

# Condensed-Phase Transitions during Effusion of Gallium Selenide

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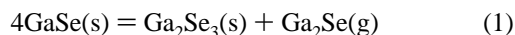
An effusion study of gallium sesquiselenide,  $\text{Ga}_2\text{Se}_3$ , was conducted by simultaneous Knudsen effusion and torsion (Volmer) effusion in the range 1105–1289 K for the purpose of testing a theory of equilibrium condensed-phase transitions<sup>1</sup> in the presence of the vapor and of improving, on that basis, understanding of this important substance at high temperatures. Below  $1225 \pm 10$  K a phase nominally  $\text{Ga}_2\text{Se} \cdot \text{Se}_2(\text{s})$  effused congruently, principally as  $\text{Ga}_2\text{Se}(\text{g})$  and  $\text{Se}_2(\text{g})$ , and above that temperature a phase nominally  $(\text{Ga}_2\text{Se})_{1+x} \cdot (\text{Se}_2)_{1-x}(\text{l})$ ,  $x = 0.10$ , effused congruently as the same species; at  $1225 \pm 10$  K the vapor pressure was  $14 \pm 1$  Pa. Detailed observations of chemical events during the transition were made. A quadruple point involving  $\text{GaSe}(\text{s})$  was found at  $1155 \pm 5$  K and  $5 \pm 1$  Pa. On plots of  $\log P$  vs  $1/T$  data fell in an envelope bounded above by curved three-phase lines in projection and below by straight two-phase lines, in conformity with theory. The  $\Delta H^\circ(298 \text{ K})$  of congruent vaporization of 1 mol of  $\text{Ga}_2\text{Se}_3(\text{s})$  to give  $\text{Ga}_2\text{Se}(\text{g})$  and  $\text{Se}_2(\text{g})$  was  $649 \pm 3$  kJ.

## Introduction

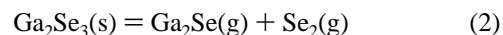
Owing to interest in the semiconducting properties<sup>2</sup> of compounds in the Ga/Se system, a number of studies have been done on the growth of thin films of  $\text{GaSe}$  and  $\text{Ga}_2\text{Se}_3$  as pure phases,<sup>3–6</sup> with substitution of Te for Se,  $\text{GaSe}_{1-x}\text{Te}_x$ ,<sup>7</sup> with substitution of Tl for Ga,  $\text{TlGaSe}_2$ ,<sup>8</sup> with substitution of In for Ga,  $(\text{In}_x\text{Ga}_{1-x})_2\text{Se}_3$ ,<sup>9</sup> or as heterointerfaces, e.g.,  $\text{GaSe}/\text{InSe}$ <sup>10</sup> or  $\text{GaSe}/\text{WSe}_2$ .<sup>11,12</sup> Knowledge of the phase equilibria and of the vaporization chemistry of the various phases in the Ga/Se system is important in such work and should be thorough. A primary goal of this work is to gain such thorough knowledge through experimental observations with fast, high-capacity, automatic equipment and current theoretical understanding. Principal motivation comes from a desire to resolve previous observations of anomalous effects during vaporization studies of gallium selenide.

The abbreviations VP for vapor pressure and  $T$  for temperature will be used.

Detailed studies of the phase diagram and structures in the Ga/Se system have been reported.<sup>13–26</sup> According to the extensive study of the Ga/Se phase diagram by Dieleman et al.,<sup>20</sup> two solid compound phases exist:  $\text{GaSe}$ , effectively as a line compound, and  $\text{Ga}_2\text{Se}_3$  with homogeneity range of  $\approx 0.012$  atomic fraction of Se at  $T \approx 1205$  K. From reported vaporization studies on the Ga/Se system,<sup>20,27–33</sup> one deduces that  $\text{GaSe}(\text{s})$  vaporizes incongruently by<sup>27</sup>



with minor contributions by other vapor species (vide infra, eq 9) and that  $\text{Ga}_2\text{Se}_3(\text{s})$  vaporizes congruently<sup>28,33</sup> by



In fact, the congruent vaporization of  $\text{Ga}_2\text{Se}_3(\text{s})$  by eq 2 is a simplification of results that call for closer examination. Uy et al.<sup>28</sup> showed by Knudsen cell mass spectrometry and X-ray analysis that no condensed-phase transformation of  $\text{Ga}_2\text{Se}_3$  occurs in the range 931–1094 K. Edwards and Uram<sup>34</sup> pointed out and discussed apparent anomalies in reported results by Vendrikh and Pashinkin<sup>31</sup> and Grimes<sup>33</sup> from effusion experiments on  $\text{Ga}_2\text{Se}_3$  at  $T$  above 1227 K, anomalies that might be attributable to phase transitions. By mass-loss effusion measurements, Vendrikh and Pashinkin<sup>31</sup> found VP that varied from 18 to 11 Pa in the small range 1228–1231 K and then increased to 19 Pa at 1235 K. The same work gave nearly constant VP of 29–30 Pa over a range of 1249–1269 K. Grimes<sup>33</sup> consistently observed anomalously high VP over  $\text{Ga}_2\text{Se}_3$  at  $T < 1220$  K immediately following measurements at  $T > 1235$  K by the simultaneous mass-loss and torsion effusion method.

Unusual phenomena associated with condensed-phase transitions during dynamic vaporization experiments were explained with a chemical–thermodynamic theory by Edwards and Franzen,<sup>1</sup> and conditions that give such phenomena were predicted. They explained anomalous effects observed in the case of gallium sesquisulfide,  $\text{Ga}_2\text{S}_3$ .<sup>34–36</sup> The theory predicts that data plotted as  $\log P$  vs  $1/T$  may fall into four groups in the region of a condensed-phase transition during an effusion experiment. Group 1: When the condensed phase stable at low  $T$  is effusing congruently, data lie, ideally, on a Clausius–Clapeyron straight line with slope determined by thermodynamics of the condensed and vapor phases. Group 2: When the condensed phase stable at high  $T$  is effusing congruently, the data lie, ideally, on a Clausius–Clapeyron straight line with slope determined by thermodynamics of the condensed and vapor phases. Group 3: In the course of the phase transition, with three phases in equilibrium, the data follow a curved line

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with continuous and monotonic slope, convex from the low-pressure side and, except possibly in a small range around the transition temperatures, lying at higher pressures than either of the Clausius–Clapeyron lines. Group 4: In the course of the phase transition, after the unstable condensed phase is exhausted, and the stable condensed phase is effusing incongruently, the data fall between the curved three-phase line and the Clausius–Clapeyron line of the stable condensed phase. With time, as the excess volatile component vaporizes from the stable condensed phase, the VP changes in the direction of the Clausius–Clapeyron line.

Further investigation guided by new theory would provide information necessary to improve current understanding<sup>1</sup> of vaporization processes during condensed-phase transformations of Ga<sub>2</sub>Se<sub>3</sub>. It would be especially interesting in view of the proposal made by Dieleman et al.<sup>20</sup> to the effect that Ga<sub>2</sub>Se<sub>3</sub>(s) would cease to effuse congruently at  $T > 1208$  K. In this paper, we report an investigation of the effusion of Ga<sub>2</sub>Se<sub>3</sub>(s) conducted with the primary goal of examining the nature and reproducibility of the anomalous effects and clarification of the chemical reactions that occur during effusion of Ga<sub>2</sub>Se<sub>3</sub> and then of establishing, with the resulting new understanding, the VP and, where possible, other thermodynamic properties as functions of  $T$  in this important system.

## Experimental Section

Gallium (ingots, AESAR, 99.999%) and selenium (shot, Alfa Products, 99.99%) were used for sample preparation. By a set procedure,<sup>37</sup> a single batch of about 3 g of Ga<sub>2</sub>Se<sub>3</sub> was prepared by direct reaction of appropriate amounts of the elements in an evacuated, sealed Vycor tube at  $T \approx 1073$  K for 17 days and then at  $T \approx 1173$  K for 1 day. X-ray analysis confirmed the batch to be Ga<sub>2</sub>Se<sub>3</sub>(s). VP measurements were done with samples taken from this batch.

Details of the apparatus are given elsewhere.<sup>38,39</sup> In brief, it enables simultaneous measurement of VP by the torsion, or Volmer, effusion method<sup>40</sup> and the mass-loss, or Knudsen, effusion method.<sup>41</sup> Operation of the torsion-effusion pendulum in the dynamic mode<sup>38</sup> with automatic data acquisition<sup>39</sup> facilitates continuous measurement of absolute VP as a function of time. Simultaneous automatic measurement of rate of mass loss provides redundancy of observation when the effusion process is univariant, reveals immediately when a measurable change in the effusion process occurs, and facilitates continuous measurement of VP from the Knudsen equation (vide infra) from a running average of the mass vs time data. If all mass lost can be attributed to effusion of the sample, then the mass of the sample can be monitored automatically from the mass record, and the composition of the sample can be monitored if the composition of the effusing vapor is known. If the vapor composition is unknown or changes during the course of effusion, the simultaneous mass-loss and torsion effusion record can yield information about the composition of the equilibrium vapor or changes in it.

Automatically acquired data from both the torsion–effusion pendulum and the vacuum balance were accumulated in ring buffers, and the most recently acquired were used every 60 s to calculate VP. In principle, the midpoint of the pendulum could be calculated from as few as three data, but in practice, observations over at least one period were used. In this work, the period of the pendulum was ca. 35 s; the most recent 100 observations in the buffer were used to calculate torsion pressures, and the time span always included more than one period of the pendulum. Again in principle, the rate of mass

**TABLE 1: Graphite Torsion–Effusion Cells and Properties of Effusion Orifices<sup>a</sup>**

	used cell	in set	orifice	$L$ ( $\pm 0.02$ ), mm	$a$ ( $\pm 4\%$ ), mm <sup>2</sup>	$d$ ( $\pm 0.02$ ), mm	$W$	$F$
i	A	1		2.10	0.109	8.24	0.174	0.199
		2		2.10	0.100	8.06	0.168	0.192
ii	B	1		2.15	0.876	7.89	0.353	0.399
		2		2.15	0.902	7.74	0.356	0.402
iii	C, D	1		2.10	0.355	7.89	0.268	0.304
		2		2.10	0.342	8.03	0.271	0.307

<sup>a</sup>  $L$  = length (cylindrical);  $a$  = area;  $d$  = moment arm;  $W$  = transmission probability;  $F$  = recoil force correction factor.

loss could be calculated from as few as two data, but in practice, loss of at least 0.5 mg, 50 times the sensitivity of the balance, was required even at the lowest VP. At higher VP, multiples of more than 100 times the sensitivity were used, and at the highest VP, a measurement could be done in a time as short as 2 min.

Four sets of effusion experiments, denoted set A, set B, set C, and set D, were conducted, each with a different aliquot of Ga<sub>2</sub>Se<sub>3</sub>. Three graphite torsion effusion cells denoted cell i, cell ii, and cell iii were used, cell i in set A, cell ii in set B, and cell iii in sets C and D. The cells were of three-piece design<sup>42</sup> with two cylindrical orifices; all orifices were of the same length, but the diameters varied from cell to cell. Table 1 lists the mensural properties of the cells and the transmission probabilities and recoil force correction factors of the orifices calculated with a computer program using equations from Freeman and Edwards.<sup>43</sup> In the four sets, VP was measured several thousand times and at several hundred temperature settings in the range 1105–1289 K. Each set of experiments lasted several days. A typical procedure included heating the cell up to a desired  $T$  at the start of the day and maintaining this  $T$  for at least 1 h before changing it and then measuring VP at various  $T$  for various lengths of time before cooling the cell back to room temperature at the end of the day. Heating was done such that residual pressure in the vacuum system did not exceed  $4 \times 10^{-4}$  Pa.

Temperatures were measured with a Leeds & Northrup optical pyrometer focused through a right-angle prism and window onto a blackbody cavity at the bottom of the effusion cell. This optical pyrometer was calibrated with a certified Pyro optical pyrometer<sup>44</sup> by sighting both pyrometers on a tungsten-strip lamp at several lamp temperatures. The same lamp was also employed to determine the temperature correction factor for window and right-angle prism in the optical path between the blackbody hole and the pyrometer.

The Volmer equation<sup>46</sup> was used to calculate VP,  $P_t$ , from torsion–effusion experiments:

$$P_t = 2k(\beta_v - \beta_{nv})/(A_1 d_1 F_1 + A_2 d_2 F_2) \quad (3)$$

where  $k$  is the torsion constant of the suspension fiber,  $\beta_{nv}$  is the rest position of the pendulum when no vapor is effusing, and  $\beta_v$  is the rest position of the torsion pendulum with vapor effusing. The factors  $A$ ,  $d$ , and  $F$  are the area, moment arm, and recoil-force correction factor, respectively, and the subscripts 1 and 2 refer to orifices denoted as 1 and 2. Values are given in Table 1. The torsion constant was determined in a separate experiment that involved measurements of periods of oscillations when cylinders of known dimensions and mass, and thus of known moments of inertia, were hung in situ from the same torsion fiber to be used for the effusion studies.<sup>40</sup> As described in detail elsewhere,<sup>38,39</sup> the rest position of the pendulum was

determined by solving Newton's second law of angular motion from records of times at which the pendulum reached preset angular positions as the pendulum oscillated.

The Knudsen equation was used to calculate VP,  $P_k$ , from mass-effusion experiments:

$$P_k = (dg/dt)/(2\pi RT/M)^{1/2}/(A_1 W_1 + A_2 W_2) \quad (4)$$

where  $(dg/dt)$  represents the rate of mass loss of the sample,  $R$  is the gas constant,  $T$  is temperature,  $M$  is the assigned molecular weight, and  $W$  is transmission probability. Values of  $W$  are given in Table 1. Mass-time data, usually 50 values of masses within a selected duration, were continually accumulated, but only the latest were retained in the buffer; values of  $(dg/dt)$  were the slopes of least-squares straight lines. A value of  $M = 189.4 \text{ g mol}^{-1}$  was assigned, as though the atomic fraction of Se in the condensed phase were always 0.6, effusion were congruent, and the equilibrium vapor comprised  $\text{Ga}_2\text{Se(g)}$  and  $\text{Se}_2(\text{g})$ .

The equilibrium constant of reaction 2 was expressed by

$$K_p = p(\text{Ga}_2\text{Se}) p(\text{Se}_2) = X(\text{Ga}_2\text{Se}) X(\text{Se}_2) P^2 = 0.2483 P^2 \quad (5)$$

where  $p$  is partial pressure,  $X(\text{Ga}_2\text{Se})$ , 0.5404, is the mole fraction of  $\text{Ga}_2\text{Se(g)}$ ,  $X(\text{Se}_2)$ , 0.4596, is the mole fraction of  $\text{Se}_2(\text{g})$  in the vapor within the effusion cell during congruent effusion, and  $P$  is the VP,  $P_t$  or  $P_k$ . The thermal functions for  $\text{Ga}_2\text{Se}_3(\text{s})$  and  $\text{Ga}_2\text{Se(g)}$  were taken from Mills,<sup>45</sup> and those for  $\text{Se}_2(\text{g})$  were taken from Grønvold et al.<sup>47</sup>

An important application of measured VP can be in the calculation of changes in thermodynamic properties for the chemical reactions involved.<sup>48</sup> When the effusion reaction is known, and values of thermal functions are known for all species involved, the enthalpy change  $\Delta_r H_m^\circ(298 \text{ K})$  of the reaction can be calculated by the third-law method, and the result will be the same within experimental error from each measurement of VP. Second-law  $\Delta_r H_m^\circ(298 \text{ K})$  can be calculated from the slope of  $\log K_p$  vs  $1/T$ .

But such results depend on no experimental information except the measured  $T$  and VP. When the chemical reaction changes during an effusion process, the values of third-law  $\Delta_r H_m^\circ(298 \text{ K})$  calculated on the basis of a fixed chemical effusion reaction change, and such variations indicate the changes in the chemical reaction more precisely than does variation of VP.<sup>48</sup> If chemical compositions of phases involved in vaporization vary with  $T$ , then the relation between  $\log P$  and  $1/T$  may depart from a straight line.<sup>49</sup> Therefore, in pursuit of the primary goal of this work, third-law analyses of measured VP in terms of the congruent effusion reaction 2 were done in order to gain useful information about chemical changes even though other reactions were occurring.

## Results

Calibration of the torsion fiber yielded  $k = (3.331 \pm 0.004) \times 10^{-8} \text{ N m rad}^{-1}$ .

A freshly loaded sample always yielded relatively high VP for short periods even at estimated  $T$  as low as 600 K. Continued effusion led to the removal of volatile materials, and subsequently VP became measurable only above  $T \approx 1000 \text{ K}$ . This initial outgassing involved some 1–2% of the mass of the sample. Data obtained after initial outgassing were assignable to four groups in accordance with the classification of Edwards and Franzen described in the Introduction of the present paper.

VP measurements from all sets, A–D, were consistent, and thus no kinetic effects on VP were evident within the range of

**TABLE 2: Vapor Pressures Measured in Set B and Third-Law Enthalpies for the Reaction  $\text{Ga}_2\text{Se}_3(\text{s}) = \text{Ga}_2\text{Se(g)} + \text{Se}_2(\text{g})$**

torsion effusion			mass-loss effusion	
$T, \text{ K}$	$P_t, \text{ Pa}$	$\Delta_r H_m^\circ(298 \text{ K}), \text{ kJ mol}^{-1}$	$P_k, \text{ Pa}$	$\Delta_r H_m^\circ(298 \text{ K}), \text{ kJ mol}^{-1}$
1171	3.0	645.3	2.6	648.1
1151	1.4	649.4	1.3	650.8
1139	0.93	650.7	0.80	653.5
1118	0.65	645.8	0.67	645.3
1136	0.85	650.7	0.81	651.6
1110	0.37	651.8	0.44	648.6
1163	1.9	649.9	1.8	651.0
1139	0.94	650.5	0.91	651.1
1141	1.0	650.4	0.96	651.1
1154	1.5	649.7	1.4	651.0
1118	0.49	651.1	0.48	651.5
1169	2.3	649.4	2.1	651.2
1166	2.1	649.6	2.0	650.5
1182	3.4	648.6	3.2	649.8
1182	3.4	648.6	3.1	650.4
1143	1.0	651.5	0.98	651.8
1123	0.53	652.4	0.47	654.7
1119	0.55	649.5	0.56	649.2
1146	1.16	651.3	0.97	653.7
1158	1.8	648.3	1.7	649.4
1171	2.7	647.4	2.5	648.9
1174	2.7	648.9	2.5	650.4
1222	11.6	644.6	10.8	646.0
1178	3.4	646.5	3.2	647.7
1140	1.1	648.0	1.0	649.8
1136	0.90	649.6	0.91	649.4
1142	1.1	649.1	1.0	650.9
1203	6.9	645.4	6.2	647.6
1199	6.1	645.9	5.6	647.6
1198	5.8	646.3	5.4	647.8
1196	5.7	645.7	5.2	647.5
1152	1.4	649.9	1.5	648.6
1151	1.4	649.4	1.4	649.4
av		648.8 ± 0.4		649.9 ± 0.4

orifice areas used. In Table 2, columns 2 and 4, are listed respectively the isothermally invariant values of  $P_t$  and  $P_k$  from set B, which were measured at the  $T$  in column 1, before the sample had been heated at  $T > 1222 \text{ K}$ . These values when subjected to least-squares treatment yielded the following pressure-temperature relations:

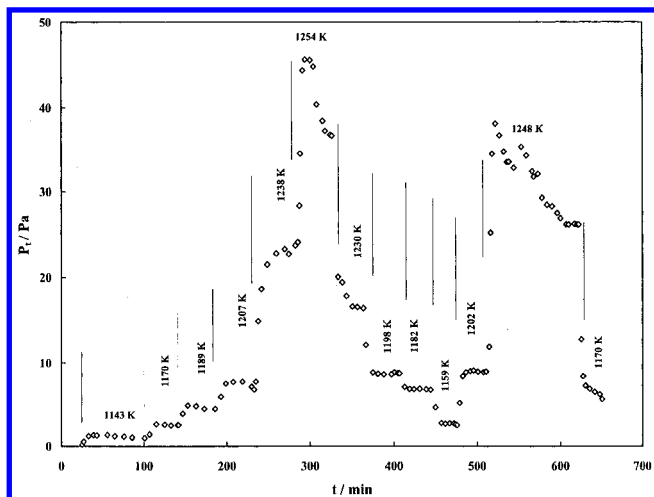
$$\log(P_t/\text{Pa}) = -(1.782 \pm 0.029) \times 10^4(\text{K}/T - 8.646 \times 10^{-4}) + 0.2261 \pm 0.0058 \quad (6)$$

$$\log(P_k/\text{Pa}) = -(1.719 \pm 0.037) \times 10^4(\text{K}/T - 8.646 \times 10^{-4}) + 0.2026 \pm 0.0075 \quad (7)$$

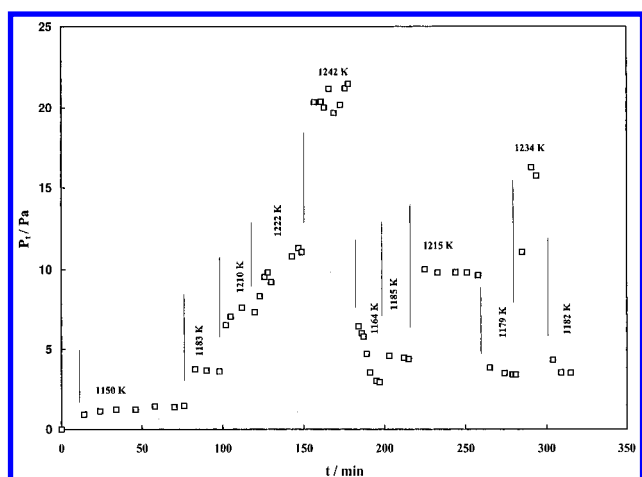
The uncertainties are standard deviations. With the data used to obtain eqs 6 and 7 a third-law treatment was done to obtain  $\Delta_r H_m^\circ(298 \text{ K})$  of reaction 2; values are in columns 3 and 5, respectively, of Table 2. Average values were, from torsion data,  $648.8 \pm 0.4 \text{ kJ}$  and from Knudsen data,  $649.9 \pm 0.4 \text{ kJ}$ , where uncertainties are standard deviations of the means.

From coefficients of  $T^{-1}$  in eqs 6 and 7, values of  $\Delta_r H_m^\circ$  (1141 K) for reaction 2 were  $682 \pm 11$  and  $658 \pm 14 \text{ kJ}$ , respectively. These when combined with auxiliary enthalpy functions for  $\text{Ga}_2\text{Se}_3(\text{s})$ ,<sup>45</sup>  $\text{Ga}_2\text{Se(g)}$ ,<sup>45</sup> and  $\text{Se}_2(\text{g})$ <sup>47</sup> gave second-law  $\Delta_r H_m^\circ(298 \text{ K}) = 712 \pm 11$  and  $688 \pm 14 \text{ kJ}$ , respectively. The uncertainties were deduced from those in eqs 6 and 7.

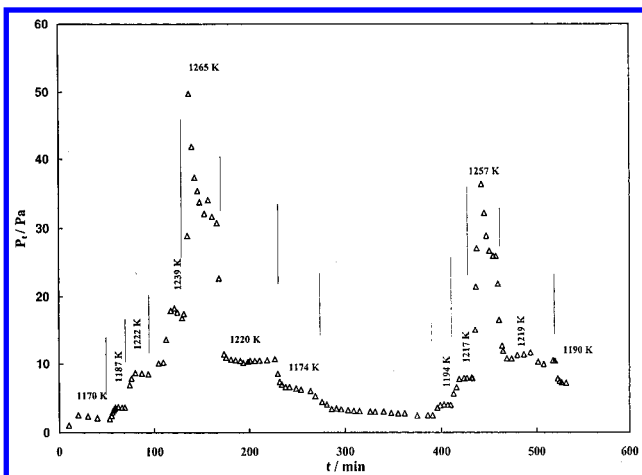
Observation of the anomalous effect sought in these experiments is illustrated by data in Figures 1–4, from sets A–D, respectively. In these figures, typical sequential measurements



**Figure 1.** Measurements of vapor pressure with time on a typical day during set A.

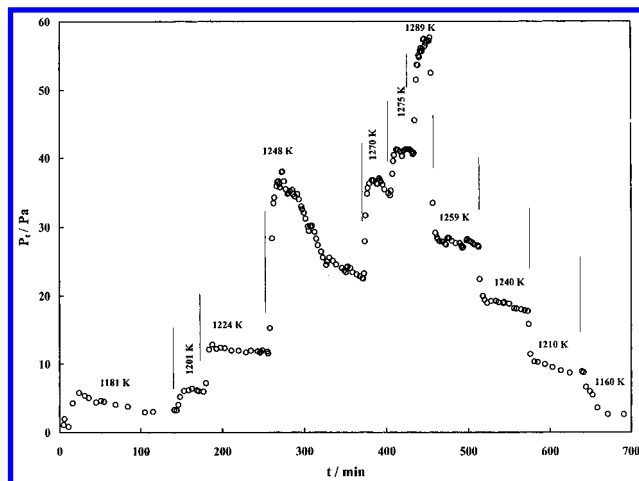


**Figure 2.** Measurements of vapor pressure with time on a typical day during set B.

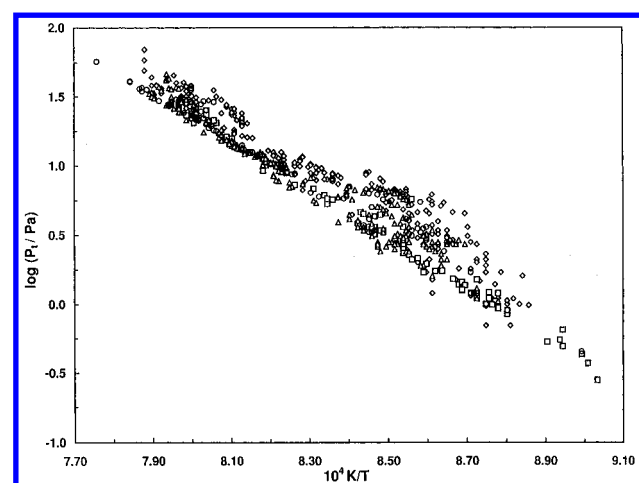


**Figure 3.** Measurements of vapor pressure with time on a typical day during set C.

of  $P_t$  are given, and the values of  $T$  are written on the figure at each stage; times when  $T$  was changed are marked by vertical lines. In each sequence,  $T$  was cycled at least once from below 1225 K to above 1225 K and again to below 1225 K. Within experimental error, variations of  $P_k$  in the same sequences were the same as those of  $P_t$ , with appropriate accounting for variations in the molecular weight of the vapor.



**Figure 4.** Measurements of vapor pressure with time on a typical day during set D.



**Figure 5.** Plot of  $\log P_t/\text{Pa}$  vs  $10^4 K/T$  from sets A, B, C, and D. Envelope is bounded above by curved three-phase lines and below by straight two-phase lines. Triple "point" at  $1225 \pm 10$  K and  $15 \pm 1$  Pa; quadruple point at  $1155 \pm 5$  K and  $5 \pm 1$  Pa.

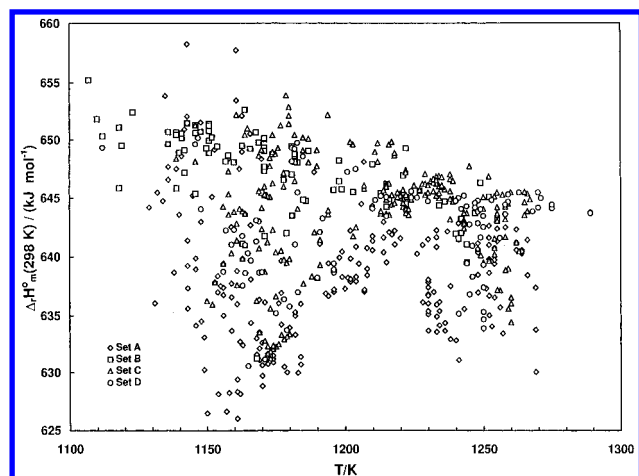
In combination with theory,<sup>1</sup> these results show that a condensed-phase transition occurred in the sample within the effusion cell in the range  $1225 \pm 10$  K.

The  $T$  dependence of  $P_t$  is plotted as  $\log(P_t/\text{Pa})$  vs  $10^4 K/T$  in Figure 5, where results from set A are represented by diamonds, those from set B by squares, those from set C by triangles, and those from set D by circles. These results comprise isothermally invariant values of  $P_t$ , data in groups 1–3, and values of  $P_t$  that varied with time at constant  $T$ , data in group 4. Within experimental error, measurements of  $P_k$  agreed with those of  $P_t$  (*mutatis mutandis*).

Each value of  $P_t$  shown in Figure 5 was used to calculate the third-law enthalpy  $\Delta_r H_m^\circ(298 \text{ K})$  of reaction 2 with the expectation that such enthalpies would be more sensitive indicators of chemical variations than values of VP.<sup>48</sup> In Figure 6 is a plot of the resulting values of  $\Delta_r H_m^\circ(298 \text{ K})$  against  $T$ . Again, results from set A are represented by diamonds, those from set B by squares, those from set C by triangles, and those from set D by circles.

## Discussion

This work demonstrates that anomalous effects during effusion studies of gallium sesquiselenide,  $\text{Ga}_2\text{Se}_3(\text{c})$ ,<sup>31,33</sup> result from a transition in the condensed phase at  $1225 \pm 10$  K while both condensed phases are in equilibrium with the vapor. During



**Figure 6.** Vapor pressures and temperatures in Figure 5 transformed through  $K_p$  into third-law  $\Delta_f H^\circ$  (298 K) of  $\text{Ga}_2\text{Se}_3(\text{s}) = \text{Ga}_2\text{Se}(\text{g}) + \text{Se}_2(\text{g})$ . Chemical variations and differences between sets are enhanced by the transformation.

transition, the condensed phases and the vapor all have different compositions, and the composition of the effusing vapor varies measurably with  $T$  while both condensed phases are present. Both pure condensed phases vaporize congruently under Knudsen effusion conditions at  $T$  near that of the transition. The VP was measured and expressed as a function of  $T$  by eqs 6 and 7 for the low- $T$  congruently effusing phase, and the third-law  $\Delta_f H_m^\circ(298 \text{ K})$  of the corresponding effusion reaction 2 was  $648.8 \pm 0.4 \text{ kJ}$  from torsion results and  $649.9 \pm 0.4 \text{ kJ}$  from Knudsen results. In view of these results and those of Uy et al., we select  $\Delta_f H_m^\circ(298 \text{ K}) = 649 \pm 3 \text{ kJ}$  for reaction 2. Thermodynamic properties of the high- $T$  phase were not calculated because of various uncertainties discussed below.

The results of set A as well as those of Vendrikh and Pashinkin<sup>31</sup> showed changes in composition of the gas phase with  $T$  and time at  $T > 1225 \text{ K}$ . For this reason, VP- $T$  relations reported in this work, those in eqs 6 and 7; were obtained only from VP up to  $1222 \text{ K}$  and before the sample had been heated above  $1222 \text{ K}$  in the effusion experiment. The observed agreement between values of VP measured by torsion and by mass-loss effusion may be taken to indicate the validity of eqs 6 and 7. Where there are slight differences between  $P_t$  and  $P_k$  we consider VP and enthalpy from torsion-effusion results to be better, because measurement of  $P_t$  is absolute and, therefore, does not depend on measurements of  $T$  or assumptions about vapor composition. Moreover, the sensitivity of the torsion-effusion method is 5–10 times that of the Knudsen effusion method in the present setup, and thus, fractional uncertainties in measurement of  $P_k$  are greater, especially at low VP.

Variations between second-law values of  $\Delta_f H_m^\circ(298 \text{ K})$  of reaction 2 by torsion effusion and Knudsen effusion and their differences from third-law results likely arise from composition changes and other structural changes in the sample as  $T$  approaches a transition temperature at  $1225 \text{ K}$  (vide infra). The third-law values are considered to be more dependable because such effects influence them less.

Uy et al.<sup>28</sup> studied the effusion of  $\text{Ga}_2\text{Se}_3(\text{s})$  by mass spectrometry in the lower range  $931\text{--}1094 \text{ K}$  and obtained for reaction 2 a second-law value of  $\Delta_f H_m^\circ(1010 \text{ K}) = 628 \pm 17 \text{ kJ}$ , which with the enthalpy functions used in the present work gives  $\Delta_f H_m^\circ(298 \text{ K}) = 650 \pm 17 \text{ kJ}$ , with which our third-law results agree exactly. The value  $\Delta_f H_m^\circ(298 \text{ K}) = 703 \pm 29 \text{ kJ mol}^{-1}$  reported by Uy et al. was based on the thermal functions they used. Because values of VP were not reported, we could

not deduce third-law enthalpies from Uy et al. for comparison with our results. The difference in second-law values from their and our results likely owes to the difference in temperature ranges of the experiments, theirs far from the  $T$  of the phase transition and ours near it. Near the phase transition, phase compositions are expected to be strongly dependent on  $T$ , and this effect would affect significantly the dependence of VP and vapor composition on  $T$ . Far from  $T$  of the transition, where Uy et al. made measurements, dependence of phase composition on  $T$  would be small.

Berger et al.<sup>29</sup> reported a mass spectrometric study of  $\text{Ga}_2\text{Se}_3$  in the range  $970\text{--}1180 \text{ K}$ , but their results are difficult to compare with those from the present study because Berger et al. gave results at only eight temperatures and gave partial pressures of both species,  $\text{Ga}_2\text{Se}(\text{g})$  and  $\text{Se}_2(\text{g})$ , at only two temperatures,  $1090$  and  $1120 \text{ K}$ . At these temperatures, the ratio  $p(\text{Ga}_2\text{Se})/p(\text{Se}_2)$  was  $9.3$  and  $5.5$ , respectively, which ratios imply incongruent effusion in both cases. Partial pressure of  $\text{Ga}_2\text{Se}(\text{g})$  only was given at  $970$ ,  $1000$ ,  $1030$ , and  $1060 \text{ K}$ , and partial pressure of  $\text{Se}_2(\text{g})$  only was given at  $1150$  and  $1180 \text{ K}$ . One surmises from trends in the results that ionic intensity of  $\text{Se}_2^+$  was unmeasurably low at low  $T$  and measurable only at high  $T$  in the range of their study; by the same token, ionic intensity of  $\text{Ga}_2\text{Se}^+$  was unmeasurably low at high temperatures. Dieleman et al.<sup>20</sup> interpreted the results of Berger et al.: "... Berger et al. who noted that the vapor in equilibrium with solid  $\text{Ga}_2\text{Se}_3$  just above the eutectic temperature consisted of almost pure  $\text{Se}_2$  ...". Neither the results of the present study nor those of Grimes<sup>33</sup> yielded apparent average molar mass corresponding to  $\text{Se}_2$ -rich vapor at  $T < 1180 \text{ K}$ . Explanation of observations by Berger et al., such as high ratios of  $p(\text{Ga}_2\text{Se})/p(\text{Se}_2)$  at  $T \approx 1120 \text{ K}$  and dominance of  $\text{Se}_2(\text{g})$  at  $T$  just  $60 \text{ K}$  higher, may require the model of three-phase equilibria on the basis of which Edwards et al.<sup>50</sup> explained similar observations in a high-temperature mass spectrometric study of  $\text{Ga}_2\text{S}_3(\text{s})$ . In the present study too, we observed  $P_k < P_t$ , and thus  $\text{Se}_2(\text{g})$  dominated when the sample was heated above  $1225 \text{ K}$ .

Results from sets A, C, and D yielded VP consistent with eqs 6 and 7, which are based solely on results from set B. Our results are also in accord with those reported by Vendrikh and Pashinkin,<sup>31</sup> who used the mass-loss effusion method, as well as those measured by Grimes,<sup>33</sup> who used the apparatus used in the present study. However, in view of the fact that their results might be subject to errors of interpretation from effects described below, eq 6 from the present study may be considered more reliable. Equation 6 provided a basis on which we could normalize all our results, including those measured after heating the samples to  $T > 1225 \text{ K}$ . Values of  $P_t$  calculated with eq 6 will henceforth be referred to as  $P_{\text{ref}}$ .

Figures 1–4 contain data from experiments of 1 day in each set, but they reasonably represent all results as the condensed phase, initially  $\text{Ga}_2\text{Se}_3(\text{s})$ , was heated or cooled across  $T \approx 1225 \text{ K}$  in effusion cells. The observations may be summarized: (1) Heating to  $T > 1225 \text{ K}$  from lower  $T$  caused VP to increase to a value consistently higher than  $P_{\text{ref}}$ ; then the isothermal VP always decreased monotonically to a value close to  $P_{\text{ref}}$ . (2) Subsequent cooling from  $T > 1225 \text{ K}$  caused VP to decrease to a value higher than  $P_{\text{ref}}$  and often isothermally invariant for a considerable length of time. (3) The duration of the isothermal invariance depended (a) directly on the duration over which the sample was heated above  $1225 \text{ K}$  immediately before the cooling, (b) directly on the temperature at which the sample had been heated, and (c) inversely on the effective area of the

**TABLE 3: Selected Salient Details of Torsion Experiments in Sets A–D<sup>a</sup>**

<i>T</i> , K	$\Delta t$ , min	$\Delta m$ , mg	$P_t$ , Pa	<i>t</i> , min	$P_t/P_{\text{ref}}$	<i>T</i> , K	$\Delta t$ , min	$\Delta m$ , mg	$P_t$ , Pa	<i>t</i> , min	$P_t/P_{\text{ref}}$	<i>T</i> , K	$\Delta t$ , min	$\Delta m$ , mg	$P_t$ , Pa	<i>t</i> , min	$P_t/P_{\text{ref}}$
set A, starting mass = 303.0 mg; day 10, starting mass = 115.0 mg																	
1143	69	0.4	1.0	101	0.91	1238	53	4.0	24.1	286	1.39	1202	35	1.3	8.9	511	1.38
1170	41	0.4	2.6	115	1.03	1254	41	5.3	45.6	295	1.72	1248	112	11.6	38.1	523	1.69
			2.5	142	0.99				36.7	327	1.39				26.2	623	1.16
1189	44	0.8	4.9	153	1.10	1230	37	2.9	16.4	364	1.17	1170	28	0.8	6.8	636	2.70
			4.4	186	0.99	1198	43	1.7	8.7	407	1.52				6.5	642	2.58
1207	47	1.2	7.7	208	1.04	1182	37	1.2	6.7	444	1.86				6.2	648	2.46
			6.7	233	0.95	1159	32	0.6	2.5	476	1.38				5.6	651	2.22
set B, starting mass = 596.0 mg; day 6, starting mass = 352.7 mg																	
1150	50	5.4	1.4	76	1.02	1242	29	32.8	21.5	178	1.11	1179	23	5.5	3.4	281	1.03
1183	22	4.8	3.6	98	0.97	1164	19	6.1	2.9	197	1.37	1234	13	13.4	15.7	294	1.01
1210	22	9.9	7.3	120	0.91	1185	18	4.8	4.4	215	1.11	1182	21	5.6	3.5	315	0.97
1222	29	18.6	11.1	149	0.99	1215	43	24.2	9.6	258	1.03						
set C, starting mass = 434.9 mg; day 6, starting mass = 162.7 mg																	
1164	38	2.2	2.0	53	0.95	1174	164	11.6	6.5	242	2.29	1257	25	12.5	36.4	443	1.27
1187	16	1.3	3.6	69	0.86				6.2	254	2.18				25.9	458	0.91
1222	41	6.3	10.2	110	0.91				6.0	264	2.11	1219	62	12.0	10.4	520	1.00
1239	22	6.6	17.4	132	0.98				4.4	276	1.54	1190	55	6.3	7.2	532	1.58
1265	35	20.6	49.8	138	1.41				3.3	296	1.16				7.0	538	1.53
			30.8	167	0.88				2.7	362	0.95				6.9	542	1.52
1220	60	11.6	10.6	181	0.99				2.4	375	0.84				5.7	552	1.52
			10.7	227	1.00				2.5	391	0.88				4.4	562	1.22
						1194	19	1.4	3.9	410	0.76				4.1	575	0.90
						1217	23	3.2	7.8	433	0.80						
set D, starting mass = 447.7 mg; day 2, starting mass = 442.3 mg																	
1181	128	9.2	3.2	144	0.91	1270	33	20.2	36.8	383	0.92	1240	60	20.2	19.3	534	1.05
1201	33	3.9	6.4	163	1.03				34.6	405	0.87				17.8	573	0.98
			6.0	177	0.96	1275	29	20.3	41.3	413	0.91	1210	68	11.8	8.8	641	1.10
1224	79	17.1	12.9	188	1.09				40.7	434	0.90	1160	50	4.2	3.6	658	1.93
			11.6	256	1.06	1289	20	20.0	57.6	454	0.90				2.6	671	1.40
1248	116	56.8	36.6	269	1.62	1259	59	29.8	27.1	513	0.90				2.6	691	1.40
			22.5	372	0.99												

<sup>a</sup>  $T$  = temperature during measurements.  $\Delta t$  = time elapsed during current furnace setting; ca. 10 min required to attain  $T$ ; for the first  $T$  in a set, however,  $\Delta t$  is the time for which the system was at  $T$ .  $\Delta m$  = the mass lost during  $\Delta t$ .  $P_t$  = the total vapor pressure from torsion-effusion measurements at the time  $t$  given in the next column.  $t$  = the time elapsed from the start of the experiment.  $P_t/P_{\text{ref}}$  = vapor pressure  $P_t$  relative to  $P_{\text{ref}}$  computed from eq 6.

orifice in the effusion cell. (4) After prolonged isothermal heating the VP decreased monotonically to a value near  $P_{\text{ref}}$ .

To explain the observations above and for the discussion that follows, we give in Table 3 selected salient details of the experiments whose results are shown in Figures 1–4. These four experiments were selected for presentation because the initial compositions of the samples were near to the congruently effusing composition of  $\text{Ga}_2\text{Se}_3(\text{s})$ . In the figures, vertical lines mark the times of temperature changes. The mass lost and duration at each  $T$  are given to emphasize their role in enhancement of VP. The ratios  $P_t/P_{\text{ref}}$  are given to show the unusual magnitude of the VP in comparison to  $P_{\text{ref}}$  at various times. Values of  $P_t$  consistently became higher than  $P_{\text{ref}}$  when the samples were first heated above 1225 K. Often these higher ratios persisted for periods sufficiently long to identify  $P_t$  as isothermally invariant: (1) In set A, a stable value of  $P_t = 6.7$  Pa was obtained at  $T = 1182$  K after the sample had been heated at  $T > 1225$  K for more than 2 h and subsequently was at  $T < 1200$  K for 80 min, whereas, prior to heating at  $T > 1225$  K, the same value of  $P_t$  was measured only at  $T = 1207$  K, some 25 K higher. (2) In set B,  $P_t/P_{\text{ref}} = 1.37$  at 1164 K, after the sample had been heated at 1239 K. (3) In set C, the increases in  $P_t/P_{\text{ref}}$  during cooling cycles are apparent; at  $T = 1174$  K,  $P_t$  remained steady at a value as high as 6.5 Pa for about 30 min before decreasing monotonically to another steady value in the range 2.4–2.7 Pa in 2 h; upon heating the sample again to  $T = 1257$  K and cooling back to  $T = 1190$  K through an intermediate  $T$  of 1219 K, a high value of  $P_t$  in the range 6.9–7.2 Pa obtained for about 15 min before  $P_t$  decreased to 4.1 Pa, in accord with

the value of 3.9 Pa at  $T = 1194$  K measured earlier in the same experiment. (4) In set D, the sample was kept at high  $T$  for long periods, and the cooling step yielded  $P_t = 2.6$  Pa at  $T = 1160$  K,  $P_t/P_{\text{ref}} = 1.38$ , an effect consistent with that seen in set B at similar  $T$ .

The observations given in Table 3 and Figures 1–4 suggest that heating a congruently effusing sample of  $\text{Ga}_2\text{Se}_3$  to  $T > 1225$  K initiated a composition change in the condensed phase, and subsequent cooling to  $T < 1225$  K caused reversal of that change. We examine two hypotheses to explain such composition changes: (1) that the composition of the congruently effusing phase changes strongly with  $T$ ; (2) that a condensed-phase transition occurs near 1225 K and that the two condensed phases have different compositions. Comparison of the values of  $P_t$  and  $P_k$  and assumption that  $\text{Ga}_2\text{Se}(\text{g})$  and  $\text{Se}_2(\text{g})$  are the only species in the vapor indicate that the composition change at  $T > 1225$  K resulted from selenium depletion ( $P_k < P_t$  usually) and the reversal at  $T < 1225$  K resulted from gallium depletion ( $P_k > P_t$ ). These indications are in line with results of Berger et al.<sup>29</sup> When heated to  $T > 1240$  K, samples lost at least 10% of their masses before  $P_t/P_{\text{ref}}$  became unity. Such high mass loss, if assumed to occur as a result of preferential removal of selenium, would require a composition change much greater than the known homogeneity range of  $\text{Ga}_2\text{Se}_3(\text{s})$ .<sup>20</sup> We suggest that the high ratios of  $P_t/P_{\text{ref}}$  and the continuous decrease in VP for long durations at  $T > 1225$  K imply that vapor constituents  $\text{Ga}_2\text{Se}(\text{g})$  and  $\text{Se}_2(\text{g})$  are of varying importance in the temperature range of this work and that another congruently effusing phase exists, Ga-rich relative to  $\text{Ga}_2\text{Se}_3(\text{s})$ , probably a



liquid phase, as proposed by Dieleman et al.<sup>20</sup> Those authors reported residues corresponding to compositions ranging from  $\text{Ga}_{0.432}\text{Se}_{0.568}$  to  $\text{Ga}_{0.44}\text{Se}_{0.56}$  upon heating  $\text{GaSe(c)}$  or  $\text{Ga}_2\text{Se}_3\text{(c)}$  at  $1203\text{ K} < T < 1393\text{ K}$  in effusion cells. Any estimate of sample compositions from our mass-loss experiments will have large uncertainty, but if the entire mass lost at  $T > 1225\text{ K}$  during transformation to the new condensed phase were in the form of  $\text{Se}_2\text{(g)}$ , then a 10% mass loss would correspond to a composition change of  $\approx 0.04$  atomic fraction Se.

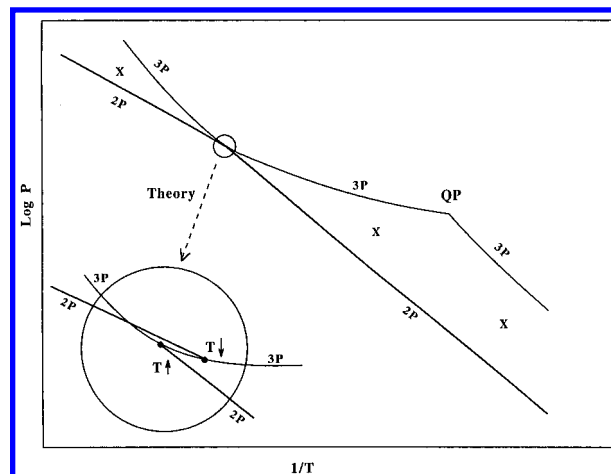
VP measured with Knudsen effusion by Dieleman et al.<sup>20</sup> for the high- $T$  congruently effusing phase in the range of  $T$  studied by us, viz.  $P(1234\text{ K}) = 6.8\text{ Pa}$  and  $P(1274\text{ K}) = 16.6\text{ Pa}$ , are lower by a factor of  $\approx 2$  than those measured by us. Dieleman et al. reported that their values from Knudsen effusion measurements agreed within a factor of 2 with theirs from levitation of loose lids of the effusion cells but did not state which technique yielded higher VP. A reasonable kinetic model could explain VP low by a factor of 2 with the unusually large orifice used in their effusion experiments,  $20\text{ mm}^2$ , if their sample size was approximately the same as that used in our experiments. With the assumption that the uncertainties in their pressures were independent of  $T$ , we subjected their results to a least-squares treatment and deduced the following equation:

$$\log(P/\text{Pa}) = -(1.626 \pm 0.072) \times 10^4(K/T - 7.708 \times 10^{-4}) + 1.463 \pm 0.018 \quad (8)$$

where the uncertainties are standard deviations. This equation, treated as though it represents reaction 2, yields very nearly the same second-law enthalpy as does our eq 7, the slopes agree within a standard deviation, and at  $1200\text{ K}$ , eq 7 gives  $5.5\text{ Pa}$  and eq 8 gives  $2.8$ , in line with the factor of  $\approx 2$  discussed above. We realize, as did Dieleman et al., that our values of VP at  $T > 1245\text{ K}$  are subject to errors owing to failure of molecular flow conditions at high pressures. However, no measurable differences from straight lines were found at high VP in plots of  $\log P$  vs  $1/T$ , and thus failure of molecular flow was insignificant in the present terms.

In Figure 5 the maximum VP form a curved upper boundary, and the curve ends at  $T = 1155 \pm 5\text{ K}$  (discussed henceforth without the uncertainty). Values of VP on the curve were assumed to be from three-phase equilibria, viz. two condensed phases and vapor, although only those at  $T < 1240\text{ K}$  remained invariant during measurement. The composition of the system within the effusion cell could vary while three phases were present, because the amount of each condensed phase could vary. The curved boundary, then, is the projection of a surface along the composition axis onto the transformed  $P$ - $T$  plane. The minimum values of VP could be interpreted as straight lines and were assumed to represent two-phase equilibria during congruent effusion of condensed phases. The straight line from eq 6 and the putative ones through minimum values of VP meet the putative curved boundary practically tangentially at  $T \approx 1225\text{ K}$ . Hence,  $T = 1225 \pm 10\text{ K}$  (discussed henceforth without the uncertainty) is taken to be  $T$  of the subject phase transition of  $\text{Ga}_2\text{Se}_3\text{(s)}$ . Within the range implied by the uncertainty lie the maximum  $T$  at which the low- $T$  condensed phase effuses congruently and the minimum  $T$  at which the high- $T$  condensed phase effuses congruently.

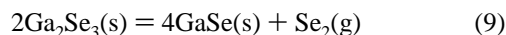
The effects described in the last paragraph are seen in Figure 6 as well, where VP is transformed to third-law enthalpy and the abscissa is  $T$ . The effects are amplified by the transformation. Larger VP gives lower enthalpy, and so the curved boundary is found at the bottom in Figure 6. The narrow waist at  $1225\text{ K}$  is at  $T$  of the transformation.



**Figure 7.** Schematic representation of the envelope in Figure 5 explained theoretically by Edwards and Franzen.<sup>1</sup>

Data that fall between the curved upper boundary and the straight lower boundaries above  $1155\text{ K}$  in Figure 5 (and in Figure 6, mutatis mutandis) were obtained while incongruent effusion of a single condensed phase was occurring, i.e., after the unstable condensed phase was exhausted from a three-phase equilibrium but before the congruently effusing composition of the stable condensed phase had been reached. As it must, the VP decreased continually during each of these measurements, and measurements were made at arbitrary times during such transitions.

Termination in the decreasing- $T$  direction at  $1155\text{ K}$  of the curved boundaries in Figures 5 and 6 resulted from stabilization of the phase  $\text{GaSe(s)}$  and onset of the three-phase equilibrium represented by eq 1 and the necessary accompanying simultaneous equilibrium represented by



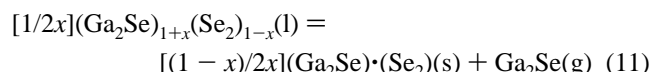
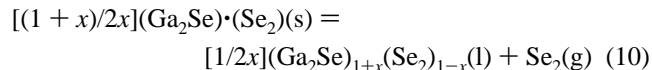
At the terminal  $T$ , the VP was  $5.0 \pm 1.0\text{ Pa}$ . This VP is within  $1\text{ Pa}$  of that measured by Piacente et al.<sup>27</sup> for reaction 1 with assumed insignificant contribution by  $\text{Se}_2\text{(g)}$ . One concludes that the termination owes to intersection of two three-phase equilibrium surfaces in pressure, temperature, composition space, so that at  $T$  below the intersection the maximum values of VP are determined by the simultaneous reactions 1 and 9. If the system is taken to be two-component, the cusp in Figure 5 or Figure 6 at  $1155 \pm 5\text{ K}$  and  $5.0 \pm 1.0\text{ Pa}$  is a quadruple point at which the pressure and temperature are fixed by equilibrium among  $\text{GaSe(s)}$ , the high- $T$  and the low- $T$  condensed phases of  $\text{Ga}_2\text{Se}_3$ , and the vapor, and at which the compositions of all four phases are fixed. The composition of the system at the quadruple point could be varied by varying the amounts of the four phases in the system.

The data in Figure 5 lie within an envelope whose upper and lower boundaries are fixed by the properties of isothermally invariant chemical equilibria. The envelope is shown schematically in Figure 7, which is patterned after the data in Figure 5 and after Figures 4 and 5 of Edwards and Franzen.<sup>1</sup> From the highest  $T$  in this study,  $1289\text{ K}$ , to  $1155\text{ K}$ , the upper boundary is determined by the three-phase (3P) equilibrium among the high- $T$  and the low- $T$  congruently effusing condensed phases and the vapor. From  $1289$  to  $1225\text{ K}$  the lower boundary is determined by the two-phase (2P) equilibrium between the high- $T$  congruently effusing condensed phase and its vapor. From  $1225\text{ K}$  to the lowest  $T$  in this study,  $1110\text{ K}$ , the lower boundary is determined by the two-phase (2P) equilibrium

between the low- $T$  congruently effusing phase, written as  $\text{Ga}_2\text{Se}_3(\text{s})$ , and its vapor. And from 1155 K to the lowest  $T$ , the upper boundary is determined by the three-phase (3P) equilibrium represented by eqs 1 and 9. Within the envelope, VP is determined by isothermally univariant two-phase (X) equilibria between the stable condensed phase at its temporal composition and the vapor.

The envelopes in Figures 5–7 were explained theoretically by Edwards and Franzen;<sup>1</sup> cf. their Figures 4 and 5. In Figure 7 theory is used to imply the expanded circular inset from around the region of condensed-phase transition.  $T^\uparrow$  denotes  $T$  of the increasing- $T$  transition and  $T^\downarrow$  that of the decreasing- $T$  transition. The difference in compositions of the high- $T$  and low- $T$  congruently effusing phases in the present work is higher than that used for illustration by Edwards and Franzen, and in consequence the three-phase equilibrium curve in the present work has no minimum above 1155 K. Below that  $T$ ,  $\text{GaSe}(\text{s})$  is stable in the effusion cell, and the upper boundary of the envelope assumes a negative slope, as shown by Piacente et al.<sup>27</sup> VP in this work below 1155 K always were lower than those of Piacente et al., because the small amount of  $\text{GaSe}(\text{s})$  formed in the transition at 1155 K was exhausted before stable measurements could be made. However, curvature in the upper boundary of the envelope above 1155 K, greatest at the  $T$  of the phase transition, 1225 K, supports the theory.<sup>1</sup>

If the formula of the low- $T$  phase is  $\text{Ga}_2\text{Se}_3(\text{s})$ , or  $(\text{Ga}_2\text{Se})\cdot(\text{Se}_2)(\text{s})$ , and that of the high- $T$  condensed phase is  $\text{Ga}_{2(1+x)}\text{Se}_{3-x}(\text{l})$ , or  $(\text{Ga}_2\text{Se})_{1+x}(\text{Se}_2)_{1-x}(\text{l})$ ,  $x = 0.1$ , after Dieleman et al.,<sup>20</sup> then the effusion reaction near  $T$  of the phase transition is represented by the simultaneous chemical equations



To analyze the equilibrium, more information such as the vapor-phase composition as well as the compositions of the congruently effusing condensed phases as functions of  $T$  is required. A high-temperature mass spectrometric study of effusion of  $\text{Ga}_2\text{Se}_3$  in the range 1100–1289 K would be highly desirable.<sup>50</sup>

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