfer. The entire assembly was supported by three tungsten rods inside an Inghram-type mass spectrometer and was heated by radiation from two concentric tungsten filaments.

Temperatures were measured with a Pt-Pt 10% Rh thermocouple embedded in a cavity in the bottom of the tantalum crucible. The thermocouple was calibrated against another Pt-Pt 10% Rh thermocouple inserted through the orifice into the Knudsen cell and immersed in an indium sesquisulfide sample. Two independent calibration runs deviated by 8° at 600°C and 3° at 800°C.

Identification of $In_2S_{2.96}(s) = In_2S(g) + .98S_2(g)$ as the principal reaction at the composition of congruent sublimation was reported in our previous paper.[3] Recent analyses of our samples by Pankratz[8] indicate that the composition of congruent sublimation is $In_2S_{2.90}$ or $InS_{1.45}$. Our thermodynamic data are not significantly altered by this compositional change.

As a test of the reliability of our mass spectrometer studies, variations of ion intensities with temperature at the congruent composition were measured for comparison with our previous weight-low measurements, which are inherently more precise. Plots of $-R\ \ell n\ (I_{In_2S} I_{S_2} T^2)$ vs 1/T for indium sesquisulfide at the composition of congruent sublimation yielded for the heat of reaction 130, 136, 141, 142, 143, and 145 kcal/mole at 1000°K with an average of 139.5 ± 4.4 kcal/mole, compared to 141 kcal/mole from the weight-loss experiments. The variations in the temperature scale noted during the calibration runs are enough to cause 6 kcal variation in the measured slopes.

Indium-rich samples were heated at 600°, 650°, 700°, 750°, and 800°C and sulfur-rich samples were heated at 600°, 650°, 700°, and 750°C. During each run the intensities of the ions $In_2S^+$ and $S_2^+$ were alternately recorded on a strip chart until the ion intensities became constant with time (Fig. 1). The sample was then quickly cooled to room temperature. The samples were weighed before and after heating, and x-ray diffraction photographs of the powders were made before and after each run.

Several samples, initially about 50-at.% indium, were heated in the temperature range 600° to 750°C; all showed constant ion intensities at first, then a rapid change in intensities in a very short time period (Fig. 2). The rapid change indicated that a narrow, single-phase region was being traversed. The experiment was repeated, therefore, at 700°C and the sample was quickly cooled when the middle of the composition of sharp intensity change was reached. An x-ray diffraction pattern was obtained for the product, which was calculated to have an overall composition of 47.1 at.% indium, corresponding to $InS_{1.12}$, with an uncertainty of about 0.5% in this composition.

The ion $In_2O^+$ was observable during heating of indium sesquisulfide whenever an air leak developed in the vacuum system, even though the residual pressure was less than $10^{-6}$ torr. The ion $InGaS^+$ was seen when indium sesquisulfide was heated subsequent to several runs during which large amounts of GaN had been vaporized in the mass spectrometer. These ions were at negligible intensities during the studies reported in the remainder of this paper.

Pressure-vs-Composition Data from Ion Intensity vs Time. --- Provided that the intensity of an ion that is produced from each major vapor species can be followed as a function of time at constant temperature, a pressure-vs-composition plot can be derived.

The pressure $P_i$ at any given time is related to the intensity $I_i$ by the equation $P_i = U I_i T$, where T is the absolute temperature and U is a constant which is dependent on the ionization cross section of the vapor species and on the response of the electron multiplier to each particular kind of ion.

The constant can be evaluated for $In_2S$ and $S_2$ because the partial pressure of each of these species is known at the known composition of congruent sublimation. The composition for congruent sublimation is fixed at $InS_{1.45\pm0.03}$ at 600°C to 825°C by analytical studies of Pankratz[8] of samples heated at 825°C in vacuo and by the fact, demonstrated in experiments discussed later, that temperature changes in the 600 to 825°C range of a sample, which was known from its unchanging ratio $In_2S^+/S_2^+$ to sublime congruently, produced only small, temporary variations in the ion ratio. From the Knudsen-effusion weight loss experiments, the partial pressures of $In_2S(g)$ and $S_2(g)$ can be calculated with a probable absolute error of about 20%, compared to estimated errors of factors of 2 to 3 when usual calibration techniques that require estimation of ionization cross sections[9] are employed.

With pressures determined from the ion intensities, the remaining problem is to calculate the compositions that correspond to these pressures. The total weight loss $\Sigma Y_j$ for each ion must first be related to the intensity-vs-time data to obtain the relationship. For each ion $\Sigma Y_j$ was calculated from

$$\sum_0^t Y_j = \frac{\sum_0^t I_j P_f A k \Delta t}{I_f} \left( \frac{M_j}{T} \right)^{\frac{1}{2}} 2.66 \times 10^6 \quad , \qquad (1)$$

where $\Sigma I_j$ is the sum of the average intensities over time intervals $\Delta t$ in minutes for ion j, $I_f$ is the final intensity of ion j (at the compositions for congruent sublimation), $P_f$ is the partial pressure at the congruent sublimation point (i.e., the pressure that produced the measured intensity $I_f$), A is the orifice area in square cm, k is the Clausing correction,[10] and M is the molecular weight of the vapor species.

As a first approximation, the composition for congruent sublimation was assumed to correspond to stoichiometric indium sesquisulfide. The sums of the calculated losses by vaporization of $In_2S$ and $S_2$ are compared with directly measured losses in Table I. Most of the claculated weight losses agree with the directly measured weight losses to within a factor of 2. However, at 758°C the vaporization of the 46.1 at.% indium sample produced a measured weight loss 6 times the calculated value, and at 600°C vaporization of the sulfur-rich sample produced a weight loss of 5 times the calculated value. These high losses are believed to be due in part to escape of vapor between the crucible and lid rather than through the orifice, and in part to errors in temperature measurement.

A constant factor, $\alpha$, was applied to Eq. (1) to correct both $Y_{In_2S}$ and $Y_{S_2}$ so that the calculated weight loss would agree with the directly measured loss. The final composition was then calculated from the known initial weight and composition of the condensed phase, the weight of $In_2S$ and $S_2$ molecules vaporized, and the final weight of sample.

If this calculated composition for congruent sublimation differed from the stoichiometric composition, a second approximation was made in which the partial pressures that characterize the composition for congruent sublimation, calculated in the first approximation, were assumed to be the final pressures. These pressures were calculated assuming that the free energy of vaporization per gram atom for the indium sesquisulfide solid solution region is independent of composition. The final results of this study demonstrate this approximation to be valid to within a few tenths of a kilocalorie, except possibly at the lowest temperatures studied.

Table I. Comparison of observed and calculated weight losses.

| Temp (°C) | Initial composition | Obs wt. loss (Mg) | Calc wt. loss (Mg) | Calc / Obs |
|---|---|---|---|---|
| 598 ± 8 | $In_{.44}S_{.56}$ | 0.2 | 0.500 | 2.5 |
| 650 ± 7 | $In_{.44}S_{.56}$ | 0.8 | 0.602 | 0.75 |
| 703 ± 6 | $In_{.44}S_{.56}$ | 7.2 | 2.98 | 0.41 |
| 700 ± 6 | $In_{.50}S_{.50}$ | 15.1 | 12.8 | 0.85 |
| 758 ± 5 | $In_{.461}S_{.539}$ | 4.8 | 0.78 | 0.16 |
| 809 ± 3 | $In_{.44}S_{.56}$ | 16.5 | 30.7 | 1.8 |
| 600 ± 8 | Sulfur-rich | 0.2 | 0.04 | 0.2 |
| 650 ± 7 | " | 0.7 | 0.57 | 0.81 |
| 701 ± 6 | " | 2.2 | 1.00 | 0.45 |
| 754 ± 5 | " | 2.4 | 1.3 | 0.54 |

This gives the relationships

$$[P^{\circ}_{In_2S}]^{0.2}\,[P^{\circ}_{S_2}]^{0.2} = [P_{In_2S}]^{(1-x)/2}\,[P_{S_2}]^{(3x-1)/4}\ , \qquad (2)$$

and

$$\frac{P_{In_2S}}{P_{S_2}} = \left(\frac{1-x}{2}\right)\left(\frac{4}{3x-1}\right)\left(\frac{M_{In_2S}}{M_{S_2}}\right)^{\frac{1}{2}} \qquad (3)$$

where $P^{\circ}$ is the partial pressure at stoichiometry and x is the mole fraction of sulfur in the solid phase. The simultaneous solution of (2) and (3) provides partial pressures closer to those at the congruent-subliming composition.

The end composition calculated in the second approximation usually agreed to within 0.1 at.% with that of the first approximation, but this small correction is necessary to prevent anomalous reversal of calculated slopes of the partial pressure-vs-composition curves.

The composition at any time t could be obtained by correcting the initial sample composition for the summation of the losses of $In_2S$ and of $S_2$ by effusion. For each gas species

$$\sum_{o}^{t} Y_i = \frac{\sum_{o}^{t} I_i}{I_f}\, P_f A k \Delta t \left(\frac{M}{T}\right)^{\frac{1}{2}} c\ 2.66 \times 10^{6}\ , \qquad (4)$$

The compositions for congruent sublimation were calculated by the method described to be 40.5, 41.0, 41.2, 40.8, and 40.8 at.% indium at 600°, 650°, 700°, 750°, and 800°C. Experiments described below lead us to believe that the composition for congruent sublimation varies by only about 0.1 at.% in the temperature range studied. So the composition 40.8 at.% indium found by chemical analysis best identifies the composition of congruent sublimation over this temperature range. This composition of congruent sublimation must be considered uncertain by about 0.5 at.%. From similar analysis of samples prepared with excess sulfur, initial compositions are found to have been 40.3, 40.7, 40.6, and 40.5 at.% indium at 600°, 650°, 700°, and 750°C, i.e., all samples were sulfur-deficient relative to the stoichiometric composition.

By the procedure just outlined, the composition of the phase designated $InS_{1.12}$ was calculated to have compositions 47.9, 48.0 and 47.2 at.% indium at 600°, 650°, and 700°C, compared to 47.1 found by quenching a single-phase sample in the mass spectrometer. The width of this phase was found to decrease with increasing temperature. The calculated phase widths are: 3.3 ± 0.4, 2.8 ± 0.2, and 0.8 ± 0.1 at.% at 600°, 650°, and 700°C, respectively.

The results of an experiment in a fused-silica crucible to determine the variation in composition of congruent sublimation with temperature are summarized in Table IIA, which shows the temperatures, in the sequence followed, at which the sample was held, and the initial and final (i.e., steady-state) intensity ratios of $S_2^+$ to $In_2S^+$ that resulted.

A value of 0.6 to 0.7 is characteristic of the $S_2^+/In_2S^+$ ratio for congruent sublimation in our mass spectrometer. The high initial $S_2^+/In_2S^+$ ratio obtained when the temperature was first dropped to 768°C presumably resulted because the composition for congruent sublimation at 838°C was richer in sulfur than the composition for congruent sublimation at 768°C. Similarly the composition for congruent sublimation at 726°C presumably contains less sulfur than does the composition for congruent sublimation at either 768 or 838°C.

Table II. The $S_2^+/In_2S^+$ ratio above indium sesquisulfide immediately after a temperature change (initial) and after the composition has attained that for congruent sublimation at the same temperature (final).

| | Temp (°C) | Initial $S_2^+/In_2S^+$ | Final $S_2^+/In_2S^+$ |
|---|---|---|---|
| A | 838 | -- | 0.72 |
| | 768 | 1.2 | 0.67 |
| | 726 | 0.5 | 0.7 |
| | 838 | 0.4 | 0.7 |
| B | 800 | -- | 0.46 |
| | 750 | 4.1 | 0.59 |
| | 700 | 0.36 | 0.56 |
| | 800 | 0.61 | 0.55 |

That the composition for congruent sublimation did not shift continuously in a single direction with temperature was surprising. The experiment was repeated, therefore, in a graphite crucible for which the interior temperature had been carefully calibrated against the temperature on a thermocouple wedged against the bottom. The temperature sequence followed and the measured initial and final $S_2^+/In_2S^+$ intensity ratios are summarized in Table IIB. The results are similar to those found in silica.

From the time-vs-temperature plots obtained during the second of these composition-variation experiments, the maximum variation of the composition for congruent sublimation is calculated to be less than 0.1 at.%. However, when samples that had been equilibrated in the mass spectrometer at a composition for congruent sublimation at temperatures below 850°C were raised to a temperature of 880° to 950°C, the $S_2^+/In_2S^+$ intensity ratio initially rose from about 0.6 to 2.2. When a sample was held at these higher temperatures, the $S_2^+/In_2S^+$ ratio decreased to a constant value of 0.5. Samples quenched after this treatment have the same x-ray diffraction pattern as samples of overall composition 43 to 45 at.% indium.

Presumably, at about 850°C the composition for congruent sublimation under the steady-state conditions of our experiments coincides with the indium-rich phase boundary of the indium sesquisulfide solid solution, and at higher temperatures the composition for congruent vaporization moves to about $InS_{1.3}$ or $InS_{1.2}$ in the liquid solution range.

Samples whose initial compositions corresponded to InS were heated to 600°, 650°, 700°, and 750°C in the mass spectrometer long enough to move their compositions into the two-phase region between the $InS_{1.12}$

and indium sesquisulfide phases. The pressure-vs-composition plots derived from these data are presented in Fig. 3. At 750°C only the pressures in the two-phase region are known because the weight of the sample was not measured.

## DISCUSSION

Our diffraction pattern-vs-composition study indicates that a single-phase region extends from about $InS_{1.5}$ on the sulfur-rich side (the limit depends on the sulfur pressure and the temperature) to about $InS_{1.35}$ at the indium-rich phase boundary, and the pressure-vs-composition studies indicate still lower sulfur contents for the indium-rich phase boundary, $InS_{1.26}$ at 600°C and $InS_{1.17}$ at 700°C.

Quenching is often ineffective in preserving the compositions stable at annealing temperatures, and the limits of the partial pressure-vs-composition studies should be accepted as providing the better measure of the high-temperature solid solution limits.

On the other hand, the pressure-vs-composition curves show distinctly that no discrete phase of composition near $In_3S_4$ is stable in the temperature range between 600°C and 650°C, the approximate temperature at which the sesquisulfide phase boundary reaches this composition. Probably the thermal effect noted by Stubbs et al.[4] at 370°C was the precipitation of $InS_{1.12}$ from the supersaturated solution of indium in the indium sesquisulfide phase. Such precipitation reactions are necessarily exothermic.[11]

By means of the expression $\Delta F° = -RT \ln P_{In_2S}^{(1-x)/2} \cdot P_{S_2}^{(3x-1)/4}$, the free energy of formation per gram atom was calculated for the indium sesquisulfide solid solution region as a function of composition. These free energies can be combined with data that we have reported for the stability of $In_2S$ gas[3] to yield the free energy of formation of the indium sesquisulfide phase as a function of composition, i.e., for the reaction:

$$(1-x)\ In(\ell) + \left(\frac{x}{2}\right) S_2(g) = In_{1-x}S_x(s) \quad . \tag{5}$$

The results are shown in Fig. 4 as solid lines.

The slope of a $\Delta F°$ -vs-composition plot for (5) should change smoothly with temperature and must always have a positive curvature[12] instead of the negative curvature indicated by the experimental data at 600° and 650°C. To obtain values of the proper curvature as a function of composition at 600°, 650°, 700°, and 750°C from the experimental curve at 800°C, the entropy of formation was assumed to be given by

$$S°_{In_{(1-x)}S_x} - (1-x)S°_{In(\ell)} - \frac{x}{2} S°_{S_2} + \Delta S°_m , \tag{6}$$

where $S°_{In_{(1-x)}S_x}$ is the weighted average of the entropy of the sesquisulfide phase[13] and of solid indium[14] and where $\Delta S_m$ is the difference between the entropy of mixing of the elements and vacant lattice sites[15] at the desired composition and at 40 at.% indium.

The $\Delta H°$ of formation per gram atom at each composition, which must be essentially temperature independent over the temperature region studied because $\Delta C_p$ for condensed-phase reactions are small, was calculated from the expression $\Delta F°_T = \Delta H° - T\,\Delta S°_T$ by use of the values of $\Delta F°$ at 800°C and $\Delta S°_{800}$. These values of $\Delta H°$ can be expressed as $\Delta H° = 0.37y - 44.3$ (where y is at.% indium). The heat of formation of stoichiometric $In_2S_3$(s) from liquid indium and $S_2$ gas is then calculated to be -147.5 ± 2 kcal/mole. The expression for the heat of formation was used with expression (6) to calculate the values of $\Delta F°$ at various compositions between 40 and 44 at.% indium (shown as dashed lines in Fig. 4). The resultant calculated curves agree with the solid curves to within the experimental error, but the calculated curves probably represent the true composition dependence of $\Delta F°$ for formation more correctly than do the curves of negative curvature.

The free energy of formation of $InS_{1.12}$ at the sulfur-rich boundary was determined at 600°, 650°, 700°, and 750°C by the method used for indium sesquisulfide. The entropy of solid $InS_{1.12}$ was estimated by use of (7) which averages the entropy of $In_2S_3$ and solid indium.

$$0.119\ In(s) + 0.176\ In_2S_3(s) = In_{0.471}S_{0.529}(s) \qquad (7)$$

The heat of formation per gram atom from liquid indium and $S_2$ gas was calculated from the free energy of formation and these entropies to be -27.5 kcal at 600°C and 650°C, -27.7 at 700°C and -28.0 at 750°C. A nearly constant value of $\Delta H = 27.7 \pm 0.3$ kcal/g at. or $58.7 \pm 0.7$ kcal/mole is an indication of internal consistency of the data. The free energy of formation per gram atom can be expressed as $\Delta F = -20.97 + 7.4 \times 10^{-3}$ T°C kcal/mole. Since the $InS_{1.12}$ phase is only 1 to 3 at.% wide, $\Delta F$ and $\Delta H$ for formation per gram atom must be essentially constant with composition across the phase.

The heat and free energy of formation of InS from liquid indium and $S_2$ gas were calculated at 600°, 650°, and 700°C at the sulfur-rich boundary using the $In_2S(g)$ and $S_2(g)$ partial pressure in the two-phase region between $InS_{1.12}$ and InS. The $S_2(g)$ partial pressure was calculated from the measured $In_2S(g)$ partial pressure and the free energy of formation of the $InS_{1.12}$ phase. (The intensities of $S_2^+$ were just measureable at 650°C and 700°C. The measured $S_2^+$ intensities gave free energy values 0.3 and 0.1 kcal/g at. less negative than values for calculated $S_2$ pressures at 650° and 700°C, respectively.)

The free energy of formation, determined in the same manner as for the other phases, was found to be -15.9, -15.7, and -15.4 kcal/g at. at 600°, 650°, and 650°C, respectively. The entropy of solid InS was estimated by use of (8)

$$0.167\ In(s) + 0.167\ In_2S_3(s) = In_{0.5}S_{0.5}(s) \qquad (8)$$

The heat of formation was calculated from the free energy of formation and these entropies. A nearly constant value of $\Delta H = -26.5 \pm 0.3$ kcal/g at. or $-53.0 \pm 0.6$ kcal/mole was obtained.

## FOOTNOTES AND REFERENCES

1. This work was supported in part by a contract with the Office of Naval Research and the Advanced Research Projects Agency and in part by the U. S. Atomic Energy Commission.

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# FIGURE LEGENDS

Fig. 1 Ion ($In_2S^+$ and $S_2^+$) intensities vs time in the indium sesquisulfide region.

Fig. 2 Ion ($In_2S^+$ and $S_2^+$) intensities as functions of time in the $InS_{1.12}$ region.

Fig. 3 Vapor pressures of $In_2S(g)$ and $S_2(g)$ vs composition in the $InS_{1.12}$ region.

Fig. 4 Free energy of formation of indium sesquisulfide as a function of composition and temperature. Solid line calculated from experimental data. Dashed line calculated from solid curve at 800°C and the assumption of a model described in text.

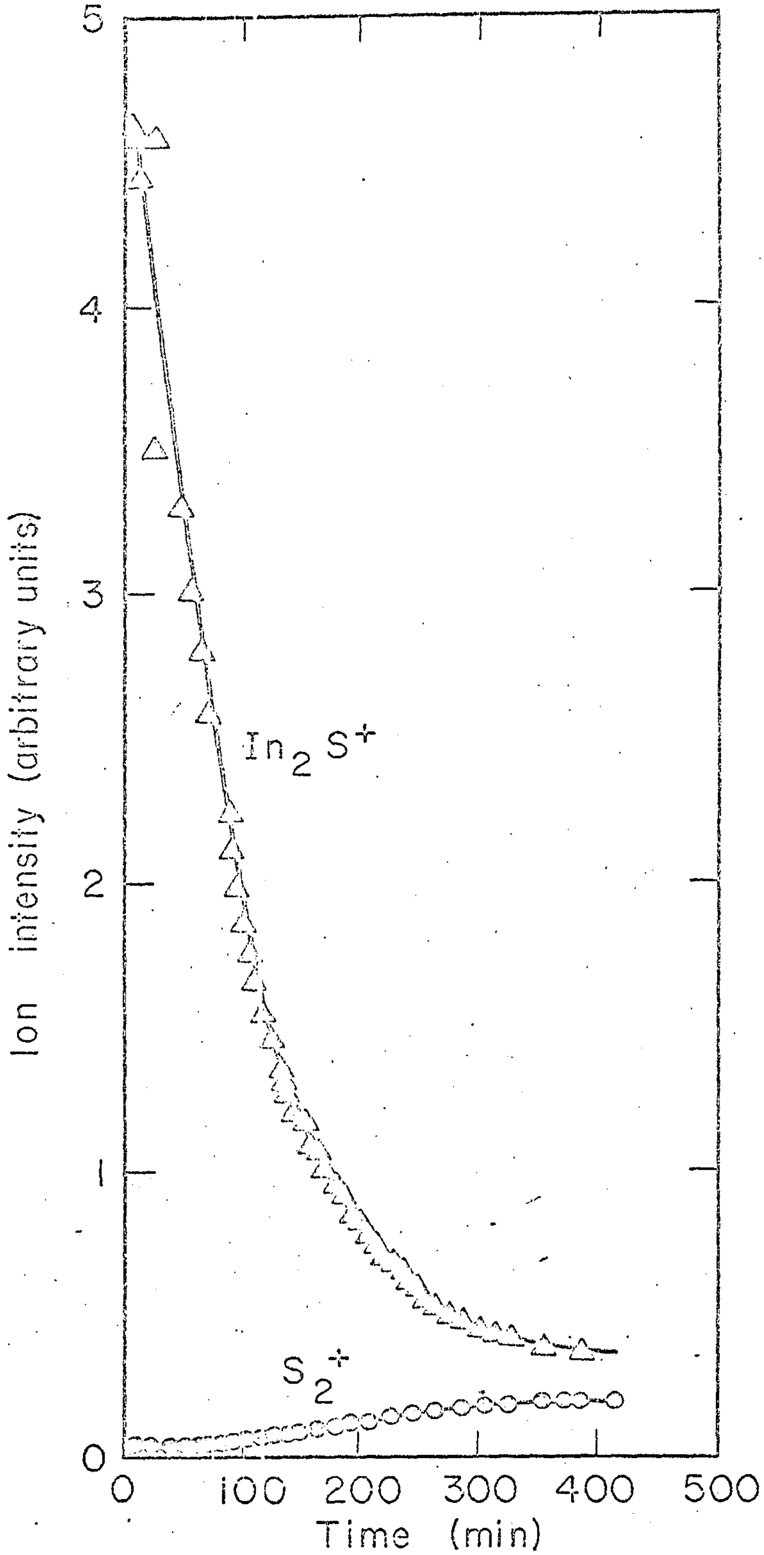


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Fig. 1

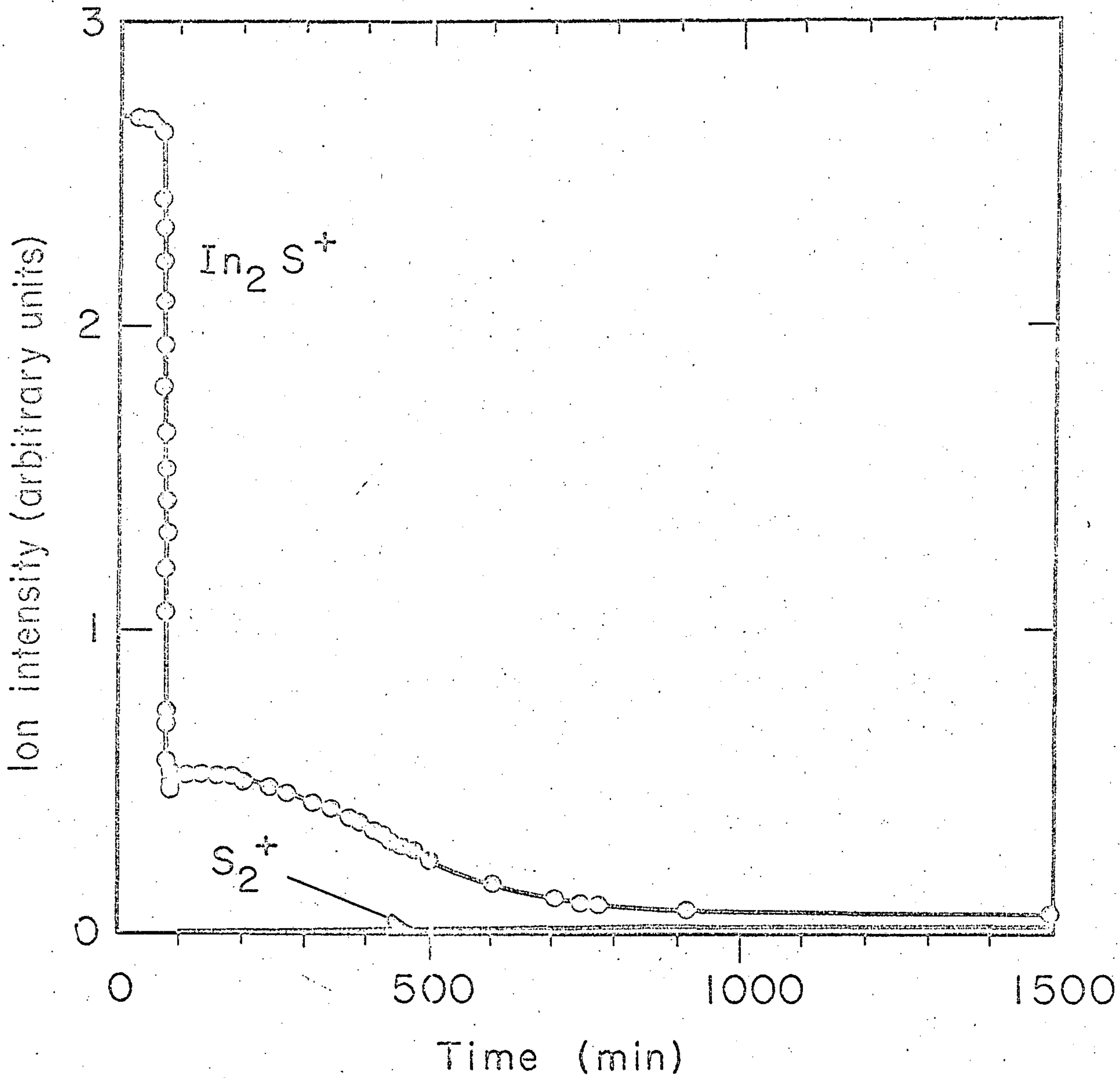


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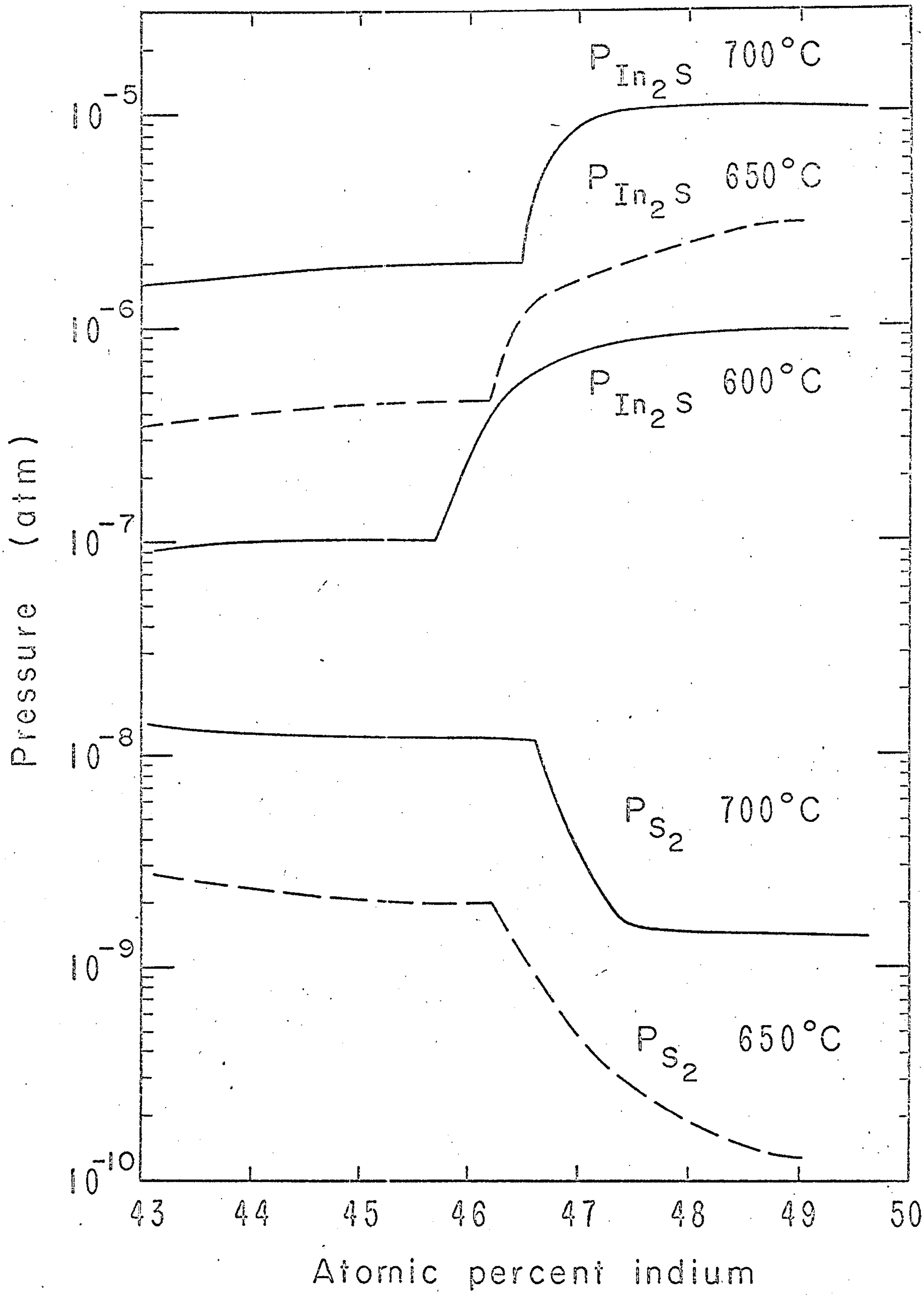
Fig. 2




MU-32309

Fig. 3

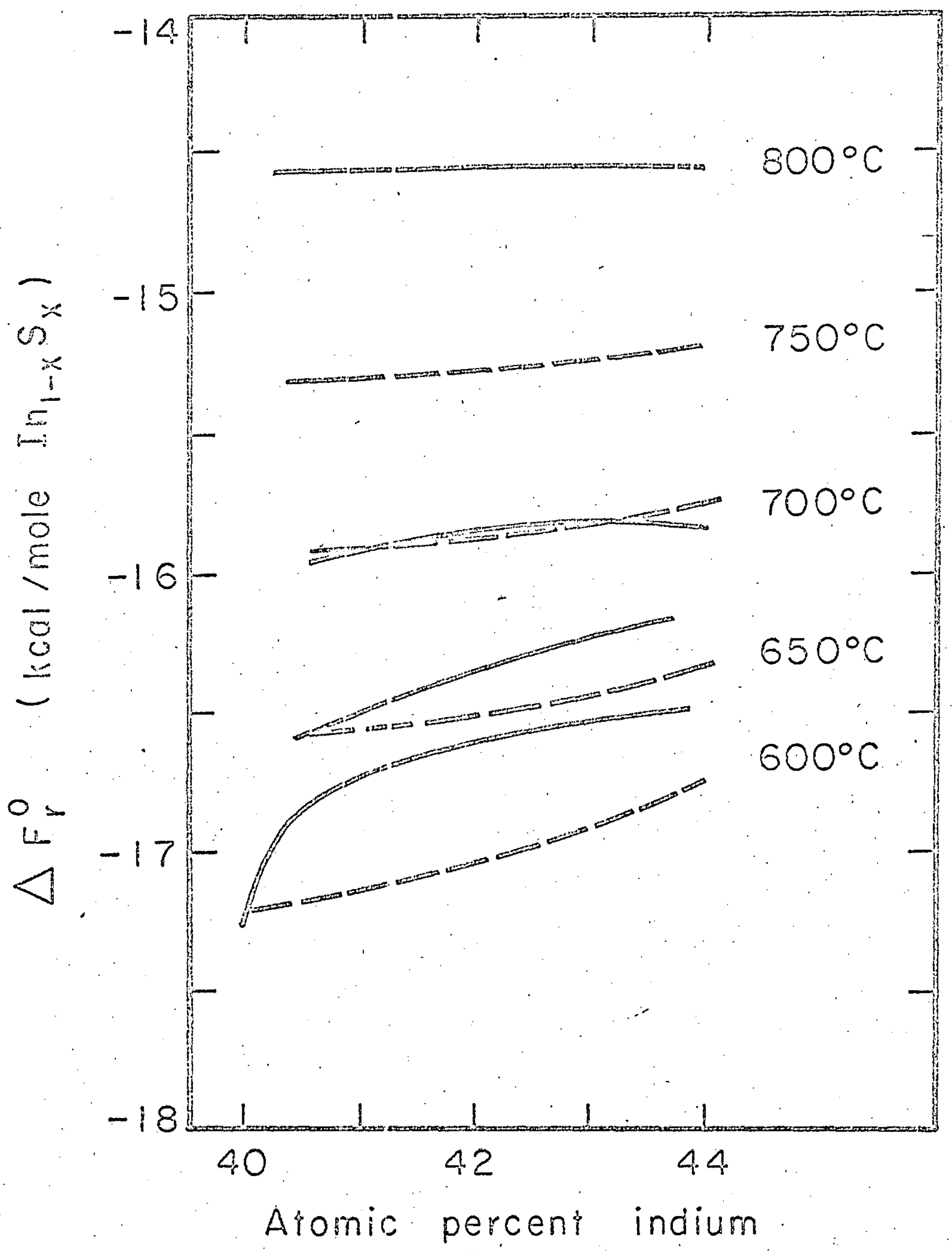

-14
-15
-16
-17
-18
800°C
750°C
700°C
650°C
600°C
$\Delta F_f^0$ (kcal/mole $In_{1-x}S_x$)
40
42
44
Atomic percent indium
MU-32510

Fig. 4