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Effusion reactions in the ZnSe–$ZnIn_2Se_4$ system

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Abstract

Chemical changes during effusion of substances in the binary ZnSe–$ZnIn_2Se_4$ system were observed during 21 studies by the simultaneous Knudsen- and torsion-effusion method. Principal vapor species were taken to be Zn(g), In_2Se(g), and Se_2(g). Two intermediate solid phases were found in the temperature range 1100–1200 K, $ZnIn_2Se_4$(s) and $(ZnSe)_5In_2Se_3$(s). The latter phase vaporized congruently throughout the temperature range, but it effused congruently only above 1150 K; it was not observed at room temperature. $ZnIn_2Se_4$(s) effused incongruently to a vapor rich in zinc sulfide and a condensed phase rich in indium selenide. Here, proposed binary pressure-composition phase diagrams of this system at approximately 1120 and 1190 K are given, and equations for all effusion reactions in the system are presented. Stability of the two intermediate condensed phases relative to the chemically binary constituents are small, $\Delta H^\circ(298\ \mathrm{K}) = -12.5 \pm 3.5$ kJ/mol for $ZnIn_2Se_4$(s), and for the other phase it was less than the experimental error. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Binary system; Knudsen-effusion method; Torsion-effusion method

1. Introduction

Zinc diindium selenide, $ZnIn_2Se_4$(s) is an important solid-state material and model compound. Its photoconductivity [1–4] and electrooptical memory effect [5] have been reported. The first report of $ZnIn_2Se_4$ was by Hahn et al. [6] who gave crystallographic data. Its unit cell is tetragonal in space group S_4^2, with lattice constant $a = 0.569$ nm and $c = 1.149$ nm [6]. Veliev et al. [7] gave $a = 0.5715$ nm and $c = 1.143$ nm. Other reports [1,3,4] agree with Hahn et al. The melting point of $ZnIn_2Se_4$(s) is 1253 K [7]. Measurements of the heat capacity in the range from 15 to 300 K by adiabatic calorimetry gave the standard entropy, $S^\circ(298\ \mathrm{K}) = 299.20 \pm 0.88$ J/mol K [7]. No information exists on the thermochemical properties of $ZnIn_2Se_4$(s) at higher T or about its vaporization chemistry.

Considerable information is available about the binary components zinc selenide, ZnSe, and indium sesquiselenide, In_2Se_3. The stable form of ZnSe at low T is cubic [8] (zinc blende) with $a = 0.5667$ nm [9], 0.56782 ± 0.00081 nm [10], or 0.567 nm [11]. Above 1300 K the hexagonal form [8,9] was observed. Values of the lattice constants were $a = 0.4003 \pm 0.0001$ nm and $c = 0.6540 \pm 0.0003$ nm [9] or $a = 0.398$ nm and $c = 0.655$ nm [11]. In the T range from 1150 to 1250 K a mixture of both forms was found [8].

The cubic/hexagonal transition occurred at 1339 K by DTA [12]. C_p at 300 K has been reported [13–15]. The formation enthalpy of ZnSe was determined by direct measurement with a differential calorimeter

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Table 1
Literature data about formation enthalpy of ZnSe(s)

No.	Source	Method	Temperature (K)	ΔH° (298 K, ZnSe) (kJ/mol)
1	Korneeva et al. [22]	Knudsen cell mass loss	916–1095	–175.0 ± 1.2[a]
2	Wösten and Geers [18]	Transport in N_2	1060–1393	–196.6, –183.4 ± 13.3[a]
3	Goldfinger and Jeunehomme [20]	Knudsen cell mass loss	980–1220	–164.4
4	Sedgwick and Agule [19]	Bourdon gauge reaction ZnSe+I	900–1200	–184.9
5	Terpilowski and Ratajczak [17]	EMF in concentration cell	360–420	–163.2 ± 2.9
6	Wagman et al. [28]	Estimated	–	–163.2
7	Charlot et al. [16]	DSC	About 700	–156.5 ± 3.8
8	Karapet'yans and Karapet'yans [29]	Estimated		–129.7
9	Hassan and Munir [21]	Knudsen cell torsion	952–1209	–176.7 ± 1.1[a]
10	Mills [27]	Selected		–159.0 ± 8.4
11	This work	Knudsen cell mass loss	1086–1220	–179.5 ± 1.1
12	This work	Knudsen cell torsion	1086–1220	–180.0 ± 1.2
13	Brebrick and Liu [30]	Optical density measurements	1273–1400	–177.8

[a] Calculated from Knudsen pressure.

[16], by e.m.f. measurements with a concentration cell [17], and by measurements of the equilibrium constant of the vaporization reaction of ZnSe(s) [18–25]; values from these works are given in Table 1.

The melting point of ZnSe is 1788 K with heat of fusion 66.9 ± 5.0 kJ/mol (16.0 ± 1.2 kcal/mol) [26]. In the tabulation by Mills [27] the melting point is given as 1799 K. A reversible transition at 1698 K was reported [12].

Thermodynamic properties of ZnSe reported before 1974 were tabulated by Mills [27]. Other tabulations include Wagman et al. [28] and Karapet'yans and Karapet'yans [29]. Latest values, including standard molar enthalpy of formation at 298 K of –177.8 kJ, were given by Brebrick and Liu [30] in 1996.

The vaporization reaction of ZnSe(s) has been studied by transport [18,25,23], Knudsen-effusion [20,22], torsion-effusion [21], and mass spectrometry [31]. Mass spectrometry showed that the major vapor species are Zn(g) and Se_2(g). Goldfinger and Jeunehomme [20] reported that ZnSe(s) effused congruently by the reaction

$$2/3\mathrm{ZnSe(s)} = 2/3\mathrm{Zn(g)} + 1/3\ \mathrm{Se_2(g)}. \qquad (1)$$

Third-law ΔH°(298 K) of reaction (1) recalculated from vapor pressures of Hassan and Munir [21] but with our thermal functions is 251.5 ± 1.0 kJ. From free evaporation and effusion studies. Hassan and Munir found significant kinetic limitations to the vaporization of ZnSe(s) and measured its condensation coefficient to be in the range 0.07–0.2.

An experimental study and literature review on the effusion of indium sesquiselenide, In_2Se_3, has been presented [32]. Effusion of In_2Se_3(s) in the range 1004–1156 K was incongruent, with net loss of Se_2(g) until In_5Se_6(1) effused congruently;

$$4/17\mathrm{In_5Se_6(l)} = 10/17\ \mathrm{In_2Se(g)} + 7/17\ \mathrm{Se_2(g)} \qquad (2)$$

ΔH°(298 K) of reaction (2) was 263.6 ± 1.3 kJ, and ΔH°(298 K) of the reaction

$$1/2\mathrm{In_2Se_3(s)} = 1/2\mathrm{In_2Se(g)} + 1/2\mathrm{Se_2(g)} \qquad (3)$$

was 30 1 ± 2 kJ [32]. In a concurrent study of the effusion of $CdIn_2Se_4$(s) [33], the system remained thermodynamically binary, on the CdSe–In_2Se_3 join, until the composition of In_2Se_3(s) was reached by net loss of CdSe to the vapor as Cd(g) and 1/2Se_2(g).

In this paper, the word "effuse" and its derivatives are used both transitively and intransitively to represent the composite process by which a condensed phase within an effusion cell evaporates, passes through the vapor phase within the cell, and finally effuses through the orifice. The chemical reactions in this process can be different from those in other types of vaporization processes, e.g., those in a closed system or those in transpiration [34].

The established term "euatmotic point" [35] is applied here in two-component systems to denote a point in pressure(P)–temperature(T)–composition(C) space at which a mixture of two condensed phases with overall composition C is in equilibrium with a vapor of the same C. The C of a euatmotic point must lie in the range between the individual compositions of the two condensed phases. When C of the vapor in equilibrium with two condensed phases lies outside the range between their individual compositions, the corresponding point on the vapor composition (VC) curve will be called a "periatmotic point".

To represent C, the lower-case x will be used for the molar ratio [ZnSe]/[In_2Se_3], e.g., for the phase $ZnIn_2Se_4$(s), $x = 1$, and the label upper-case X will be used for mole fraction, e.g., when $x = 1$, $X(\mathrm{ZnSe}) = 0.5$. It will be the convention here to balance all chemical equations for effusion reactions to produce 1 mol of vapor, as was done with Eqs. (1)–(3).

The goals of the present work were: learn the effusion reactions in the ZnSe–$ZnIn_2Se_4$ system by use of the simultaneous Knudsen-effusion and torsion-effusion method and ancillary experiments; measure equilibrium constants (K_p) and calculate the thermodynamic properties of the effusion reactions and the reacting substances; establish parts of the P–C phase diagram of the ZnSe–In_2Se_3 system.

2. Experimental

2.1. Samples

Zinc shot 3.2 mm, m6N (Alfa Products), selenium shot 1.6 mm, m5N$^+$ (Alfa Products) and indium wire 99.99% (Indium Corporation of America) were used. Samples with $x = 19$, 9, 5.67, 4, 2.33, 1.5, 1.0, and 0.67, and a sample of ZnSe, $x = \infty$, were prepared by heating the elements in evacuated, sealed Vycor tubes in a tube furnace. The T of the furnace was increased slowly to 900°C over several days until the product appeared homogeneous. The tube was removed, quenched in water, and opened. The product was ground with an agate mortar and pestle and stored in a closed glass vial in a desiccator over $CaSO_4$. Each sample was analyzed for phase content by X-ray powder diffraction. A sample with $x = 5.86$ was prepared by thoroughly mixing equal masses of samples with $x = 9$ and $x = 4$; no further treatment of this sample was done before it was placed in a cell for effusion study.

2.2. Apparatus

The apparatus used for vapor pressure (VP) measurements has been described [36–39]. It comprises two effectively independent systems operating simultaneously with the same sample: a dynamically operated torsion-effusion pendulum and a balance for mass measurements. The pendulum was used to measure the rate of momentum loss from the effusion cell. The balance was used to measure mass and the rate of mass loss from the effusion cell.

Graphite torsion-effusion cells labeled 5 and 109, with cylindrical orifices, were used. The design of the cells has been described [40]. Moment arms, diameters of the orifices, and thicknesses of the walls in which orifices were drilled were measured with a traveling microscope. The photographic method [41] was used for measurements of the orifice areas, A. From these data the transmission probabilities, W, and recoil-force factor, f, of the orifices were calculated with a computer program using equations from Freeman and Edwards [42]. The mensural properties of the effusion cells are given in Table 2.

T was measured with an optical pyrometer calibrated through a tungsten band lamp against a

Table 2
Mensural properties of the effusion cells

Cell	Orifice	r (cm)	L (cm)	10^3 A (cm^2)	d (cm)	W	f
5	1	0.0312 ± 0.0006	0.1194 ± 0.0020	3.06 ± 0.12	0.8123 ± 0.0060	0.366 ± 0.011	0.413 ± 0.012
	2	0.0314 ± 0.0007	0.1245 ± 0.0019	3.10 ± 0.14	0.8123 ± 0.0060	0.358 ± 0.007	0.405 ± 0.006
109	1	0.0329 ± 0.0002	0.2144 ± 0.0042	3.40 ± 0.04	0.7930 ± 0.0072	0.260 ± 0.003	0.296 ± 0.003
	2	0.0321 ± 0.0003	0.2144 ± 0.0061	3.24 ± 0.05	0.7930 ± 0.0085	0.256 ± 0.006	0.291 ± 0.007

calibrated optical pyrometer [43]. Calibration of the window and prism between the pyrometer and the cell during VP measurements was by a standard method [44,45].

2.3. Data collection and treatment

In the course of a study, primary data were considered to be: type (a), cell and orifice parameters: type (b), initial C of samples; type (c), T; type (d), mass of the pendulum; type (e), time, t; and type (f), times at which the torsion pendulum was at a set of preselected positions. Data of types (d) and (e) were combined to give type (g), the rate of mass loss by effusion of the sample, $\dot{g}$. The Knudsen pressure P_K was calculated from types (a), (c), and (g) with the Knudsen equation [45]

$$P_K = \dot{g}(2\pi RT/M^*)^{1/2}/(W_1A_1 + W_2A_2), \qquad (4)$$

W and A are orifice transmission probability [42] and area, respectively, the indexes on W and A identify the orifices, and M^* is an assigned molecular weight (MW) and can be any positive real number. If P_K is to be the "true" P, then the VC must be known, and M^* must be set equal to the Knudsen average MW, M_K,

$$M_K = \left(\sum_{J=1}^{n} m_j M_j^{-1/2}\right)^2 \qquad (5)$$

in which n is the number of molecular species effusing, m_j is the mass fraction, and M_j is the MW of species j in the effusing vapor. To the extent that VC is uncertain, P_K is uncertain as revealed by Eqs. (4) and (5).

Data of type (f) were used to solve the equation of motion of the torsion pendulum. Each solution, with the torsion constant of the torsion fiber, k, and data of type (a) yielded the torsion pressure, P_t, through the Volmer equation [46,47].

$$P_t = 2k\Delta\theta/(d_1f_1A_1 + d_2f_2A_2), \qquad (6)$$

where k is the torsion constant of the torsion pendulum, $\Delta\theta$ is the deflection by effusing vapor of the pendulum from its rest point with no vapor effusing, and d is moment arm and f is recoil force correction factor [42] of each orifice. P_t is the "true" pressure and is independent of T and the nature of the effusing vapor. The apparent MW, M_a can be calculated with the equation

$$M_a = M^*(P_K/P_t)^2. \qquad (7)$$

M_a is independent of M^* because the same M^* is used in both Eqs. (4) and (7).

In calculating P_K with Eq. (4), the arbitrary value $M^* = 188.4$ was used. That value would be M_K from Eq. (5) of a hypothetical effusing vapor comprising Zn(g), In_2Se(g), and Se_2(g) effusing in the molar ratios 1 : 1 : 1.5, respectively. Within the bonds of the stoichiometry assumption of Eq. (11) a value of $M < 188.4$ from Eq. (7) would indicate relatively more of the vapor of ZnSe(s), i.e., Zn(g) + $\frac{1}{2}$$Se_2$(g), and $M > 188.4$ would indicate relatively more of the vapor of In_2Se_3(s), i.e., In_2Se(g) + Se_2(g).

2.4. Vapor analysis

P_K and P_t were used to analyze the vapor [41]. The effusing vapor was taken to comprise Zn(g), Se_2(g), and In_2Se(g) [20,48].

The sum of the partial pressures equaled total P,

$$P_{\text{total}} = P_{\text{Zn}} + P_{\text{Se}_2} + P_{\text{In}_2\text{Se}}. \qquad (8)$$

The mass of the system was conserved,

$$\dot{g} = \dot{g}_{\text{Zn}} + \dot{g}_{\text{Se}_2} + \dot{g}_{\text{In}_2\text{Se}}. \qquad (9)$$

With Eq. (4), Eq. (9) became

$$P_K(M^*)^{1/2} = P_{\text{Zn}}(M_{\text{Zn}})^{1/2} + P_{\text{Se}_2}(M_{\text{Se}_2})^{1/2} + P_{\text{In}_2\text{Se}}(M_{\text{In}_2\text{Se}})^{1/2}. \qquad (10)$$

The binary, ZnSe/In_2Se_3, chemical stoichiometry of the system was assumed to be conserved as it was conserved in the CdSe/In_2Se_3 system [33], and thus it was required that

$$\dot{n}_{\text{Se}_2} = \dot{n}_{\text{In}_2\text{Se}} + 1/2\dot{n}_{\text{Zn}}, \qquad (11)$$

where $\dot{n}$ is the rate of molar loss. With Eqs. (4) and (9), Eq. (11) became

$$P_{\text{Se}_2}/(M_{\text{Se}_2})^{1/2} = P_{\text{In}_2\text{Se}}/(M_{\text{In}_2\text{Se}})^{1/2} + 1/2P_{\text{Zn}}/(M_{\text{Zn}})^{1/2}. \qquad (12)$$

Simultaneous solution of Eqs. (8), (10), and (12) gave partial pressures of Zn(g), Se_2(g), and In_2Se(g) in the effusion cell. With the values $M_{\text{Zn}} = 65.37$, $M_{\text{Se}_2} = 157.9$ and $M_{\text{In}_2\text{Se}} = 308.6$ the solution was

$$P_{\mathrm{Zn}} = 1.602\, P_{\mathrm{t}} - 0.1035\, P_{\mathrm{K}} M^{*^{1/2}}, \quad (13)$$

$$P_{\mathrm{Se_2}} = 0.475\, P_{\mathrm{t}} - 0.00373\, P_{\mathrm{K}} M^{*^{1/2}}, \quad (14)$$

$$P_{\mathrm{In_2Se}} = -1.077\, P_{\mathrm{t}} + 0.1072\, P_{\mathrm{K}} M^{*^{1/2}}. \quad (15)$$

Again, the solution was not dependent on the value chosen for M^*.

Examination of Eqs. (13)–(15) reveals that sufficient variation in the experimental values of P_K and P_t can yield a negative partial pressure of Zn(g) or In_2Se(g), particularly when the partial pressure is a small fraction of the total P. Such an outcome is especially likely when the fraction of either component (ZnSe or In_2Se_3) in the sample is small. Results from vapor analyses were recorded but not used when negative partial pressures were produced.

2.5. Thermodynamics

After the effusion reactions in the ZnSe–$ZnIn_2Se_4$ system were deduced, vide infra, K_p were calculated with P from Eqs. (13)–(15). Standard enthalpy increments at 298.15 K, ΔH°(298 K) of the effusion reactions were calculated by the usual methods [49,50] from K_p and T with Gibbs-energy functions (fef) given in the literature. The values of fef were from Mills [27] for ZnSe(s) and Se_2(g), from Hultgren et al. [51] for Zn(g), from Srinivasa et al. [33] for In_2Se_3(s), and from Greenberg et al. [52] for In_2Se(g). The fef of ZnSe(s), In_2Se_3(s), Zn(g), In_2Se(g), and Se_2(g) are given in Table 3. The fef of $ZnIn_2Se_4$(s) were estimated by Kopp's rule [49] to be equal to the sum of the fef of the constituent selenides, ZnSe(s) and In_2Se_3(s).

The result form Eqs. (13)–(15) could be used in thermodynamic analyses of condensed phases present during the effusion experiments. When the condensed phase had C between those of ZnSe and In_2Se_3, two effusion reactions occurred simultaneously and could, for purposes of reference, be represented by the chemical equations

$$2/3\ \mathrm{ZnSe\ (in\ condensed\ phase)} = 2/3\ \mathrm{Zn(g)} + 1/3\ \mathrm{Se_2(g)}$$

$$1/2\ \mathrm{In_2Se_3\ (in\ condensed\ phase)} = 1/2\ \mathrm{In_2Se(g)} + 1/2\ \mathrm{Se_2(g)}. \quad (17)$$

Of course, the nature of the condensed phase depended on C and T. Third-law analysis, with activities in the condensed phase arbitrarily set at unity, would yield values of ΔH°(298 K) of reactions (16) and (17) that gave information about the energy with which ZnSe(s) and In_2Se_3(s) were bound into the condensed phase when the same values were compared with ΔH°(298 K) of reactions (1) and (3).

2.6. Procedure

Twenty-one effusion studies of samples in the ZnSe–In_2Se_3 system were done. Details are given in Table 4. Each study began with a new sample loaded into an outgassed effusion cell attached to a torsion pendulum with calibrated fiber. Four types of studies were done:

Type A: the VP of a sample was studied as a function of T. T was set and held constant for as long as was required to make the VP measurement, then it was changed to a new value according to a program which produced a dispersed distribution of T [53].

Type I1: isothermal experiments in which T was held as constant as possible throughout the study. T was measured periodically. The term isothermal is not perfectly applied here because T typically did drift by a few Kelvins during experiments lasting several hours.

Table 3
Values of free energy function (J mol^{-1} K^{-1}) − [$G^\circ(T)$–H°(298 K)]/T

T (K)	ZnSe(s) [20]	In_2Se_3(s) [31]	Zn(g) [48]	In_2Se(g) [52]	Se_2(g) [20]	Reaction		
						(1)	(23) or (25)	(20)
1000	97.2	270.8	171.5	362.6	264.8	206.7	356.6	145.5
1100	100.9	280.7	172.9	366.4	267.7	205.9	353.4	144.7
1200	104.4	290.2	174.2	370.2	270.4	205.0	350.4	144.0
1300	107.7	299.7	175.5	373.8	273.0	204.3	347.1	143.3

Table 4
Characteristics of the 21 studies

Study No.	Study type	Effusion cell	Ratio [ZnSe]/[In_2Se_3]	Initial mass (mg)	Mass lost (mg)	Range or Average T (K)	No. measurements of T
1	A	5	1.00	300.2	121.5	1068–1087	2
2	A	5	1.00	299.4	120.7	1065–1205	8
3	A	5	1.00	300.4	201.4	1048–1205	18
4	A	5	0.67	300.6	All	1078–1221	30
5	I1	5	0.67	201.0	All	1186 ± 2	17
6	I1	5	0.67	201.6	All	1195 ± 1	30
7	I1	5	0.67	201.4	All	1202 ± 4	10
8	A	5	1.50	201.1	All	1057–1232	34
9	I1	5	1.50	201.2	All	1189 ± 6	15
10	12	5	4.00	201.1	All	1085–1197	7
11	I1	5	4.00	201.6	All	1201 ± 5	8
12	12	109	9.00	200.9	All	1153–1195	12
13	I1	109	9.00	100.3	All	1178 ± 4	8
14	A	5	4.00	201.8	All	1084–1212	22
15	A	5	∞	201.0	144.2	1086–1220	10
16	12	5	9.00	141.6	All	1110–1205	16
17	D	5	4.00	70.0	44.5	1115–1231	12
			9.00	103.9	43.8		
18	D	5	9.00	100.4	25.5	1091–1210	12
			4.00	100.1	28.5		
19	D	5	4.00	101.2	65.3	1092–1205	21
			5.86	101.1	63.7		
20	I1	5	9.00	141.6	All	1193 ± 4	9
21	I1	5	5.67	141.6	All	1198 ± 4	16

Type I2: for various reasons, the attempt to keep T constant failed, and the study was done in long-term isothermal steps.

Type D: differential studies in which samples with different C were placed in the two chambers of the effusion cell, the orifices were directed in parallel directions rather than the usual antiparallel directions [46], and the difference between the torques generated by effusion of vapor from the two chambers was measured by the torsion-effusion method, while the usual measurements by the Knudsen method were done.

In some studies all of the sample was exhausted, and in some the study was stopped with sample remaining in the effusion cell.

Table 4 outlines the 21 studies. The first column gives the number of the study in chronological sequence. i.e., study $n+1$ was done after study n, the second column gives the type of study as defined in the previous paragraph, and the third column gives the number of the effusion cell used in the study. The fourth column gives the initial C of the sample as x, and the fifth and sixth columns give the initial mass of the sample and the mass lost during the study, respectively. The seventh column gives the range of T, and the eighth column gives the number of measurements of the T, roughly evenly distributed in time throughout the study. In cases of studies of type A, column eight is the number of measurements of VP versus T.

Study 15 was done with ZnSe(s) in order to obtain VP of ZnSe(s) with the same equipment and by the same procedures for comparison during analyses of the ZnSe/In_2Se_3 systems in the other studies. Moreover, results from study 15 could be compared with results of other workers by various methods on the VP of ZnSe(s).

Where VP was isothermally invariant in studies of type A, the data were fitted by least-squares to the equation

$$\mathrm{Log}_{10}(P/\mathrm{Pa}) = -D \cdot (K/T - F) + E, \qquad (18)$$

where P is the VP in Pa, T is temperature in K, F is the mean of the values of $1/T$, and D and E are parameters from the least-squares fit. For normally distributed data that fit the Clausius–Clapeyron model, this form gives uncorrelated coefficients, D and E.

The mean M_a during studies of Type I was calculated from observations made at intervals of about 1 min during the study. Because of the high correlations among such observations, uncertainties in these averages were estimated; the reported uncertainties are those estimates.

3. Results

3.1. Visual observations and X-ray analysis

Samples with $x < 4.0$ were black and were indistinguishable visually. The sample with $x = 5.67$ was black-red, and the sample with $x = 9.0$ was black with a yellow hue, the sample $x = 19$ was brick-red. The sample of ZnSe was yellow.

In X-ray diffraction patterns at room T of samples with C from $x = 1.0$ to $x = \infty$, that of ZnSe, changes from $ZnIn_2Se_4$ to ZnSe were seen. With $x = 1.0$, only lines of $ZnIn_2Se_4(s)$ were seen; with $x = \infty$, the X-ray diffraction pattern matched that reported in the literature [54] for the face-centered cubic form of ZnSe(s); at intermediate values of x, lines from both phases were seen. No indication of an intermediate phase in this range of C was found at room T.

3.2. Vapor-pressure measurements

The parameters in Eq. (18) from the least-squares analysis of data in Studies 2, 3, 4, and 15 are given in Table 5. Column 1 gives the Study number, column 2 gives the initial C of the sample as x, column 3 gives the method, columns 4 and 5 give the parameters D and E and their uncertainties, and column 6 gives the mean value of $1/T$ of the Study.

Third-law analysis of results from Study 15 with fef from Mills [27] yielded, for reaction (1), $\Delta H^\circ(298\ \mathrm{K}) = 253.42 \pm 0.35$ kJ and $\Delta H^\circ(298\ \mathrm{K}) = 253.06 \pm 0.31$ kJ from torsion-effusion measurements and from Knudsen-effusion measurements, respectively. An average of these results, 253.24 ± 0.47 kJ, was used with $\Delta H^\circ(298\ \mathrm{K})$ of Zn(g) [51], 130.42 ± 0.42 kJ/mol, and $Se_2(g)$ [27], 139.3 ± 2.1 kJ/mol, to obtain $\Delta H^\circ(298\ \mathrm{K})$ of formation of ZnSe(s), -179.8 ± 1.2 kJ/mol. Kinetic limitations to the sublimation of ZnSe(s), reported by Hassan and Munir [21], could decrease the magnitude of this result by as much as 1 kJ/mol, and thus the value -178 ± 3 kJ/mol may be better. This result compares favorably with the value given by Brebrick and Liu [30], -177.8 kJ/mol, and will be used with other results from Study 15 in subsequent analyses of the present results.

Results from Type I1 isothermal studies on samples with initial $x = 0.67$ and 1.5 (Studies 5, 6, 7, and 9) were consistent and can be illustrated with results from Study 9 with $x = 1.5$. The latter results are presented schematically but accurately in Fig. 1, where P_K, P_t, and M_a are plotted against percentage of the sample remaining in the cell. Fig. 1 reveals that isothermal effusion occurred in three stages bounded on the horizontal axis at 95% and 70%, at 70% and 40%, and at 25% and 2% of the original sample mass. The stages were separated by relatively rapid decreases in P from 69 to 71%, from 40 to 25%, and at 2% mass remaining. Slower decrease in P with decreasing sample mass occurred continuously during each stage.

Table 5
Parameters in Eq. (18) from least-squares

Study	Composition	Method	$(D \pm \sigma_D)\times 10^{-4}$ K	$E \pm \sigma_E$	$F\times 10^4$ K
2	1.00	Knudsen	1.608 ± 0.064	0.822 ± 0.022	8.81
		Torsion	1.678 ± 0.076	0.809 ± 0.026	8.81
3	1.00	Knudsen	1.477 ± 0.039	0.879 ± 0.019	8.66
		Torsion	1.372 ± 0.059	0.892 ± 0.029	8.66
4	0.67	Knudsen	1.300 ± 0.044	0.953 ± 0.014	8.66
		Torsion	1.320 ± 0.054	0.927 ± 0.017	8.66
15	∞	Knudsen	1.409 ± 0.228	0.959 ± 0.007	8.69
		Torsion	1.428 ± 0.278	0.942 ± 0.008	8.69

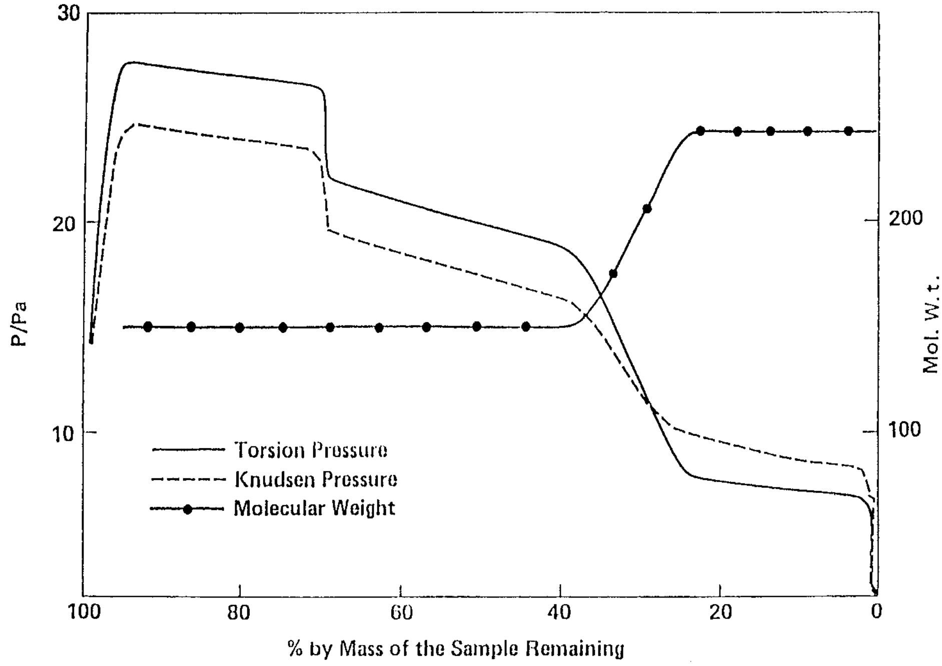

Fig. 1. Study 9: isothermal VP/Pa vs. percentage of sample remaining. Initial $x = 1.5$, $T = 1189 \pm 6$ K.

The initial rapid increase in VP was caused by the initial increase in T of the effusion cell. The relatively rapid decreases in VP at 69–71% and from 40% to 25% resulted from chemical changes in the sample. The relatively rapid decrease at 2% resulted from exhaustion of the sample. The slower decrease in P during the three stages was caused principally by a downward drift in T from 1196 ± 2 K in stage 1 to 1178 ± 1 K in the third stage.

The mass loss of the sample after the first stage was $30.6 \pm 0.5\%$ of the initial mass. If the euatmotic point during the first stage is taken to be at $x = 1.84 \pm 0.45$, an effusing composition of $x = 4 \pm 1$ (vide infra), then C at the end of the first stage was $x = 0.89 \pm 0.20$, which is adequate confirmation of the hypothesis that the first stage ended when C of $ZnIn_2Se_4$ was reached. The mean values of M_a during the first, second and third stages were 153 ± 5, 150 ± 5, and 242 ± 10 g mol^{-1}, respectively. By Eqs. (13)–(15) with typical P_K and P_t, VC within the effusion cell during Stage 1 was $x = 1.40 \pm 0.40$, which yields an effusing VC of $x = 3.1 \pm 1$. This result too, within the uncertainties, confirms the hypothesis. Similar calculations gave an effusing VC during Stage 2 of $x \approx 3.5$ and were concordant with the hypothesis that only In_2Se_3 or a phase with <10% by mass of ZnSe remained in the effusion cell at the end of the second stage.

Studies 5, 6 and 7, with $x = 0.67$ initially, showed only the Stages 2 and 3 seen in Study 9. The results from all four of these experiments are given in Table 6. The first column identifies the Study and the second column the average T. The third to the eleventh columns are in three groups of three with results from the first, second, and third stages, respectively. Within each group or stage, the first column gives the average P_K, the second column gives the average P_t, and the third column gives the mean of M_a from Eq. (7).

The results of Study 9 implied the existence of a congruently effusing composition (CEC), i.e., at least a euatmotic point [35] and perhaps one congruently effusing condensed phase, between those of $ZnIn_2Se_4$ and ZnSe. Study 11 was designed to locate the CEC. Effusion cell 5 was used with 201.6 mg of sample with $x = 4.00$. The Study was Type I at 1201 ± 5 K. The results from this study are shown in Fig. 2. During the study, after the initial rapid increase of T. T drifted downward slowly by ca. 5 K until an upward correc-

Table 6
Average values of the temperature, Knudsen and torsion pressures, and apparent molecular weight calculated from isothermal studies with samples with composition $x \leq 1.5$

Study	First stage				Second stage			Third stage		
	T (K)	P_K (Pa)	P_T (Pa)	M	P_K (Pa)	P_T (Pa)	M	P_K (Pa)	P_T (Pa)	M
5	1186 ± 2	–	–	–	16.5 ± 2.0	17.4 ± 1.0	170 ± 10	14.9 ± 3.0	13.1 ± 2.0	244 ± 10
6	1195 ± 1	–	–	–	22.7 ± 2.0	25.2 ± 1.5	153 ± 10	21.9 ± 3.0	18.2 ± 2.0	273 ± 15
7	1202 ± 4	–	–	–	28.3 ± 3.9	30.8 ± 3.0	159 ± 15	–	–	–
9	1189 ± 6	24.3 ± 1.0	26.9 ± 1.0	153 ± 5	18.3 ± 1.0	20.5 ± 1.0	150 ± 5	10.2 ± 1.5	9.0 ± 1.5	242 ± 10

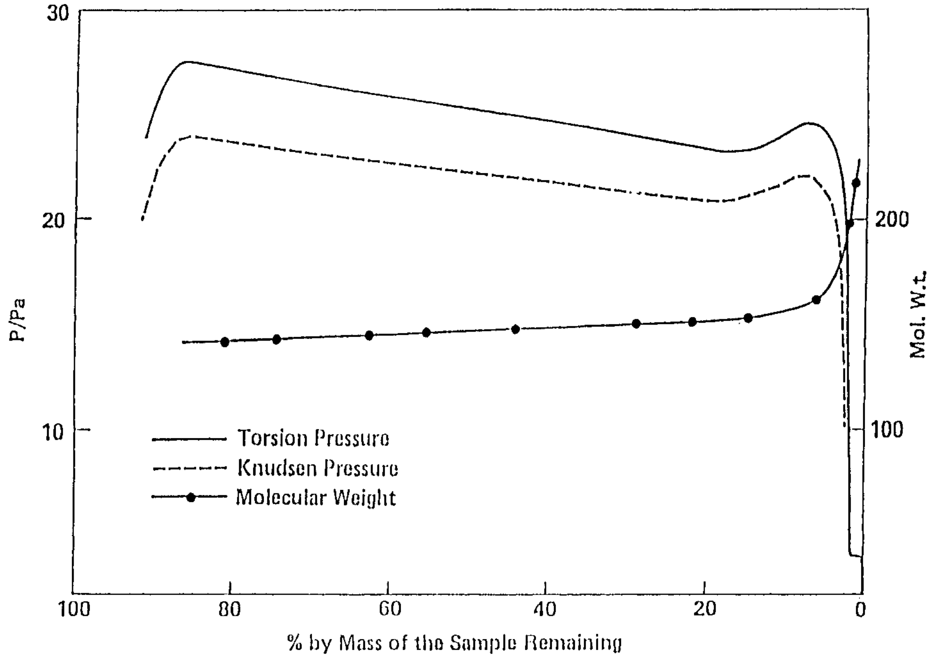

Fig. 2. Study 11: isothermal VP/Pa vs. percentage of sample remaining. Initial $x = 4.0$, T=1201 ± 5 K.

tion was made when ca. 85% of the mass had been lost. The uncertainty of ±5 K includes drifts, corrections, and random effects, but not the initial steep rise in T. P_t and P_K are plotted on the left ordinate and M_a plotted on the right ordinate as functions of the percentage of the original 201.6 mg of sample remaining in the effusion cell.

The VP rose sharply initially and reached a nearly constant value that corresponded to the nearly constant T. Each VP drifted downward with T and then rose with the correction. When the sample was 98% exhausted, P_t dropped sharply to a short plateau. As the sample was exhausted, each VP dropped sharply to 0. Since data accumulation of several minutes is needed for a measurement of P_K, such measurements could not be made in the last several minutes of the experiment, while the VP was dropping steeply, and thus the curve representing P_K ends before sample exhaustion.

The results shown in Fig. 2 are what one would expect from a two-component sample comprising two solid phases and vapor and whose initial C is near to that at a local maximum, a euatmotic point, [35] in the P–C phase diagram. Had the initial C been exactly that at the euatmotic point, the short plateau at the end of the Study in Fig. 2 would not have been seen. M_a of the

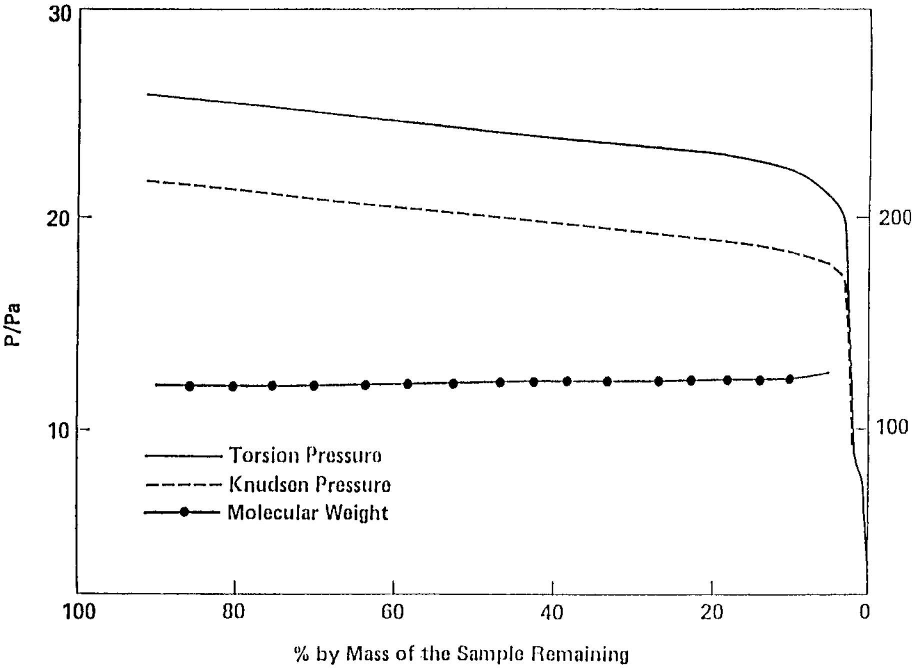

Fig. 3. Study 20: isothermal VP/Pa vs. percentage of sample remaining. Initial $x = 9.0$, $T = 1193 \pm 4$ K.

vapor was nearly constant through most of the Study but rose sharply at the end. Its average value between 20% and 85% mass loss was 152 ± 5 g mol^{-1}. The implication is that C of the condensed phase became richer in indium selenide and that the short plateau corresponded to the terminal stage in Study 9 and probably modified by exhaustion of sample from one chamber of the effusion cell before the other.

The results of Studies 9 and 11 implied the existence of a CEC between that of ZnSe and $x = 4.00$. Study 20 was designed to isolate that CEC. Effusion cell 5 was used with 141.9 mg of sample with $x = 9.00$. The Study was Type I with $T = 1193 \pm 4$ K. The results are displayed in Fig. 3. T drifted downward slightly during the Study, but no correction was made.

Fig. 3 gives the results of Study 20 as does Fig. 2 for Study 11. The mean M_a was 121 ± 5 g mol^{-1}. Indication of a short plateau, at lower P_t, was seen at the end, but not as distinctly as in Study 11. Fig. 3 presents the same picture as does Fig. 2, viz., that one would expect from a two-component sample comprising two solid phases and the vapor and whose initial C is very near to that at a euatmotic point in the P–C phase diagram. It should be noted, however, that Fig. 3 could as well be interpreted in terms of a single, congruently effusing phase.

Between two euatmotic compositions there must be at least one congruently effusing phase. The results of Studies 11 and 20 suggest the possibility of such a congruently effusing phase with C between $x = 4$ and $x = 9$. To locate C of such a phase more accurately, Studies 17, 18, and 19, Type D were done. Studies 17 and 18 established the difference in P (ΔP) between samples with initial $x = 4.00$ and $x = 9.00$. Study 19 established ΔP between samples with initial $x = 4.00$ and $x = 5.86$ and its results were very revealing. Studies 17 and 18 yielded the same results within experimental variation, and so, of these two studies, the results of Study 17 only are reported here. In Fig. 4 the points represented as diamonds are ΔP in Pa plotted against T/K as measured in Study 17 and the solid curve was drawn through the diamonds by visual comparison. Study 18 confirmed these observations.

The rest of the points in Fig. 4 represent results from Study 19. The data represented by circles were obtained initially, before 29% of the initial mass in the cell was lost; the curve broken by single dots was

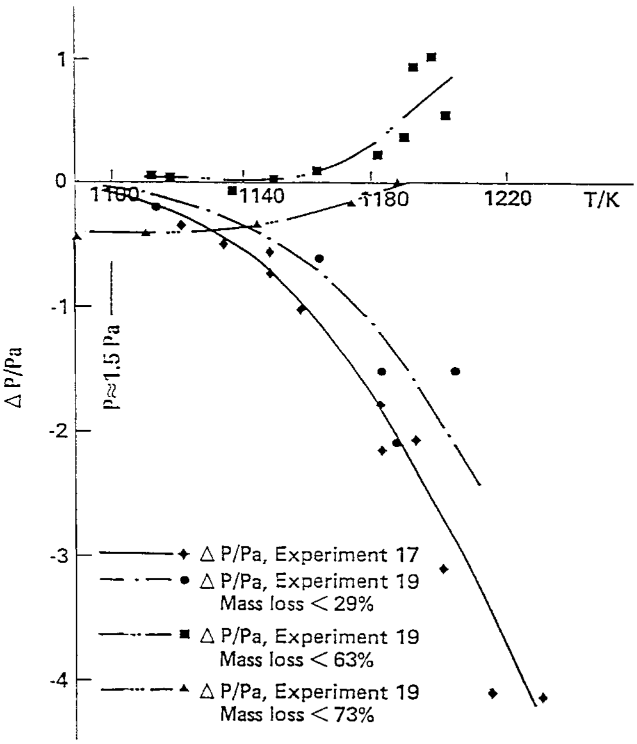

Fig. 4. Studies 17 (initially $x = 4$ vs. $x = 9$) and 19 (initially $x = 4$ vs. $x = 5.86$): differential P/Pa vs. T/K.

drawn through the circles. The data represented by squares were obtained next, after 31%, but before 63% of the initial mass was lost; the curve broken by double dots was drawn through the squares. Then data represented by triangles were obtained, after 65%, but before 73% of the initial mass was lost; the curve broken by triple dots was drawn through them. Clearly, the relationship between T of the cell and momentum loss from the cell changed abruptly between these mass-loss regions. Only 2–4 mg or 1–2% of the initial mass was lost during the changes. The study was terminated with 27% of the initial sample mass remaining in the cell.

In Studies 17 and 18, ΔP was negative; its magnitude increased monotonically with T throughout the Studies. Three stages occurred in Study 19 as described in the previous paragraph. During the first stage, represented by circles in Fig. 4, the results were the same, within acceptable uncertainty, as those in Studies 17 and 18. During the second stage, represented by squares in Fig. 4, ΔP increased monotonically with T, but with opposite sign to that in the first stage. During the third stage, represented by triangles in Fig. 4, the sign of ΔP was the same as in the first stage, but the magnitude decreased monotonically with T.

Study 21 was designed to locate more closely C of the congruently effusing phase between $x = 4.00$ and $x = 9.00$. The Study was Type I with cell 5, T of 1198 ± 4 K, and initial $x = 5.67$. The results are shown in Fig. 5. After the initial rapid increase of T, the VP was nearly constant until it rose as T increased, owing to a correction, as the last 10% of the initial mass of the sample was lost. Without intermediate stages, the VP dropped precipitously to zero when the sample was exhausted. M_a was practically constant at 133 ± 5 g mol^{-1} throughout.

Partial pressures of Zn, Se_2, and In_2Se were calculated by Eq. (13)–(15) with all 261 data from all experiments type A, I1, and I2 described in Table 4. A few negative values of Zn or Se_2 partial pressures resulted. and these data were rejected on statistical

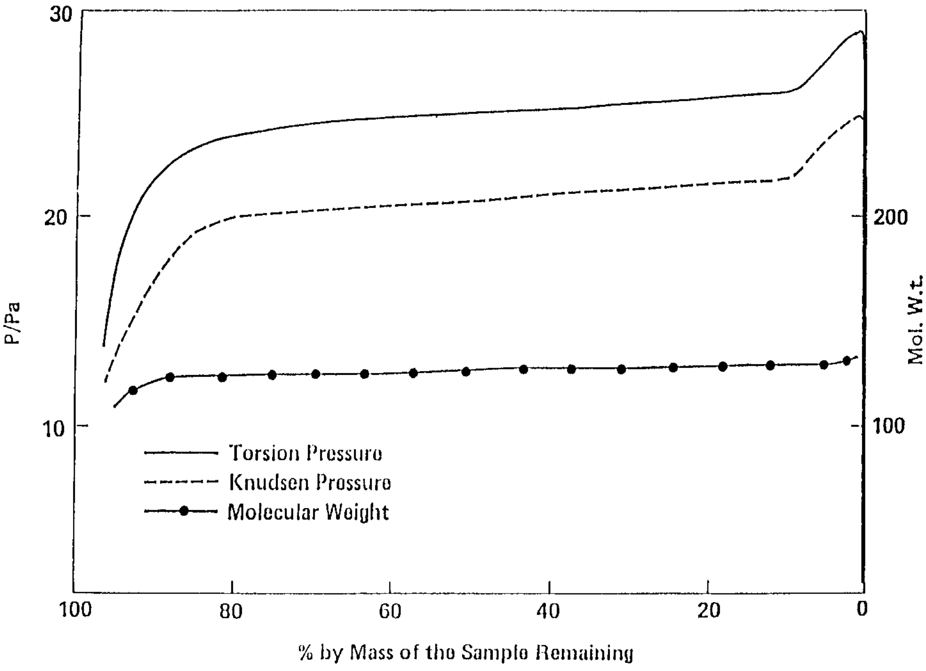

Fig. 5. Study 21: isothermal VP/Pa vs. percentage of sample remaining. Initial $x = 5.67$, $T = 1198 \pm 4$ K.

grounds; one datum was deleted from Study 2, three data from Study 3, eight data from each of Studies 4 and 5, 16 data from Study 16, and one datum from Study 21. The negative values of the partial pressure of In_2Se were observed in the first points in Studies in which samples have initial $x > 1.00$, i.e., when there might have been little $In_2Se(g)$ present, and negative values of the partial pressure of Zn were observed in the final points in the Studies in which samples have initial $x < 1.50$, i.e., where the amount of Zn(g) in the vapor approached 0. The results confirmed, within experimental error, assumptions about VC made in the following sections.

4. Discussion

The first studies, 1–10, in this work were done to test the hypothesis that $ZnIn_2Se_4(s)$ or a phase with nearly the same *C*, would effuse congruently. Samples with initial *x* in the range 0.67–1.5 were chosen for this purpose. This hypothesis failed in every case, and the failure is clearly shown by the results of Study 9, with $x = 1.5$. The trends in M_a from those expected for high concentrations of ZnSe vapor [$Zn(g) + 1/2\ Se_2(g)$] to those expected from vapor with significant concentrations of $In_2Se(g)$ and $Se_2(g)$ demonstrated that effusion was not congruent. Moreover, *C* of the condensed residue after Study 9 was rich in indium selenide. Those observations required the conclusion that any CEC in the system was at $x > 1.5$.

The results of all Studies can be explained if the *P–T–C* relationships in the ZnSe–In_2Se_3 system follow the schematic diagrams in Fig. 6 in the range of *T* of these Studies. The *P* axes (ordinates) are in arbitrary units, but the levels in the diagrams are intended to be proportional, within experimental uncertainties to the equilibrium *P*. Insufficient study was done in this work to know the region to the right of the dashed line where *C* is near that of In_2Se_3, but occurrences there can be interpreted in terms of literature reports on the ZnSe–In_2Se_3 [55] and In–Se systems [32]. Two intermediate ternary condensed phases were found, β and one with $x \approx 5$, denoted by α. It is reasonable to hypothesize that the latter phase has $x = 5$ and, for convenience, to write its formula as $(ZnSe)_5In_2Se_3(s)$ by analogy with the known phase $(BaS)_5Ga_2S_3(s)$ [56]. This formula will be used henceforth to represent phase α. The

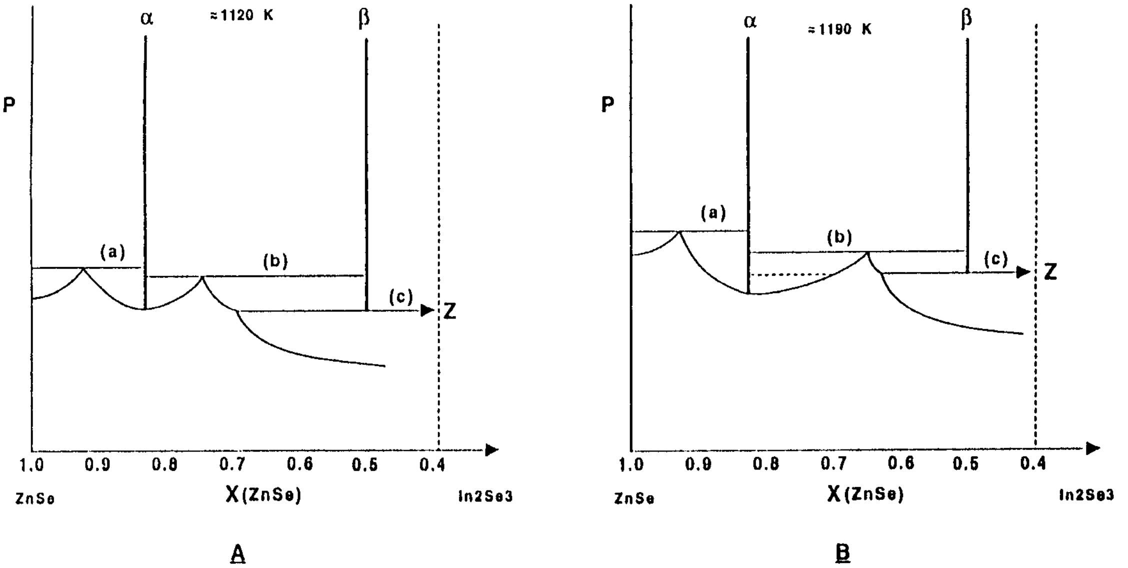

Fig. 6. Proposed P–C phase diagram at $T \approx 1120$ and $T \approx 1190$ K, C as mole fraction of ZnSe, α is $(ZnSe)_5In_2Se_3(s)$, β is $ZnIn_2Se_4(s)$.

condensed phase, $ZnIn_2Se_4(s)$, β, effuses incongruently, through vapor at the periatmotic point in Fig. 6, to yield $ZnSe(In_2Se_3)_3(s)$ [55] or, possibly, solid In_2Se_3 saturated with ZnSe, here called Z, and a vapor relatively rich in the vapor species over ZnSe(s). Above ≈ 1190 K, the VP of the three-phase tie-line (c) in Fig. 6 exceeds the VP of congruently effusing α.

In Study 9, represented in Fig. 1, the initial $x = 1.5$ was between those of α and β in Fig. 6. Initially the VP increased steeply as the cell was heated. Then T was in the range 1178–1193 K, and diagram B in Fig. 6 was applicable. During Stage 1, VP was at the euatmotic point on the three-phase tie-line (b) between α and β, and during Stage 2, VP was at the periatmotic point on the three-phase tie-line (c) between β and Z. The decrease in VP between Stages 2 and 3 and steady VP during Stage 3 occurred in the region cut off by the dashed line in Fig. 6 ; the decreasing VP likely owed to changes in C from $ZnSe(In_2Se_3)_3$ to In_2Se_3, then to an In-rich phase, i.e., incongruent effusion of In_2Se_3 [32], and perhaps to some solution of ZnSe in In_2Se_3. The nearly constant VP after 75% mass loss was that of congruently effusing, liquid, indium-rich, indium selenide [32].

In Study 11, at 1201 ± 5 K, the initial $x = 4.00$ of the solid was very near to a CEC. If a vapor in the $ZnSe/In_2Se_3$ system with species Zn(g), $In_2Se(g)$, and $Se_2(g)$ effuses with $x = 4$, then the vapor within the cell has $x = 1.84$. Then the system has a euatmotic point with x only slightly larger than 1.84 in the range 1201 ± 5 K. The VC within the cell remained at the euatmotic point until 98% of the sample was exhausted. The small initial difference between the solid and effusing VC caused C of the solid to change as vapor effused, and when 98% of the initial mass had effused, C of the solid was that of β, $ZnIn_2Se_4$. Moreover, these changes occurred at slightly different masses lost as sample was exhausted from one chamber of the cell before the other. Study 11 is seen to have gone through the same Stages as did Study 9, but with Stage 1 exaggerated, and with Stages 2 and 3 reduced to the last 2% of mass lost.

In Study 20, the initial $x = 9.00$ was very near to, but slightly to the right (In_2Se_3-rich) side, of that of the vapor which effuses when the VC within the cell is that at the euatmotic point on line (a) of Fig. 6. (The exact C of this euatmotic point is unknown, vide infra.) The VC remained at the euatmotic point until the sample was almost exhausted. The small initial difference between C of the solid and the effusing VC caused C of the solid to change as vapor effused, and finally, after 90% of the sample effused, C of the solid approached that of α. The final sloped plateau likely resulted when sample in one chamber of the effusion cell was exhausted before that in the other chamber.

In Study 17, a differential study, the initial *C* in one chamber of the effusion cell, call it side *R*, was $x = 4.00$ and in the other side, call it side *L*, was $x = 9.00$. Throughout that study, ΔP was that between the VP at euatmotic points on lines (a) and (b) in Fig. 6; ΔP decreased as *T* decreased, and approached zero below 1100 K. ΔP would become zero as α became unstable, i.e., as *C* of the euatmotic point on line (b) reached that of α. The Study was terminated before the sample in either chamber approached exhaustion. Interpretations of results from Study 18, which results were practically identical to those from Study 17, were the same.

In Study 19, another differential study, the initial *C* on side *R* of the effusion cell was $x = 4.00$, just to the right of the euatmotic point on line (b), and the initial *C* on side *L* was 5.86, just to the right of the euatmotic point on line (a) in Fig. 6. During Stage 1 the results reproduced those from Study 17, while *C* of the sample in side *L* remained between $x = 9.00$ and that of α in Fig. 6. Then when *C* in side *L* reached that of α, the sign of ΔP reversed because the VP in side *L* became lower than that of side *R*. This reversal brought the onset of Stage 2.

Stage 2 continued while *C* on side *R* was between $x = 4.00$ and that of β, and the VP there was that on line (b) in Fig. 6. When *C* on side *R* reached that of β, $ZnIn_2Se_4$, another reversal in the sign of ΔP occurred because below 1090 K, *P* on line (c) in Fig. 6 is lower than VP over α. This reversal was the onset of Stage 3. ΔP decreased with increasing *T* in Stage 3, because at *T* above 1190 K, *P* on line (c) exceeds VP over α.

Quantitative conclusions from Studies 20 and 21 were restricted by uncertainties about events during the initial heating of the samples. Apparently, mostly ZnSe was lost early in Study 21 so that congruent effusion observed during loss of the last 80% of the sample was from a condensed phase more rich in In_2Se_3 than the initial composition $x = 5.67$. Hence, the proposal that the congruently effusing phase is $(ZnSe)_5In_2Se_3$ is reasonable. And a euatmotic point intermediate between ZnSe(5) and phase α implies an effusing composition with *x* considerably greater than 9, the *x* implied by Study 20. This result suggests the vapor early in the study was relatively rich in indium selenide.

4.1. Effusion reactions

Effusion reactions were deduced from experimental results and knowledge about effusion chemistry of ZnSe and In_2Se_3. In a two-component system with two condensed phases and vapor at equilibrium and two independent species in the vapor, two independent chemical reactions are necessary and sufficient to describe the system [57]. The reactions chosen here are intended to involve the major vapor species in the system, Zn(g), $Ga_2Se(g)$, and $Se_2(g)$, and the chemical equations for vaporization reactions are balanced such that 1 mol of vapor is produced.

A phase α with assumed formula $(ZnSe)_5In_2Se_3$ exists and effuses congruently above 1150 K and incongruently below 1150 K, but becomes unstable below 1100 K; a reasonable estimate of *T* at onset of this instability is 1080 K. Above 1080 K, in the range of *C* between ZnSe and $(ZnSe)_5In_2Se_3$ the effusion reactions and their K_p were, reaction (1) with

$$K(1) = (P_{\mathrm{Zn}})^{2/3}(P_{\mathrm{Se_2}})^{1/3} \tag{19}$$

$$2/19(\mathrm{ZnSe})_5\mathrm{In_2Se_3(s)} = 10/19\mathrm{Zn(g)} + 2/19\mathrm{In_2Se(g)} + 7/19\mathrm{Se_2(g)} \tag{20}$$

$$K(20) = (P_{\mathrm{Zn}})^{10/19}(P_{\mathrm{In_2Se}})^{2/19}(P_{\mathrm{Se_2}})^{7/19}. \tag{21}$$

Above 1080 K in the range of *C* between $(ZnSe)_5In_2Se_3$ and $ZnIn_2Se_4$, the reactions were

$$1/6(\mathrm{ZnSe})_5\mathrm{In_2Se_3(s)} = 1/6\mathrm{ZnIn_2Se_4(s)} + 2/3\mathrm{Zn(g)} + 1/3\mathrm{Se_2(g)} \tag{22}$$

$$5/8\mathrm{ZnIn_2Se_4(s)} = 1/8(\mathrm{ZnSe})_5\mathrm{In_2Se_3(s)} + 1/2\mathrm{In_2Se(g)} + 1/2\mathrm{Se_2(g)} \tag{23}$$

$$K(23) = (P_{\mathrm{In_2Se}})^{1/2}(P_{\mathrm{Se_2}})^{1/2} \tag{24}$$

Below 1080 K the reactions were reaction (1) and

$$1/2\mathrm{ZnIn_2Se_4(s)} = 1/2\mathrm{ZnSe(s)} + 1/2\mathrm{In_2Se(g)} + 1/2\ \mathrm{Se_2(g)} \tag{25}$$

$$K(25) = (P_{\mathrm{In_2Se}})^{1/2}(P_{\mathrm{Se_2}})^{1/2} \tag{26}$$

Results from thermodynamic analysis on the basis of reactions (1), (23), and (25) are given in Table 7, where column 1 gives the number of the Study, column 2 gives the initial molar ratio ($ZnSe/In_2Se_3$) of the sample, and columns 3 and 4 give the

Table 7
ΔH°(298 K)/kJ of reactions (1) and (23) or (25)

Study	Molar ratio (x)	ΔH°(298 K) (kJ/mol)	
	$ZnSe/In_2Se_3$	Reaction (1)	Reaction (23) or (25)
1	1.00	255.1 ± 5.2	301.8 ± 2.5
2	1.00	260.9 ± 2.7	298.9 ± 0.6
3	1.00	263.1 ± 1.6	303.0 ± 0.6
4	0.67	264.0 ± 1.4	301.0 ± 0.4
5	0.67	266.3 ± 3.8	303.1 ± 0.3
6	0.67	258.8 ± 1.9	302.1 ± 0.4
7	0.67	260.2 ± 1.5	302.7 ± 0.7
8	1.50	257.7 ± 1.1	302.0 ± 0.3
9	1.50	255.3 ± 0.7	302.3 ± 0.6
10	4.00	255.2 ± 0.8	305.5 ± 1.8
11	4.00	257.2 ± 0.6	304.5 ± 0.6
12	9.00	255.1 ± 0.4	305.1 ± 0.4
13	9.00	259.2 ± 0.7	306.8 ± 0.5
14	4.00	258.4 ± 0.9	307.2 ± 0.9
15	∞	253.1 ± 0.3[a]	–
		253.4 ± 0.4[b]	–
16	9.00	254.9 ± 0.2	306.9 ± 0.4
20	9.00	253.8 ± 0.1	307.3 ± 0.3
21	5.67	253.6 ± 1.1	304.6 ± 1.1

[a] Calculated from Knudsen pressure.

[b] Calculated from torsion pressure.

ΔH°(298 K) of reaction (1) and reactions (23) or (25), respectively.

The value 301 ± 2 kJ/mol of ΔH°(298 K) of reaction (3) with data from Study 14 yielded the enthalpy of $ZnIn_2Se_4$ relative to its binary components, i.e., ΔH°(298 K) of

$$ZnSe(s) + In_2Se_3(s) = ZnIn_2Se_4(s) \qquad (27)$$

$\Delta H^\circ(298\ K) = -12.5 \pm 3.5$ kJ/mol.

Study 21 gave the third-law ΔH°(298 K) of reaction (20), 262.1 ± 1.1 kJ/mol. Proportional combination of the results from vapor analysis in Table 7 gives the same results. Uncertainty in this result is much greater than the standard deviation 1.1 kJ, however, owing to inherent uncertainties in the vapor analysis and in C of the condensed phase. For that reason, no value of the enthalpy of phase α relative to the binary components is given. The relative stability of α is mall, a few kJ/mol, as is implied by the proposed phase diagrams in Fig. 6.

M_a from Study 11 with $x = 4$ and from stage one in Study 9 were reasonably close to 142.0 g mol^{-1} the M_K calculated on the basis of congruent effusion. M_a measured in Studies 20 and 21 with $x = 9.0$ and $x = 5.67$ were 122.6 and 132.7 g mol^{-1}, respectively. M_a in both cases were comparable to M_K calculated on the basis of congruent effusion. These results support the assumptions that the VC in both cases was near to that of the condensed phase.

The isothermal studies revealed four CEC above 1080 K in the system $ZnSe–In_2Se_3 : ZnSe(s)$, $(ZnSe)_5{\cdot}In_2Se_3$ called α, C at the euatmotic point between ZnSe(s) and α, and that between α and $ZnSe{\cdot}In_2Se_3$ or $ZnIn_2Se_4$. No sample with C near that of In_2Se_3(s) was studied, but published work shows that In_2Se_3(s) does not effuse congruently in the range of T of the present experiments. The congruently effusing phase α has not been reported before.

In summary, interpretations here are supported by the observations. (1) Samples with $x = 9.00$ and $x = 4.00$ gave isothermally invariant VP near 1200 K until the sample was substantially exhausted. (2) M_a was different in the two cases. For the sample with $x = 4.00$, M_a was similar to that in the first stage of the effusion of sample with $x = 1.50$. M_a in the study begun with $x = 9.00$ was distinctly smaller. (3)

Samples with $x = 5.67$ gave isothermally invariant VP and the study ended with VP decreasing sharply to zero. (4) Differential experiments showed differential VP that varied in accordance with predictions from phase diagrams in Fig. 6.

ZnSe is known to effuse congruently to Zn(g) and Se_2(g) with M_K of 100.9. In the present study, M_a was 108.9 ± 1.5, where the uncertainty is standard deviation of the mean. This result shows that estimated VC obtained by comparison of P_K and P_t are reasonably dependable.

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