

Equilibrium in $\text{GeI}_4\text{-S}(\text{Se})$ systems

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Saturation vapor pressure in $\text{GeI}_4\text{-S}$ system is measured in 150-300 °C temperature range by tensiometric method using membrane null-manometer. Thermodynamic analysis of heterogeneous chemical equilibriums of $\text{GeI}_4\text{-S}$ system in 200–500°C range is carried out by the method of equilibrium constants. The degree of conversion of germanium (IV) iodide into germanium disulfide and germanium diselenide at temperature of 500°C is shown to do not excess 27 and 11 % respectively. The samples of $\text{Ge-S}(\text{Se})\text{-I}$ glass system were prepared by interaction of germanium tetraiodide and chalcogen melt in the apparatus equipped with mass-transfer section, it allowed to increase an yield of germanium chalcogenides up to 80–90%.

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1. Introduction

The $\text{GeI}_4\text{-S}$, $\text{GeI}_4\text{-Se}$ glass system is of interest due to development of low-temperature technique of preparation of special pure chalcoidide glasses by interaction of germanium (IV) iodide and chalcogen melt [1]. The data in chemical and phase composition of reaction system is necessary to determine the optimal conditions of preparation of specified composition glasses characterized by a set of required physicochemical properties.

The goal of the present work is the investigation of heterogeneous equilibrium into $\text{GeI}_4\text{-S}(\text{Se})$ systems and the preparation of $\text{Ge-S}(\text{Se})\text{-I}$ glass system.

2. Equilibrium investigation into $\text{GeI}_4\text{-S}(\text{Se})$ systems

2.1. Measurement of equilibrium vapor pressure into $\text{GeI}_4\text{-S}$ system

Measurement of vapor pressure into $\text{GeI}_4\text{-S}$ system was carried out by static method using membrane null manometer from molybdenum glass [2]. The compensating pressure was measured by deformation vacuum gauge. Systematic error of pressure measurement was 2-6 mm Hg. Heating thermostatically controlled chamber and temperature control was performed using programmed thermo-regulator Termolux-010 equipped with chromel-alumel thermocouple, that gave a temperature measurement accuracy and temperature maintenance $\pm 1^\circ\text{C}$ and $\pm 0.5^\circ\text{C}$ respectively. The germanium (IV) iodide (99.98%), subjected to a sublimation, and sulfur (99.999%), purified additionally by double distillation in vacuum, were used.

The results of measurement of equilibrium vapor pressure into $\text{GeI}_4\text{-S}$ system with 1:2.6 molar ratio of

components and 10.41 mg/cm^3 specific volume of reaction chamber are given in Fig. 1.

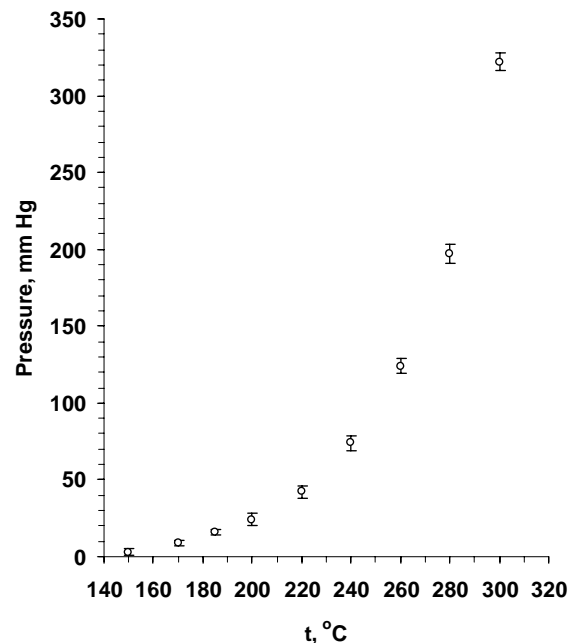


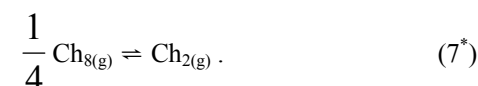
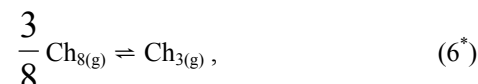
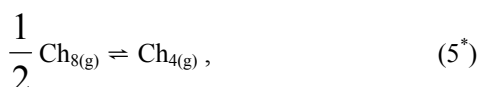
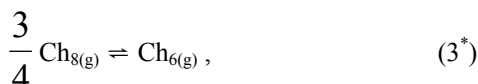
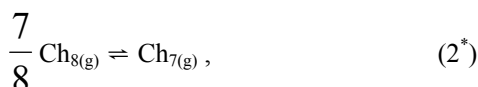
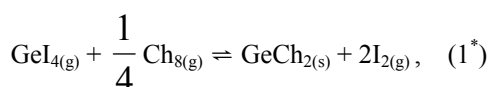
Fig. 1. Equilibrium vapor pressure $\text{GeI}_4\text{-S}$ (1:2.6) system

2.2. Thermodynamic simulation

Thermodynamic simulation of heterogeneous equilibriums into $\text{GeI}_4\text{-S}(\text{Se})$ systems was performed using a method of equilibrium constants [3]. The method includes a generation and joint solution of equation systems of following types:

1. Equations of equilibrium constants of independent (base) reactions;
2. Equations of phase equilibrium;
3. Equations of material balance;
4. Normalizing equations.

A detailed description of generation method of these equations is given in paper [4]. On assumption, that the chemical composition of system is defined by interaction of germanium tetraiodide and chalcogen, resulting to formation of germanium dichalcogenides and molecular iodine; the system is three-phase: ideal mixture of "germanium tetraiodide-chalcogen-iodine", crystal phase GeCh_2 ($\text{Ch}=\text{S}, \text{Se}$), and vapor phase containing GeI_4 , I_2 and molecules of chalcogen Ch_2 , Ch_3 , Ch_4 , Ch_5 , Ch_6 , Ch_7 , Ch_8 , - base reaction will be:



Equation system, characterizing studied equilibriums, will take on form:

$$K_1^\circ = \frac{\tilde{p}_{\text{I}_2}^2}{\tilde{p}_{\text{GeI}_4} \tilde{p}_{\text{Ch}_8}^{\frac{1}{4}}} \quad (1)$$

$$K_2^\circ = \frac{\tilde{p}_{\text{Ch}_7}}{\tilde{p}_{\text{Ch}_8}^{\frac{7}{8}}} \quad (2)$$

$$K_3^\circ = \frac{\tilde{p}_{\text{Ch}_6}}{\tilde{p}_{\text{Ch}_8}^{\frac{3}{4}}} \quad (3)$$

$$K_4^\circ = \frac{\tilde{p}_{\text{Ch}_5}}{\tilde{p}_{\text{Ch}_8}^{\frac{5}{8}}} \quad (4)$$

$$K_5^\circ = \frac{\tilde{p}_{\text{Ch}_4}}{\tilde{p}_{\text{Ch}_8}^{\frac{1}{2}}} \quad (5)$$

$$K_6^\circ = \frac{\tilde{p}_{\text{Ch}_3}}{\tilde{p}_{\text{Ch}_8}^{\frac{3}{8}}} \quad (6)$$

$$K_7^\circ = \frac{\tilde{p}_{\text{Ch}_2}}{\tilde{p}_{\text{Ch}_8}^{\frac{1}{4}}} \quad (7)$$

$$p_{\text{GeI}_4} = P_{\text{GeI}_4}^\circ x_{\text{GeI}_4}; \quad (8)$$

$$p_{\text{I}_2} = P_{\text{I}_2}^\circ x_{\text{I}_2}; \quad (9)$$

$$\sum_{k=2}^{k=8} p_{\text{Ch}_k} = P_{\text{Ch}}^\circ x_{\text{Ch}}; \quad (10)$$

$$n_{\text{GeI}_4}^\circ - \Delta\xi = x_{\text{GeI}_4} N + \frac{P_{\text{GeI}_4} V_g}{RT}; \quad (11)$$

$$n_{\text{Ch}}^\circ - 2\Delta\xi = x_{\text{Ch}} N + \frac{V_g}{RT} \sum_{k=2}^8 k p_{\text{Ch}_k}; \quad (12)$$

$$2\Delta\xi = x_{\text{I}_2} N + \frac{P_{\text{I}_2} V_g}{RT}; \quad (13)$$

$$P = p_{\text{GeI}_4} + p_{\text{I}_2} + \sum_{k=2}^{k=8} p_{\text{Ch}_k}; \quad (14)$$

$$x_{\text{GeI}_4} + x_{\text{Ch}} + x_{\text{I}_2} = 1; \quad (15)$$

were K_k° – standard equilibrium constant of k reaction; \tilde{p}_i – relative portion pressure of substance i in vapor phase; P_i° – saturated vapor pressure of individual substance i ; x_i – molar portion of substance i in the melt; $n_{\text{GeI}_4}^\circ$, n_{Ch}° – initial amounts of germanium tetraiodide and chalcogen; N – total amount of substance in liquid phase; V_g – volume of gaseous phase; T – absolute temperature; R – universal gas constant; p_i – portion pressure of substance i over the melt; P – total pressure in system; $\Delta\xi$ – change of chemical reaction variable:



The system from 15 equations with 15 unknown variables was obtained: x_{GeI_4} , x_{Ch} , x_{I_2} , P_{GeI_4} , P_{I_2} ,

p_{Ch_k} ($k = 2 \div 8$), P , $\Delta\xi$, N . The calculation of equilibrium constants of reactions (1*)–(7*) was performed using data on thermodynamic properties of substances [5, 6]. The values of saturated vapor pressures of individual components of system were taken from literature sources [7-9]. The solution of system in the form of temperature dependences of compositions of vapor and condense phases are given in Figs. 2-3.

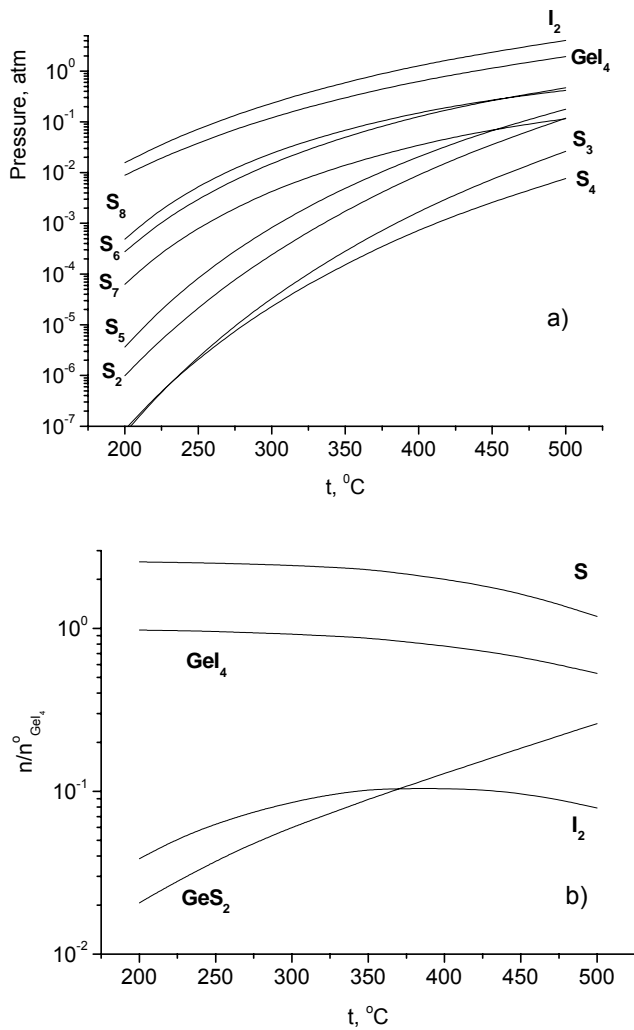


Fig. 2. Thermodynamically specified composition of vapor (a) and condense (b) phases in $\text{GeI}_4\text{-S}$ (1:2.6) System.

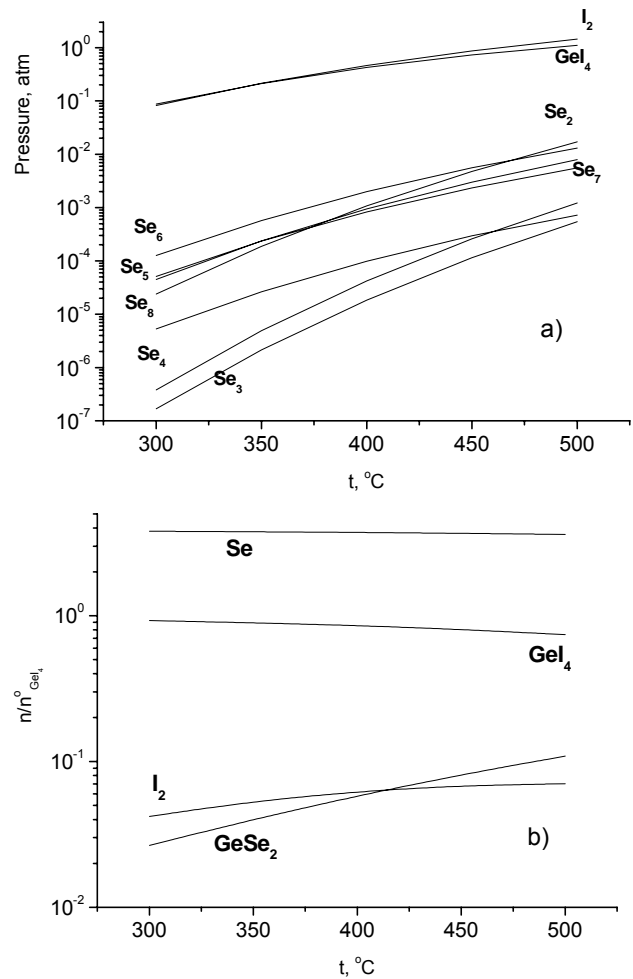


Fig. 3. Thermodynamically specified composition of vapor (a) and condense (b) phases in $\text{GeI}_4\text{-Se}$ (1:4) system

It results from calculation that the vapor phase in $\text{GeI}_4\text{-S}$ system at the temperature range of 200–500°C mainly consists iodine and germanium tetraiodide, total pressure changes from 23 mm Hg to 7.3 atm, and the conversion degree of germanium tetraiodide in germanium disulfide (appropriated curve GeS_2 in Fig.2b) increases from 2 to 26%.

Allocation of components between equilibrium phases in $\text{GeI}_4\text{-Se}$ system is close to that for $\text{GeI}_4\text{-S}$ system. The total pressure and conversion degree of germanium tetraiodide in germanium diselenide at 500°C is lower than for sulfide system and are equal to 2.6 atm and 11 % respectively. It seems to connect with lesser volatility and reaction ability of selenium in comparison with sulfur.

Table 1 compares experimental and calculated data of vapor pressure values in $\text{GeI}_4\text{-S}$ system. The mean absolute percent error (MAPE) was used as a value that characterizes adequacy of suggested thermodynamic model. It was equal to 6.8 %. At definition of conditions of glass-forming melt synthesis, it is possible to consider such value of an error satisfactory. Apparently, the principal cause of a deviation of experimental and calculated values of saturated vapor pressure consists that model doesn't consider interaction of components of a solution "germanium tetraiodide – sulfur – iodine", leading to formation of various associates (GeSI_2 , $\text{Ge}_2\text{S}_3\text{I}_2$, etc.), complicating molecular structure of a solution and causing its non-ideality [10]. Despite lacking steady chemical compounds in sulfur – iodine system [11], S – I bonds are present in the melt. Iodine breaks off high-molecular fragments of liquid sulfur, incorporating in the form of ended atoms that increases a share of low-molecular components and leads to change of its physical and chemical properties [8].

Table 1. Comparison of experimental and calculated values of vapor pressure into $\text{GeI}_4\text{-S}$ system.

$t, ^\circ\text{C}$	$P, \text{ mm Hg}$		
	Exper.	Calcul.	$\Delta, \%$
150	3 ± 2	3	<10
170	9 ± 2	8	11.1
185	16 ± 2	15	6.3
200	24 ± 4	23	4.2
220	42 ± 4	38	9.5
240	74 ± 5	69	6.7
260	124 ± 5	118	4.8
280	197 ± 6	193	2.0
300	322 ± 6	302	6.3
MAPE			<6.8

Preparation of glass-forming melts of Ge – S (Se) – I systems with low iodine content assumes an achievement of considerable degree of conversion of germanium tetraiodide in chalcogenides. Calculated and experimental data specify that in conditions of balance it is impracticable in intervals of temperature and pressure, which are acceptable for glass synthesis. In our opinion, one of the most effective ways of displacement of balance of reaction (8*) towards the product formation is selective removal of iodine from a gaseous phase. It is caused by high values of ideal coefficients of separation in $\text{GeI}_4\text{-I}_2$, S-I_2 , Se-I_2 systems which at 300°C are equal to 21, 150 and ~ 22000 respectively. It can be carried out by synthesis in the reactionary-separating apparatus that is actively used, for example, in a number of organic syntheses [12].

3. Preparation of Ge–S(Se)–I glass system

The commercial germanium iodide (IV) with purity of 99.98% subjected to double sublimation in vacuum, as well as sulfur and selenium with purity of 99.999%, additionally purified by double distillation, were used for preparation of glasses. Quartz apparatus, used for preparation of glasses, was sequentially washed with the mixture of nitric and hydrochloric acids, hydrofluoric acid, distilled water and then was annealed in tube furnace at 800°C for 12 hours.

Synthesis of glass was carried out into special reaction-separating silica set-up consisting of a reactor, heat transfer section and iodine receiver. The maximum temperatures of synthesis and homogenization of glass-forming melt were 500°C and 650°C for Ge-Se-I system; 600°C and 650°C for Ge-S-I system. The prepared glasses were in the form of cylinders with diameter of 10 mm and length of 30 – 50 mm with glossy surface. Vitreous nature of samples was proved by characteristic break on DSC heating curves.

Table 2. Comparison of preset and real compositions of Ge–S(Se)–I glass systems

Preset glass composition			Real glass composition, mol. %			$\alpha, \%$	Difference of compositions, abs. %			
Gross formula	Concentration of components, mol. %		Ge	S(Se)	I		Ge	S(Se)	I	
	Ge	S(Se)				I				Ge
$[\text{Ge}_{0.30}\text{S}_{0.70}]_{90}\text{I}_{10}$	27.0	63.0	10.0	25.1	65.7	9.2	83.2	1.9	2.7	0.8
$[\text{Ge}_{0.30}\text{S}_{0.70}]_{90}\text{I}_{10}$	27.0	63.0	10.0	26.1	64.6	9.3	83.5	0.9	1.6	0.7
$[\text{Ge}_{0.20}\text{Se}_{0.80}]_{95}\text{I}_5$	19.0	76.0	5.0	18.9	76.5	4.6	89.7	0.1	0.5	0.4
$[\text{Ge}_{0.17}\text{Se}_{0.83}]_{90}\text{I}_{10}$	15.0	75.0	10.0	14.4	77.3	8.2	79.5	0.6	2.3	1.8
Average absolute difference of compositions								0.9	2.2(1.4)	1.1
Average relative difference of compositions								4.0	3.4(1.9)	10.6

Element compositions of the charge and prepared glasses are presented in Table 2. Composition of the prepared samples was determined by the method of X-ray spectral micro-analysis (XRSA). It is possible to see, that the average relative difference of set and real concentration of atoms of germanium is 4.0 %, sulfur – 3.4 %, selenium – 1.9 %, iodine – 10.6 %. It is natural to expect, that the greatest deviation from initial composition will take

place for the most volatile components of the charge which was actually observed. These deviations are commensurable with those for the glasses obtained from simple substances with purification of the melt by distillation.

The degree of transformation of germanium tetraiodide into disulfide, calculated in assumption that the residual iodine is bound with germanium, is 80–90%. Hence, synthesis of the glass-forming melt in reaction separating

apparatus with selective withdrawal of volatile products provides a considerable increase in the yield of target components as compared with synthesis under conditions of thermodynamic equilibrium.

4. Conclusions

Equilibrium in GeI₄-S system was investigated by tensiometric method. The composition of equilibrium phases in GeI₄-S(Se) systems was calculated by the method of equilibrium constants. It is shown that the degree of transformation of germanium tetraiodide into germanium disulfide and germanium diselenide in equilibrium conditions at 500°C does not exceed 26 and 11%, respectively. The glass samples of Ge-S(Se)-I systems are produced in the reaction separating apparatus with the content of iodine from 4.6 to 9.3 % mol. The yield of germanium chalcogenides was 80–90%.

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