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An Anomalous Temperature Dependence for a Decomposition Pressure
ABSTRACT In a limited temperature range the Ga$_2$S$_3$ partial pressure above gallium sesquisulfide increases when the temperature is decreased. The anomaly is caused by changes with temperature of the equilibrium compositions of two solid phases that coexist at 1228±3 K with compositions that differ by only 0.3±0.1 atomic % sulfur.
In the course of a mass spectrometer study of the vaporization of gallium sesquisulfide \((\text{Ga}_2\text{S}_3)\) we were surprised-- and at first dismayed-- to find that near 1220° K decreases in temperature caused the partial pressure of one of the two principal vapor molecules to increase (Fig. 1). In other temperature ranges, decreases in temperature caused normal exponential decreases in partial pressures. The anomaly near 1220° K was reproducible and large; a temperature decreases of 25° K caused a pressure increase of about 50% rather than the decrease of 50% which would be expected from pressure variations in other temperature ranges.

After about an hour the anomalously high partial pressures decreased to values that were consistent with interpolations of pressures from higher and lower temperature ranges. The anomaly could not be dismissed as arising from purely kinetic factors; it must have a thermodynamic basis because partial pressures can only change, even during reactions, in directions that increase the total thermodynamic stability of the system. Although such a pressure reversal had not been observed before, it proves to be explainable in terms of familiar thermodynamic relations when applied to an unfamiliar set of experimental conditions.

The key to explaining the partial pressure anomaly lies in recognizing that two component solids like gallium sesquisulfide actually have variable compositions.\(^1\) The vaporization of gallium sesquisulfide occurs by dissociation,

\[
\text{Ga}_{(2+2\epsilon)}\text{S}_{(3-\epsilon)}(s) = (1+\epsilon) \text{Ga}_2\text{S}(g) + (1-\epsilon) \text{S}_2(g)
\]  

(1)
where \( \varepsilon \) takes small positive or negative values that depend upon conditions of preparation and subsequent treatment of the sample. When heated in an effusion cell to some fixed temperature, the solid loses either \( \text{Ga}_2\text{S} \) or \( \text{S}_2 \) preferentially. The preferential loss shifts the composition of the remaining solid in a direction that reduces the partial pressure of the more volatile vapor molecule and increases the partial pressure of the less volatile vapor molecule. A steady state is reached when the average composition of the vapor beam is the same as the composition of the solid. This composition, called the composition for congruent vaporization, can vary with temperature. However, the variation is small for solids and it had apparently never been measured for a narrow solid solution.

Variations in the composition for congruent vaporization can be measured for gallium sesquisulfide with a mass spectrometer. Gallium sesquisulfide, heated in alumina or graphite effusion cells, gave \( \text{Ga}_2\text{S}^+ \) as the principal ion product of collision of 70 eV electrons with \( \text{Ga}_2\text{S} \) molecules and \( \text{S}_2^+ \) as the principal ion from \( \text{S}_2 \). The proportionality constant between ion intensities and molecular fluxes was calculated from the steady state ion ratio \( \text{Ga}_2\text{S}^+ / \text{S}_2^+ \) of a congruently vaporizing solid for which the composition and total pressure were known. Changes in composition were calculated by correcting the known composition of a known weight of solid for the time integrals of the total \( \text{Ga}_2\text{S} \) and \( \text{S}_2 \) molecular fluxes. That pressures measured even under non-steady state conditions were close to equilibrium values is proved by the observation that pressures measured at all compositions and temperatures were
unchanged when areas of effusion orifices were changed by as much as a factor of twenty.

The sulfur content of the congruently vaporizing gallium sesquisulfide decrease linearly with temperature by very small amounts, less than 0.002 at % S/deg, except on heating through 1228 ± 3°K, where the sulfur content decreased discontinuously by 0.37 ± 0.1 at % S. The discontinuous change, which is reversible with temperature, must arise from a phase transition between a low temperature form of gallium sesquisulfide, which we will call L-Ga₂S₃, and a high temperature form, which we will call h-Ga₂S₃.⁷

Figure 2 is a schematic partial phase diagram that is consistent with the observed temperature dependence of the composition for congruent vaporization. In constructing the diagram we were guided by the knowledge that, although high and low temperature modifications of a two component solid phase are often ascribed the same fixed composition, they actually can coexist over at least a small range of compositions and temperatures.¹ Phase boundaries for both solid phases at 1228° K were determined from discontinuities in a plot of composition for congruent vaporization versus temperature (dotted line, Fig. 2). The boundary for a low temperature phase at 1203° K (pt c) was determined from variations in partial pressure with composition. Partial pressures for two component systems are independent of composition when two condensed phases are stable, but vary with composition in one phase regions.² The boundary of h-Ga₂S₃ at 1203° K was drawn to be consistent with a calculation described below.
The changes in partial pressures with time that are shown in Figure 1 can be correlated with the partial phase diagram of Figure 2. When \( \text{h-Ga}_2\text{S}_3 \) of a composition for congruent vaporization at a temperature \( T_1 \) a little above 1228° K is first quenched to a temperature at which the two solid modifications can be brought to equilibrium, say 1203° K, the \( \text{h-Ga}_2\text{S}_3 \) first supercools at essentially unchanged composition \( a \). During this cooling at constant composition the partial pressures of both vapor molecules decrease. Then \( \lambda\text{-Ga}_2\text{S}_3 \) nucleates and the untransformed portion of \( \text{h-Ga}_2\text{S}_3 \) shifts toward higher gallium content. As the gallium content increases the \( \text{Ga}_2\text{S} \) partial pressure rises and the \( \text{S}_2 \) pressure continues to fall. When the compositions become those at which the two solids can be at equilibrium at 1203° K (points b and c of Figure 2), the partial pressures of both gases become constant for about an hour under our experimental conditions, while preferential loss of \( \text{Ga}_2\text{S} \) reduces the quantity of \( \text{h-Ga}_2\text{S}_3 \). When no \( \text{h-Ga}_2\text{S}_3 \) remains, the composition of the \( \lambda\text{-Ga}_2\text{S}_3 \) phase and the partial pressures of the two vapor molecules again shift simultaneously until the composition (point d) for congruent vaporization of \( \lambda\text{-Ga}_2\text{S}_3 \) at 1203° K is reached. The product of the \( \text{Ga}_2\text{S} \) and \( \text{S}_2 \) partial pressures, which is a measure of the molar free energy of the condensed phase(s), is constant to within our limits of measurement during the isothermal pressure changes.

These partial pressure variations are unusual only in that the partial pressure of \( \text{Ga}_2\text{S} \) which is at equilibrium with the two solid phases is higher at 1203° K than it is at 1228° K. The pressure of a gas molecule which is at equilibrium with two solids of different composition is called a decomposition pressure. Decomposition pressures for conventional
decomposition reactions have always been found to decrease exponentially with decreasing temperatures.

The effect of composition changes of the solids on the decomposition pressures is commonly neglected, and when studied, the effect has proved to be small. Here, however, the changes in composition of the solid phases with temperature almost certainly cause the reversal in sign of the temperature dependence of the Ga₂S decomposition pressure.

The overall changes in partial pressures $P$ of Ga₂S as a consequence of a change in the temperature $T$ of the decomposition reaction is

$$P_{2} - P_{1} = \int_{T_{1}}^{T_{2}} \left( \frac{\partial P}{\partial T} \right)_{X} \, dT + \int_{X_{1}}^{X_{2}} \left( \frac{\partial P}{\partial X} \right)_{T} \, dX$$

where $X$ is the mole fraction of gallium in one of the solids at its equilibrium phase boundary composition (e.g. composition $a$ for $h$-Ga₂S₃ at 1228° K), and the subscripts 1 and 2 identify the initial and final states. Because the composition for congruency changes very little with temperature in the single phase regions, the value of the first integral can be obtained for $h$-Ga₂S₃ by a conventional Clausius-Clapeyron extrapolation of Ga₂S partial pressures measured above 1228° K. With $T_{1} = 1228°$ K and $T_{2} = 1203°$, the value of the integral is $-1.04 \times 10^{-5}$ atm. Two measurements were made of the variation in partial pressures with composition over a range of 0.04 at $\%$ S at 1237° K by quenching a sample from higher temperatures and measuring the variations in intensities with time until the congruent composition was reached. Both partial pressures varied linearly with the mole fraction of gallium. The two values measured for $\left( \frac{\partial P}{\partial X} \right)_{T}$ were $2 \times 10^{-2}$ and $3 \times 10^{-2}$ atm/mole Ga.
The average of these values corrected by means of the Clausius-Clapeyron equation to 1203° K is $1.0 \times 10^{-2}$. All quantities in equation 2 are now known except the limit $X_2$, and we calculate $X_2 - X_1 = 0.002$ for the change in the mole fraction of gallium along the $h$-$Ga_2S_3$ phase boundary when the temperature changes from 1228° K to 1203° K, compared to a measured change of 0.001 for the $l$-$Ga_2S_3$ phase boundary. We calculate from the phase boundary compositions a heat and an entropy of transition that are well within the ranges of values found for transitions between low and high temperature modifications of solid phases. 

Our analysis depends on measurements of differences in temperatures, pressures, and compositions. These differences can be measured with higher precision than can absolute values. The composition changes are probably uncertain by no more than a factor of two. Our measurements appear certainly precise enough to justify the conclusions that a decomposition reaction of a high temperature form of gallium sesquisulfide has an equilibrium pressure which increases with decreasing temperature and that the increase is a consequence of changes in compositions of the equilibrium solids.

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References and Notes


4. Combustion analyses by C. W. Koch and V. H. Tashinian yield 40.53 and 40.56 wt % S for the congruently vaporizing solid at 1270°K and 40.95 and 41.00 wt % S for 1210° K. Integrated weight changes in the mass spectrometer were about 20% higher than differences in analysis.


7. The transition is composition dependent and may be that reported to occur at 1285 10° K by P. G. Rustamov, B. N. Mardakhaev, and M. G. Safarov, Inorg. Materials (USSR) **3**, 429 (1967).


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FIGURE LEGENDS

Fig. 1. Variation with time of the partial pressures of Ga₂S (proportional to Ga₂S⁺, dotted line) and S₂ (proportional to S₂⁺, solid line). At about 11700 seconds the temperature was lowered from 1230° K to 1203° K.

Fig. 2. Schematic partial phase diagram showing details of the transition between high and low temperature forms of gallium sesquisulfide. The dotted line shows the variation of the composition for congruent vaporization.
Fig. 1

Intensity (arbitrary units)

Ga$_2$S$^+$

S$_2^+$

Time (seconds)

10,000

20,000
Fig. 2

- Temperature (°K)
- Atom. % Sulfur

- h-Ga₂S₃
- l-Ga₂S₃
- b
- c
- d

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