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# ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

# THERMODYNAMICS AND 3D MODELING OF PHASE EQUILIBRIUM IN Ag-$A^{IV}$ (Ge, Sn, Pb) -Se AND Ag-Pb-Te SYSTEMS

Speciality: 2303.01 – Inorganic chemistry

Field of science: Chemistry

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**Baku-2021**

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## GENERAL CHARACTERISTIC OF WORK

**Relevance and degree of study of the topic**. The phase diagram of three-component systems has a three-dimensional structure. Therefore, an urgent task is the development of methods for 3D modeling of phase diagrams of ternary systems. All modern computer programs solve 3D modeling problems. They are based on the compilation of matrices, including the coordinates of the spatial location of the object. Works in which 3D modeling of phase diagrams of ternary systems are carried out by analytical methods are very rare. In analytical methods, the coordinates of monovariant equilibria, surfaces of bivariant equilibria are expressed in the form of an explicit dependence of temperatures or pressure on the concentrations of the components of the ternary system, which allows visualizing the phase diagrams from different positions, obtaining 2D projections and tabulating the coordinates of the phase diagram of the ternary system.

The objects are Ag-AIV (Ge, Sn, Pb) -Se, Ag-Pb-Te systems. Chalcogenides of silver, germanium, tin and lead are promising materials for electronic engineering as electrochemical sensors, electrodes and electrolytes of solid-state batteries.The state diagrams of these ternary systems, due to the semiconductor nature of the phases, have been studied since the 60s of the twentieth century. In the last 5-10 years, research has significantly increased to clarify the phase diagrams and determine the thermodynamic parameters of the intermediate phases of the Ag-AIV (Ge, Sn, Pb) -Se, Ag-Pb-Te systems.

**The aim of this work** is to develop an analytical method for 3D modeling of thermodynamic functions and phase diagrams of ternary systems with a common chalcogenide anion and their approbation on Ag-AIV (Ge, Sn, Pb) -Se, Ag-Pb-Te systems.

**Tasks of the research** :

- Analysis and systematization of the most reliable data for phase diagrams and thermodynamic functions for two-component and three-component selenides of silver, germanium, tin, lead, tellurides of silver and lead.

- ❖ The obtaining equations for calculating and analytical 3D modeling of liquidus surfaces, separation boundaries and saturated vapor pressure of volatile components, two atomic molecules of selenium and tellurium.
- ❖ Thermodynamic triangulation, clarify of coordinates of mono, invariant equilibria with additional experiments to modeling liquidus surfaces, delamination and P-T-x equilibria in ternary systems selected from Ag-Ge-Se, Ag-Sn-Se, Ag systems -Pb-Se (Te), depending on the task.
- ❖ Solving the problem of 3D-modeling and visualization of crystallization surfaces of binary and ternary compounds and areas of separation of ternary systems on one graph.

**Research methods**.

The dissertation is part of a comprehensive study of Ag-$A^{IV}$ (Ge, Sn, Pb) -X (S, Se, Te) systems, conducted by a group of researchers under the leadership of Corresponding Member. ANAS Magomed Babanly at the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev, and at the Ganja State University. The studies were carried out by DTA (Netzsch 404 F1 Pegasus system) and XRF (Bruker D8 Advance powder diffractometer, CuKα1 radiation) and a membrane zero manometer for measuring the saturated vapor pressure. I partially participated in the experimental part of the study of the Ag-AIV (Ge, Sn, Pb) -Se and Ag-Pb-Te systems. At the same time, the results of processing experimental data on triangulation, mono and invariant equilibria obtained by these research groups were presented to me for thermodynamic analysis, modeling and 3D visualization of the systems under study.

The theoretical method of research is the phenomenological mathematical apparatus of thermodynamics of phase equilibria in analytical variation, using an asymmetric model of regular solutions and quantum-chemical representations of a solid state. Calculations and analytical modeling were carried out using computer programs: OriginLab, Grafikus.ru, www.matematikam.ru.

**The following are submitted for defense**:

Analytical method for calculating and 3D modeling mono-, bivariant equilibria in ternary systems with a common selenide and telluride ion;

Refined values of thermodynamic functions (standard entropy, heat capacity, entropy, enthalpy and free energy of Gibbs formation) for two-component and three-component selenides of silver, germanium, tin, lead, tellurides of silver and lead;

3D analytical models of T-x-y equilibria in Ag-Ge-Se, Ag-Sn-Se, Ag-Pb-Se (Te), P-T-x equilibria in ternary Ag-Pb-Se(Te) systems.

**Scientific novelty**.

Thermodynamic equations for phase equilibria of ternary systems are obtained, the solution of which is based on the data of double boundary systems;

The values of heat capacity and standard entropy of compounds $Ag_8GeSe_6$ and $Ag_8SnSe_6$ were determined on the basis of quantum-chemical concepts of the theory of solid state;

The problem of computer multi-3D modeling and obtaining 2D projections of liquidus surfaces, immiscibility boundaries and saturated vapor pressure of volatile components in ternary systems Ag-$A^{IV}$ (Ge, Sn, Pb) -Se, Ag-Pb-Te was solved;

For the first time were determined and 3D modeled the P (pressure) -T (temperature) -X (composition) diagrams of ternary systems Ag-Pb-Se and Ag-Pb-Te in the crystallization region of n-type (PbSe-Pb) and p-type (PbSe-Se) telluride selenide, and n-type (PbTe-Pb) and p-type (PbTe-Te) lead telluride.

**Scientific and practical significance.**

In the dissertation work, a new solution to the actual problem of inorganic chemistry is given−an analytical method for calculating and 3D modeling of phase diagrams and thermodynamic functions in inorganic ternary systems with a common anion has been developed. Analytical dependences in the form of 2D and 3D models contain, respectively, 100x100 = 10,000 and 50x50 = 2500 tabular data in the form of matrices, which can be used when choosing the optimal values of the composition, temperature and pressure of saturated

vapor in the synthesis of solid phases of ternary systems Ag-Ge -Se, Ag-Sn-Se, Ag-Pb-Se (Te) from liquid and gas phases.

The method of analytical 3D modeling of phase diagrams developed in the dissertation is included in the textbooks for masters (with reference to works 1,2,3,6,8,9 - the list of references in the abstract) and is used in the educational process.

**Approbation of work**. The results of the work were discussed at conferences: XXI International Conference on Chemical Thermodynamics in Russia (RCCT – 2017). 26-30 June 2017. Akademgorodok. Novosbirsk; THERMAM 2018. 7th Rostocker International Conference: "Thermophysical Technical Thermodynamics" 26 - 27 July 2018, Rostock, Germany;THERMAM 2019.6th Thermophysical and mechanical properties et advanced materials; 22-24 September, 2019. Çeşme-Izmir / Turkey. Abstracts and Full Text Proceedings, Conference dedicated to the 80th anniversary of the Institute of Catalysis and Inorganic Chemistry of the ANAS named after M. Nagiyev. Baku, 2016; Actual problems of modern chemistry and biology. International Scientific Conference May 12-13, 2016 Ganja; Republican scientific and technical conference of students and young researchers on the theme "Youth and scientific innovations", dedicated to the 95th anniversary of Heydar Aliyev. AzTU, May 3-5, 2018. Baku.

**The work was carried out** at the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev of ANAS.

**Publications on the topic of the dissertation**. 16 papers have been published, including 7 journal articles, 9 conference proceedings (1 article and abstracts)..

**The volume of work**. Dissertation includes introduction, chapters 6 and conclusions bibliography 170 here, is described on page 139., Includes 11 tables, 68 figures. The volume of the thesis for a conventional symbol: chapter 1 with sections Table of Contents and Introduction-44000 (22 pages); chapter 2-34000 (17); chapter 3-19000 (9.5 pp.); chapter 4-12000 (6 pp.); chapter 5-24000 (12); chapter 6 with conclusions - 27000 (13.5 pages). The total number is 160,000 conventional characters (80 pages).

## MAIN CONTENT OF THE WORK

The introduction substantiates the relevance of the dissertation work, the goal, the tasks set, the scientific novelty, the scientific and practical significance and the main provisions presented for the defense.

**The first chapter** of the thesis is devoted to the analysis of literature data on the study of TXY and PTX phase diagrams, thermodynamic functions and properties of intermediate phases of ternary systems Ag-$A^{IV}$ (Ge, Sn, Pb) -Se, Ag-Pb-Te and their boundary binary systems Ag (Ge, Sn, Pb) -Se (Te), Ag-Ge, Sn, Pb. From the performed literary analysis, it was revealed that there is conflicting information on the phase diagrams of these ternary systems, on the thermodynamic data of intermediate phases. Therefore, the task was set to clarify this information with additional experiments using modern methods of thermodynamic calculation and modeling, including analytical methods of 3D modeling.

**In the second chapter** of the dissertation, theoretical and experimental research methods are considered, in particular, thermodynamic – analytical methods for calculating and modeling phase diagrams. In particular, the equation for calculating and modeling the liquidus surface of component 1 of the 1-2-3 ternary system is:

$$T_{1(123)} = \left\{\Delta H_1^m + y_{2(23)}\left[\Delta \bar{G}_{1(12)}^{exs}\right]_{x(1)} + y_{3(23)}\left[\Delta \bar{G}_{1(13)}^{exs}\right]_{x(1)} + a_1 x_1 (1-x_2) y_{2(23)} (1-y_{2(23)}\right\} / (\Delta S_1^m - R ln x_1) \quad (1)$$

Here $y_{2(23)}=x_2/(x_2+x_3)$, $y_{3(23)}=x_3/(x_2+x_3)$, $x_1$, $x_2$ and $x_3$ – mole fraction of components 1, 2 and 3, respectively. $\Delta H_1^m, \Delta S_1^m$- enthalpy and entropy of melting of matter 1, R=8.314 J/(mol.K), $\Delta \bar{G}_{1(12)}^{exs,s}$ and $\Delta \bar{G}_{1(13)}^{exs,s}$- the partial molar excess free energies of mixing of component 1 are calculated from the liquidus coordinates of the boundary binary systems 1-2 and 1-3. The parameter $a_1$ is determined from the experimental data of the ternary system.

To determine the boundaries of immiscibility of liquid alloys, the asymmetric version of the model of regular solutions was used:

$$\Delta G_T^0 = [a + b(1-x)^2](1-x)x + RT[xlnx(1-x)\ln(1-x)] \quad (2)$$

and the thermodynamic condition for internal stability

$$(\partial^2\Delta G^0/\partial x^2)_{P,T}=-2*(a+b*x\text{^}2+2*b*x*(x-1)+b*x*(3*x-1))+8.31*T/(1-x)+8.31*T/x \quad (3)$$

For the thermodynamic triangulation of the studied ternary systems, the temperature dependences of the free energy of reactions with the participation of binary and ternary compounds are determined by the Ulich equation:

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_{298}^0 - \Delta C_{P,298}^0 T\left[\ln\left(\frac{T}{298}\right) + \frac{298}{T} - 1\right] \quad (4)$$

For 3D modeling of crystallization surfaces of phases the following equation was used:

$$T_{1(1-2-3)}=yT_{1(1-2)}(x_1)+(1-y)T_{1(1-3)}(x_1)+ax_1(1-x_1)^2y(1-y) \quad (5)$$

Here $y=x_2/(x_2+x_3)$, $y=x_3/(x_2+x_3)$, $x_1$, $x_2$ and $x_3$– mole fraction of components 1, 2, 3; $T_{1(1-2)}$ и $T_{1(1-3)}$ – liquidus temperatures for boundary binary systems 1-2 and 1-3.

For 3D modeling of surfaces of monovariant equilibria in the ternary system 1-2-3, temperature dependences on the composition are determined in the form of an explicit function T = f ($_x$, y), where *x* is the atomic fraction of the basic component, let's say component 1. In the dissertation, the basic the component is chalcogen (selenium or tellurium), which forms a compound with metals. Whereas between silver and germanium, tin, lead, there is a weak interaction.

A procedure is described for the synthesis of alloys of the Ag-$A^{IV}$ (Ge, Sn, Pb) -Se and Ag-Pb-Te systems by fusing the initial binary compounds and elementary components in evacuated quartz ampoules. Methods for determining the saturated vapor pressure of volatile components are analyzed. Due to the fact that the saturated vapor pressure of diatomic selenium and tellurium molecules is several orders of magnitude higher than their saturated vapor pressure, their one-. four-, six-atone molecules, as well as selenides and tellurides of lead, tin and germanium, a static method was used using a quartz membrane zero-manometer.

**In the third chapter** the assessment of the thermodynamic stability of the ternary compounds $Ag_8GeSe_6$ and $Ag_2GeSe_3$ is carried out with additional thermodynamic calculations using the Debye method, and the triangulation of the ternary system Ag-Ge-Se. Due to the lack of reliable information for the heat capacity of α-$Ag_8GeSe$, the values of this quantity were calculated by the Debye method. This method uses the characteristic (Debye) temperatures of the elements forming the compound, as well as the melting temperatures of the elements and compounds:

$$\theta_D^* = \theta_D (T^{m*}/T^m)^{1/2} \quad (6)$$

Here $\theta_D^*$, $\theta_D$ are the characteristic temperatures of an element in a compound and in a simple substance; $T^{m*}$, $T^m$ are the melting point of a compound and a simple substance. Based on the values of the $\theta_D^*/T$ function, the values of the isochoric heat capacity ($C_v$) are found for each component, then summing them up according to the Neumann - Kopp rule, the isochoric heat capacity for the Ag8GeSe6 compound is determined. The isochoric heat capacity was recalculated to the isobaric heat capacity using the Magnus – Lindemann equation. The value of $C_{P,298}$(α-$Ag_8GeSe_6$) = 377.1 J / (mol K) for was used to determine the temperature dependence of the free energy of formation (α-$Ag_8GeSe_6$).

Due to some discrepancy in the values of the entropy of α-$Ag_8GeSe_6$, this value was determined by calculation using the Eastman-Tsagareishvili equation, obtained on the basis of the Debye temperature functions:

$$S_{298}^0 = 0.75nR\left\{\ln\left[\frac{200(M/n)^{5/3}}{\rho^{2/3}T^m}\right]\right\}^{4/3} \quad (7)$$

n = 15 is the number of atoms in the molecule, R = 8.31 J $mol^{-1}.K^{-1}$, M = 1410 is the molar mass, $T^m$ = 1175K is the melting point, ρ = 6.21 $g.cm^{-3}$ is the density of $Ag_8GeSe_6$. As a result of the calculation, the following value was obtained for the standard entropy ofα-$Ag_8GeSe_6$. $S_{298}^0(Ag_8GeSe_6)$ = 711.6 J mol-1.K-1. This value is in

accordance with the value obtained by the method of electromotive forces 714.1 $J.mol^{-1}.K^{-1}$ [Moroz M.V., Prokhorenko M.V. Russ. J. Electrochem. 2015. No. 7. p. 697].

Triangulation of the Ag-Ge-Se system was carried out on the basis of thermodynamic calculations. The Ag-Ge-Se ternary system with the formation of one congruently melting ternary compound Ag8GeSe6 with the help of third-order matrices is divided into 6 quasi-ternary subsystems Ag-$Ag_2Se$-$Ag_8GeSe_6$, $Ag_2Se$-$Ag_8GeSe_6$-Se, $Ag_8GeSe_6$-$GeSe_2$-Se, GeSe -$Ag_8GeSe_6$-$GeSe_2$, $Ag_8GeSe_6$-GeSe-Ge, $Ag_8GeSe_6$-Ag-Ge. In the ternary system Ag-Ge-Se, a large field also occupies the areas of immiscibility of the liquid phase.

3D modeling of crystallization surfaces of congruently melting compounds and boundaries of immiscibility of liquid alloys in the Ag-Ge-Se system (Fig. 1 and Eqs. 8-12) has been carried out.

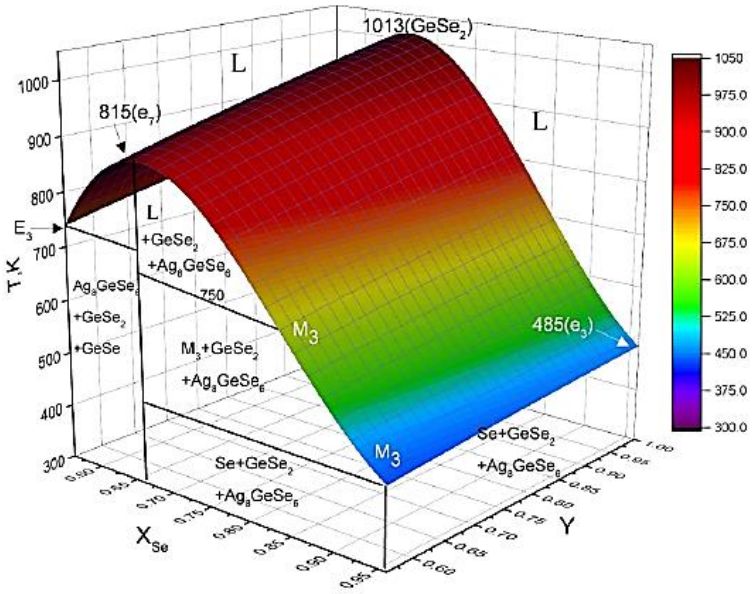


**Fig.1. 3D model of liquidus surface $GeSe_2$ around the $GeSe_2$-$Ag_8GeSe_6$ section, visualized using Eq. (8).**

The crystallization surface of $GeSe_2$ was modeled according to equation (8) (all equations are presented in computer versions):

T,K($GeSe_2$)=(-12876+52474*x-65385*x^2+
25965*x^3)*Y^0.333+273 (8)

The surfaces of $Ag_2Se$ and the ternary compound $Ag_8GeSe_6$ are modeled according to the equations:

T,K($Ag_8GeSe_6$)=(53+215*y-657*y^2+496*y^3)*x^3*(1-x)^3*
1000+25 (9)

T,K($Ag_2Se$)= (–477852*x^3 + 875875*x^2 – 531117*x +
107285)*(1-y)^0.6+273 (10)

In the ternary system Ag-Ge-Se, a large field occupies the areas of separation in the liquid phase. For the separation band between the binary subsystems Ag-$Ag_2Se$ (x, Se = 0.12 ÷ 0.3) and Ge-GeSe (x, Se = 0.12 ÷ 0.4), we obtained the analytical expressions:

T,K=(-4057+104175*x-753245*x^2+2.40816*10^6*x^3-
2.87183*10^6*x^4)*(1-y) (11)
*x*,Se=0.12÷0.3; y=$x_{Ge}/(x_{Ag}+x_{Ge})$ =0÷0.25

T,K=(–300+23268*$x$-123359*$x$^2+301913*$x$^3–
289638*$x$^4)*y^0.265 (12)
*x*,Se=0.12÷0.4; y=$x_{Ge}/(x_{Ag}+x_{Ge})$=0.25÷1

**The fourth chapter** is devoted to thermodynamic analysis and 3D modeling of the T-x-y diagram of the Ag-Sn-Se system. Due to the inconsistency of the literature data on the standard thermodynamic functions of silver, tin and ternary selenides, a comparative analysis was carried out and the most reliable data for the enthalpy, entropy, free energy of formation, and heat capacity of silver, tin selenides and ternary compounds $Ag_8SnSe_6$, $Ag_{0.84}Sn_{1.16}Se_2$ and $AgSnSe_2$ were selected. These values were used for thermodynamic triangulation of the ternary system.

In the binary side systems Ag-Se and Sn-Se of the ternary system Ag-Sn-Se, there are wide delamination regions that propagate inside the concentration triangle. To determine the separation boundary, the thermodynamic condition of internal stability $(\partial^2\Delta G^0/\partial x^2)_{P,T} > 0$ was used. The second derivative of the Gibbs free energy is defined in the following form:

$$(\partial^2\Delta G^0/\partial x^2)_{P,T}=-2*(a+b*x\text{^}2+2*b*x*(x-1)+b*x*(3*x-1))+ 8.31*T/(1-x)+8.31*T/x \quad (13)$$

Equation (13) was solved using the asymmetric model of regular solutions based on the positions of fuzzy systems. The dependences of function (13) for temperatures of 900, 950, 1000, 1050 and 1080K are shown in Fig. 2.

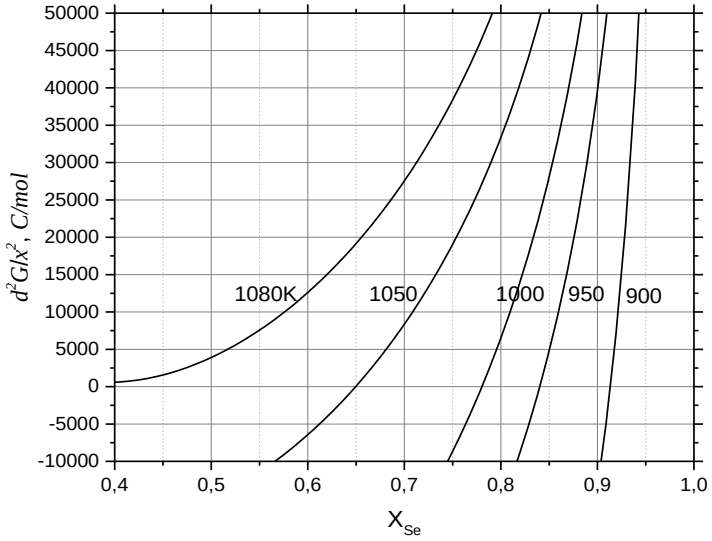


**Fig. 2 Dependences of the internal Gibbs stability function on the molar fraction of selenium for liquid alloys of the Ag-Se system in the range of compositions xSe = 0.45 ÷ 0.95. (analytical expressions of the dependencies on the graph are given below):**

-2*(16000-10000*x^2-2*10000*x*(x-1)-10000*x*(3*x-1))+8.31*1080/(1-x)+8.31*1080/x

-2*(25000-10000*x^2-2*10000*x*(x-1)-10000*x*(3*x-1))+8.31*1050/(1-x)+8.31*1050/x

-2*(40000-12000*x^2-2*12000*x*(x-1)-12000*x*(3*x-1))+8.31*1000/(1-x)+8.31*1000/x

-2*(50000-12000*x^2-2*12000*x*(x-1)-12000*x*(3*x-1))+8.31*950/(1-x)+8.31*950/x

-2*(70000-10000*x^2-2*10000*x*(x-1)-10000*x*(3*x-1))+8.31*900/(1-x)+8.31*900/x

As a result of thermodynamic calculations, it was revealed that the critical temperature of solubility in the Ag-Se system is T = 1080K. At this temperature, in the concentration range $X_{Se} = 0.45 \div 0.95$, the internal stability function is greater than zero $(\partial^2\Delta G^0/\partial x^2)_{P,T}>0$ (Fig. 2). The temperature dependence of the delamination boundary on the composition was approximated by the equation:

T,K=-6887.39418+42972.06249*x-87204.80219*x^2+79466.09268*x^3-27593.75741*x^4

Based on a limited number of DTA data for samples of the ternary system and quasi-binary sections $Ag_2Se$ –SnSe and $Ag_2Se$ –$SnSe_2$, analytical functions (Eqs. 14-20) were determined for 3D modeling of surfaces of bivariant equilibria (Fig. 3).
For the crystallization surface $Ag_2Se$, in the concentration range x = 0.31 ÷ 0.42; y = 0 ÷ 0.16 received:

T,K=( (107558-531117*(1-x)+875875*(1-x)^2-477852*(1-x)^3)*(1-y)^1.06 (14)

For the surface of crystallization SnSe, in the area of concentration X = 0.5 ÷ 0.61; Y = 0.36 ÷ 1, obtained:

T,K=( (349+4829*x-6436*x^2)*y^0.28 (15)

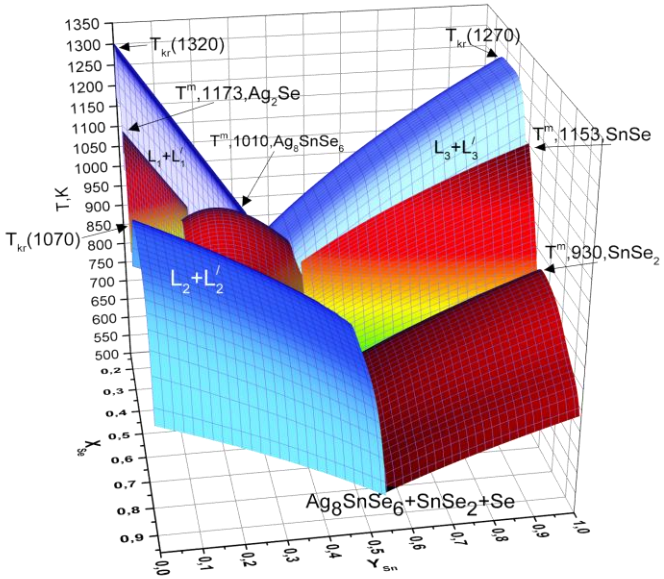


**Fig. 3. Multi 3D-model of crystallization surfaces $Ag_2Se$, $SnSe_2$, SnSe, $Ag_8SnSe_6$ and separation surfaces in the Ag-Sn-Se system.**

For the surface of crystallization $SnSe_2$, in the area of concentration x = 0.61 ÷ 0.95; y = 0.52 ÷ 1, received:

(-979787,7+7,75995E6*x^1-2,55035E7*x^2+4,45533E7*x^3-4,36243E7*x^4 +2,26954E7*x^5 -4,90063E6*x^6 )*y^0.35 (16)

For the surface of crystallization $Ag_8SnSe_6$, in the area of concentration x = 0.35 ÷ 0.55; y = 0.135 ÷ 0.62, received:

T,K=802+2044*y-6091*y^2+4237*y^3-4049+26685*x-57428*x^2+40000*x^3 (17)

For the separation surface of liquid alloys from the side Sn –Se (x = 0.16 ÷ 0.49; y = 0.33 ÷ 1), obtained:

T,K= (-1729+37308*x-173477*x^2+357612*x^3
275627*x^4)*y^0.38 (18)

For the separation surface of liquid alloys from the side Ag –Se (x = 0.12 ÷ 0.31; y = 0 ÷ 0.33), received:

T,K=(-4057+104175*x-753245*x^2+2.40816*10^6*x^3-
2.87183*10^6*x^4)*(1-y) (19)

For the separation surface of liquid alloys from the side (x = 0.44 ÷ 0.98; y = 0 ÷ 0.53), received:

T,K= (-9582+60199*x-127181*x^2+119250*x^3-
41950*x^4)*(1-y)^0.4 (20)

In the equations (14-20): $x=x_{Se}$; $y=x_{Sn}/(x_{Sn}+x_{Ag})$; $x_{Ag}$, $x_{Sn}$, $x_{Se}$ - atomic parts of components in liquid alloys of the system Ag-Sn-Se; the polynomials f(x) are defined on the basis of curved liquidity compounds and curved splits of binary border systems Ag-Se and Sn-Se; parameters associated with the change y are determined on the basis of the limited number of DTA samples of the triple system and quasi-binary cuts $Ag_2Se$ –SnSe and $Ag_2Se$ –$SnSe_2$.

**The fifth chapter** is devoted to thermodynamic analysis and 3D modeling of T-x-y diagrams of Ag-Pb-Se and Ag – Pb – Te systems. Triple connections are not formed in these systems. These systems are subdivided into the following quasi-tray systems, respectively: Ag – $Ag_2Se$– PbSe, $Ag_2Se$ – Se – PbSe, Ag – PbSe – Pb and Ag – $Ag_2Te$ – PbTe, $Ag_2Te$ – Te – PbTe, Ag – PbTe. The problem of 3D-visualization of the crystallization strengths of $Ag_2Se$ (Te), PbSe (Te) and the strength of the Ag-Pb-Se (Te) system is solved on a single graph (Fig. 4).

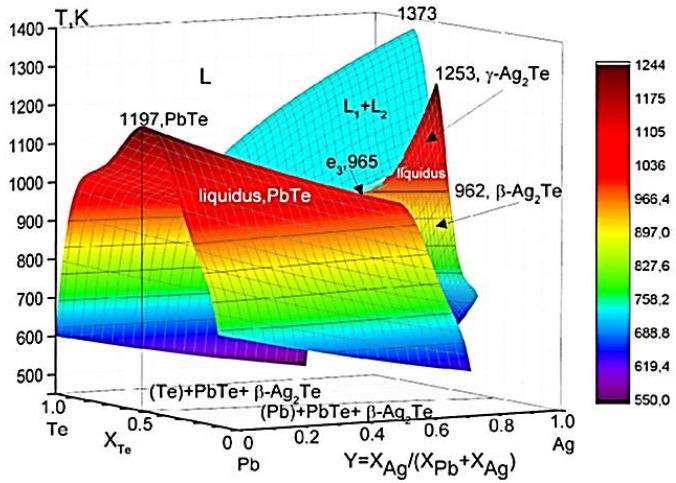


**Fig.4. 3D model of the surface of crystallization of $Ag_2Te$, PbTe and the surface of the separation in the system Ag-Pb-Te**

Due to asymmetric dependence of the liquidus temperatures of PbSe and PbTe on the composition in a wide range of concentrations, we used 7-term polynomials of the analytical option of the OriginLab program. For the crystallization surface of PbTe in the Ag-Pb-Te system, the following was obtained:

T,K(PbTe,Ag-Pb-Te)=(600+6748*x-38140*x^2+84742*x^3+ 11426*x^4-308980*x^5+408942*x^6-165767*x^7)*(0,769+ 0,1556*y + 0,0754*y^2) ; (x=$x_{Te}$=0÷0.89; y=0.2154÷1.0) (21)

**The sixth chapter** is devoted to the determination and modeling of P-T-X phase equilibria in the Ag-Pb-Se and Ag-Pb-Te systems. P (pressure) -T (temperature) -X (composition) diagrams of ternary systems are necessary to determine the conditions for obtaining a solid phase, crystallization of a liquid alloy and vapor deposition. However, such data for ternary selenide and telluride systems, which are of practical interest for semiconductor technology, were absent before this dissertation work. P-T-X diagrams were determined only for binary chalcogenide systems. This situation is associated with the

laboriousness of the experimental determination of the P-T-X phase diagrams of chalcogenide ternary systems containing volatile components, in particular, selenium and tellurium.In the dissertation work, the partial pressures of the saturated vapor of diatomic selenium and tellurium molecules over the crystallization surface of PbSe and PbTe in ternary systems Ag-Pb-Se and Ag-Pb-Te were determined and 3D modeled by experimental and computational methods. On the basis of the phenomenological mathematical apparatus, equations were obtained for calculating the partial pressure of the saturated vapor of selenium and tellurium:

$$\Delta G_{PbX}^{exl,l} = \Delta H_{298}^{0}(PbX) - T\Delta S_{298}^{0}(PbX) - \Delta c_{p,298}T\left[\ln\left(\frac{T}{298}\right) + \frac{298}{T}\right] - RTlnx_{Pb}^{l}x_{X}^{l} \quad (22a)$$

Further, on the basis of the values calculated by Eq. 22a, the values of the partial excess free energy of the chalcogen and the partial pressures of the saturated vapor of selenium or tellurium were calculated:

$$\Delta\bar{G}_{i}^{exs,l} = [\Delta G_{PbX}^{exl,l} + (1 - x_i)\frac{\partial\Delta G^{exl,l}}{\partial x_i}](1 - x_i) \quad (22b)$$

$$lnP(X_2) = \frac{2\Delta\bar{G}_{X}^{exs,l}}{RT} + \ln(x_X)^2 P_{X_2}^{0}\ ;\ \text{где X=Se; Te.} \quad (23)$$

In the equation (23):

$$\frac{2\Delta\bar{G}_{X}^{exs,l}}{RT} + \ln(x_X)^2 P_{X_2}^{0} = \ln[(x_X\gamma_X)^2 P_{X_2}^{0}] \quad (23a)$$

where $\gamma_x$ is the coefficient of activity of selenium or tellurium in a saturated liquid solution, which is associated with the thermodynamic activity and pressures of saturated vapor of chalcogen over the melt and pure chalcogen with the formulas:

$$a_X = \gamma_X x_X;\quad a_X = (P_{X_2}/P_{X_2}^{0})^{1/2} \quad (23b)$$

To check the reliability of the calculated method of saturated vapor pressure developed in this work, it was tested on the Pb-Te system (Fig. 5.), for which there are reliable experimental data in the literature. It should be noted that the vapor phase above the lead-tellurium alloys, in addition to two atomic tellurium molecules, also

contains one atomic and four atomic tellurium molecules. However, in the studied temperature range 900-1200K, the vapor phase mainly consists of diatomic tellurium molecules (within 88-90%).

The experimental data of the thesis obtained by measuring the membrane zero pressure gauge refer to the total pressure. The partial pressure of two atomic molecules in the total pressure was calculated based on the regularity of the distribution of tellurium molecules in the vapor phase. Lead telluride PbTe is a volatile component. However, the saturated vapor pressure of lead telluride PbTe is several orders of magnitude lower than the vapor pressure of other components of the vapor phase.

The 3D model of the P-T-x diagram for the isolines of the partial pressure of saturated vapor of Te2 over the surface of the liquidus PbTe in the ternary system Ag-Pb-Te is visualized in Fig. 6.

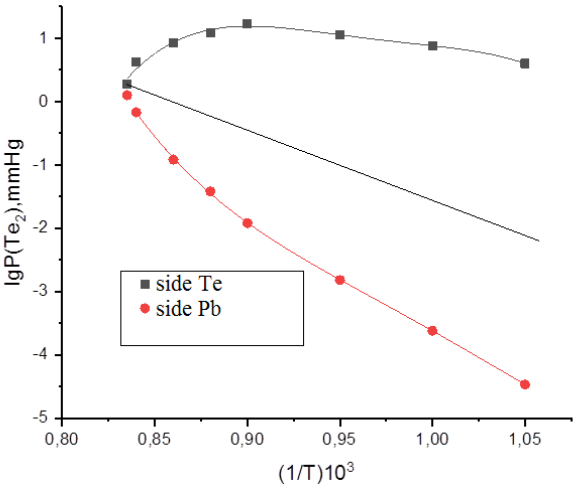


**Fig. 5. Dependences of the saturated vapor pressure of diatomic tellurium molecules on the reciprocal temperature. Symbols indicate experimental data [Hsieh K.C., Sharma R.C. // Bulletin of Alloy Phase Diagrams. August 1989. Vol. 10.p. 340]. The curves approximate the calculated data according to the equation (22,23)**

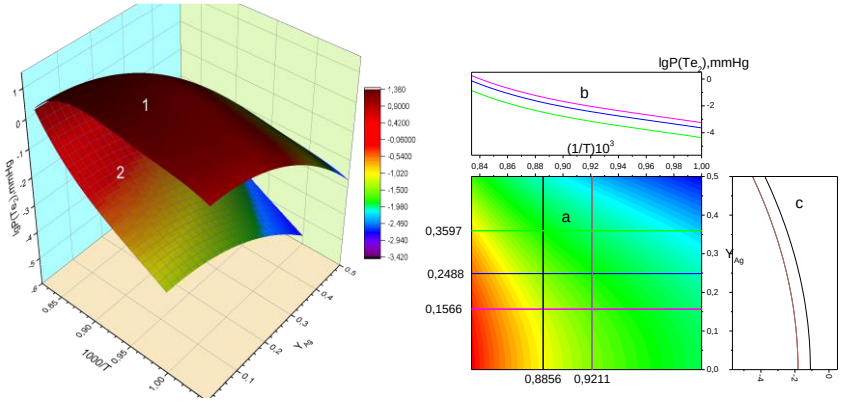


**Fig. 6. 3D model and projection of the P-T-x diagram for the isolines of the partial pressure of saturated vapor of $Te_2$ over the surface of the liquidus PbTe in the ternary system Ag-Pb-Te. 1- PbTe-Te region (p-type conductivity,eq.24a), 2- PbTe-Pb region (n-type conductivity, eq.24b).**

$lgP(Te_2,PbTe+Te),mmHg$ = Intercept + B1*x^1 + B2*x^2 + B3*x^3 + B4*x^4= -3553+14706*1000/T-22795*(1000/T)^2+15692*(1000/T)^3-4049*(1000/T)^4-13.56*y^2 ; $x=x_{Ag}$=0-0.5; y=1000/T=0.81-1.05 (24a)

$lgP(Te_2,PbTe+Pb),mmHg$ = Intercept + B1*x^1 + B2*x^2 + B3*x^3 + B4*x^4= 1575-6268*1000/T+9372*(1000/T)^2-6237*(1000/T)^3+1555*(1000/T)^4-10.7*y^2 (24b)

**Ag-Pb-Se system**. The value of the saturated vapor pressure of diselenide molecules determined by calculation is in accordance with the experimental data (Table 1), which indicates the correctness of the calculation method used.

**Table 1. Values of P ($Se_2$, mmHg) along the liquidus curve of PbSe.**

| $(1/T)10^{-3}$ / $P_{Se_2}$ (mmHg) | 0.73 | 0.75 | 0.77 | 0.80 | 0.85 | 0.90 |
|---|---|---|---|---|---|---|
| exper. (dissert.) | 8±1 | 26±2 | 52±2 | 115±3 | 118±2 | 67±2 |
| date* | 5.9 | 20.2 | 47.3 | 108.4 | 105.9 | 55.6 |
| calc. on (25, $x_{Ag}$=0) | 7.7 | 0.20 | 0.021 | 0.01 | $1.8\cdot10^{-4}$ | $1.2\cdot10^{-5}$ |
| date* | 5.9 | 0.21 | 0.023 | 0.001 | $1.5\cdot10^{-4}$ | $1.6\cdot10^{-5}$ |

*Lin, J.-C..// J. of Phase Equilibria.1996.Vol.17, N. 3. p 253

To check the reliability of the calculated data, the saturated vapor pressure of selenium was measured with a quartz null manometer for some samples along the $Ag_2Se$-PbSe sections. The calculated data are in agreement with experimental measurements.

The 3D model and 2D projections of the P-T-x diagram for the saturation vapor pressure isolines of $Se_2$ over the PbSe liquidus surface in the Ag-Pb-Se ternary system are shown in Fig. 7, 8.

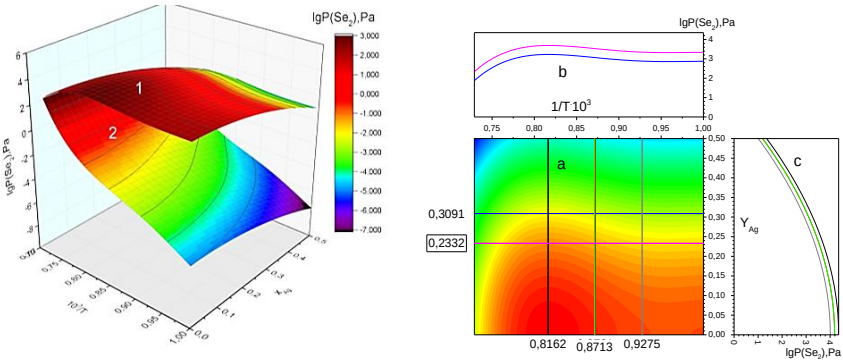


**Fig. 7. 3D model of the P-T-x diagram for isolines of the partial pressure of saturated vapor $Se_2$ over the surface of the PbSe liquidus in the Ag-Pb-Se ternary system. 1-in the PbSe-Se region (Eq. 25a), 2-in the PbSe-Pb region (Eq. 25b).**

Область PbSe-Se :

$$\lg p_{Se_2}\,(\text{Pa}) = [-1281 + 5624(1000/T) - 9190(1000/T)^2 + 6648(1000/T)^3 - 1797(1000/T)^4] - 12\,x_{Ag}^{\ 2} \qquad (25a)$$

Область PbSe- Pb:

$$\lg p_{Se_2}\,(\text{Pa}) = [2026 - 8778(1000/T) + 14247(1000/T)^2 - 10259(1000/T)^3 + 2759(1000/T)^4] - 10\,x_{Ag}^{\ 2} \qquad (25b)$$

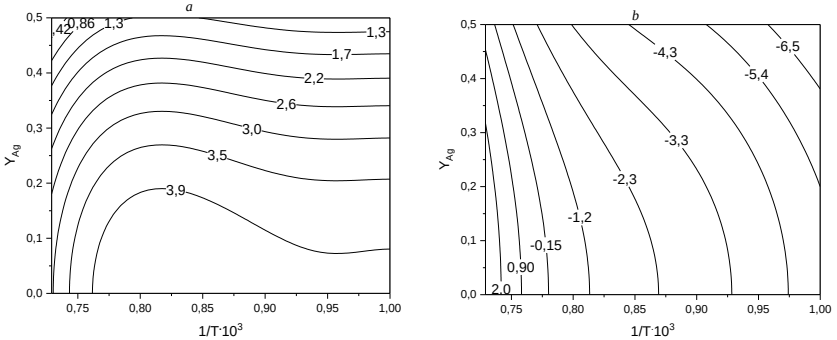


**Fig. 8. Projections of the P-T-x diagram for isolines of the partial pressure of saturated vapor of $Se_2$ over the surface of the PbSe liquidus in the Ag-Pb-Se ternary system. a - in the PbSe-Se region, b - in the PbSe-Pb region.**

## MAIN RESULT

1. An analytical-thermodynamic method for 3D modeling of thermodynamic functions and phase diagrams of ternary systems with a common chalcogenide anion has been developed and tested on the Ag-$A^{IV}$ (Ge, Sn, Pb) -Se, Ag-Pb-Te systems. Equations are obtained that explicitly relate the compositions, temperatures and thermodynamic parameters of the phases in equilibrium.

2. Analyzed, carried out additional calculations and selected the most reliable data for two-component and three-component selenides of silver, germanium, tin, lead, tellurides of silver and lead, which were used for thermodynamic triangulation of the studied systems Ag-Ge-Se and Ag-Sn- Se. In the double side systems Ag-Se and Sn-Se of the ternary system Ag-Sn-Se, there are wide delamination regions propagating within the concentration triangle. To determine the boundaries of immiscibility of liquid alloys, an asymmetric version of the model of regular solutions was used:

$$\Delta G_T^0 = [a + b(1-x)^2](1-x)x + RT[xlnx(1-x)\ln(1-x)]$$

and the thermodynamic condition for internal stability

$(\partial^2 \Delta G^0/\partial x^2)_{P,T}$=-2*(a+b*x^2+2*b*x*(x-1)+b*x*(3*x-1))+8.31*T/(1-x)+8.31*T/x

3. In the systems Ag-Pb-Se and Ag-Pb-Te, the ternary compound is not formed. These systems are divided into three stable quasi-ternary subsystems Ag – Ag2Se – PbSe, Ag2Se – Se – PbSe, Ag – PbSe – Pb and Ag – Ag2Te – PbTe, Ag2Te – Te – PbTe, Ag – PbTe – Pb. On the basis of literature data and thermodynamic calculations, the coordinates of mono- and invariant equilibria were determined, the crystallization surfaces of silver and lead selenides and tellurides, and the surface of the immiscibility boundary of liquid alloys were simulated in 3D. The problem of 3D-modeling and visualization of crystallization surfaces of binary and ternary compounds and areas of separation of ternary systems on one graph is solved.

4. Based on the phenomenological mathematical apparatus of thermodynamics of solutions, an equation was obtained for calculating the saturated vapor pressure of chalcogen $Xe_2$ molecules (in particular, two atomic selenium molecules $Se_2$ and tellurium $Te_2$) on the basis of temperature (T), composition ($x$), partial excess free energy (($\Delta \bar{\bar{G}}_{Xe}^{exs,l}$), activity coefficient ($\gamma_{Xe}$), saturated vapor pressure for pure selenium or tellurium ($P_{Xe_2}^0$). In

particular, for approximation and 3D visualization of $P(Te_2)$ over the liquidus surface of a PbTe compound with n-type and p-type conductivity, the following equations are obtained:

B1*x^1+B2*x^2+B3*x^3+B4*x^4=-3553+14706*1000/T-22795*(1000/T)^2+15692*(1000/T)^3-4049*(1000/T)^4-13.56*y^2;y=$x_{Ag}$=0-0.5;x=1000/T=0.81-1.05;
lgP($Te_2$,PbTe+Pb),mmHg=Intercept+B1*x^1+B2*x^2+B3*x^3+B4*x^4=15756268*1000/T+9372*(1000/T)^2-6237*(1000/T)^3+1555*(1000/T)^4-10.7*y^2 .

5. On the basis of literature data and conducted experiments, P-T-X diagrams of ternary systems Ag-Pb-Se and Ag-Pb-Te in the crystallization region of n-type (PbSe-Pb) and p-type ( PbSe-Se) telluride selenide and n-type (PbTe-Pb) and p-type (PbTe-Te) lead telluride. Each analytical dependence in the form of 2D or 3D models contains, respectively, 100x100 = 10,000 and 50x50 = 2,500 tabular data in the form of matrices, which can be used when choosing the optimal values of the composition, temperature and pressure of saturated vapor in the synthesis of solid phases of ternary systems Ag -Ge-Se, Ag-Sn-Se, Ag-Pb-Se and Ag-Pb-Te from liquid and gas phases.
6. Analytical functions of the state diagram in three-dimensional coordinates allow observing a three-dimensional image of phase diagrams at different angles, obtaining two-dimensional projections and classical graphs, tabulating the coordinates of the phase diagram.

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The defense will be held on 30 december 2021 at $10^{00}$ at the meeting of the Dissertation council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at at the Institute of Catalysis and Inorganic Chemistry named after academician Murtuza Nagiyev ANAS

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Abstract was sent to the required addresses on 23 november 2021

Signed for print: 19.11.2021

Paper format:A5

Volume:37709

Number of hard copies: 40