

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# The EMF Method with Solid-State Electrolyte in the Thermodynamic Investigation of Ternary Copper and Silver Chalcogenides

Mahammad Babanly, Yusif Yusibov and Nizameddin Babanly  
*Baku State University  
 Azerbaijan*

## 1. Introduction

Design and optimization of technology of creating new multicomponent inorganic materials, in particular, chalcogenides of metals are perspective functional materials in modern electronic techniques, are based on results of thermodynamic calculations. In turn, to ensure high accuracy of similar calculations is needs reliable dates on fundamental thermodynamic characteristics of corresponding phases.

However, the analysis of literature data shows that unlike binary system, the thermodynamic properties of ternary and multicomponent systems are studied quite insufficiently. In our opinion, elimination of this blank wide application of electromotive forces method (EMF) - one of the most exact experimental methods of chemical thermodynamics appreciably can promote. This method is applied with the big success to the thermodynamic studying of liquid binary and ternary metal systems, which more than 70 % of the available information is concerning to EMF method. Wide application of EMF method for studying of liquid metal systems is caused not only that the specified systems are the most suitable objects of investigation by this method, but also that the mathematical apparatus of chemical thermodynamics allows to calculate strictly integrated thermodynamic functions (ITF) homogeneous binary and ternary system on the basis of values partial thermodynamic functions (PTF) one of components in wide compositions area [M.Babanly et.al, 1992; Morachevskii et.al., 2003; Wagner, 1952].

Unfortunately, specific features and conditions of application EMF method to the heterogeneous systems have not been considered in long time. In the 80th years of last century we have undertaken attempts of elimination of this blank and have developed conditions of application EMF method to heterogeneous metal and semi-conductor systems [M.Babanly, 1985, 1992]. In this chapter we offer the rational method of calculation integral thermodynamic functions of intermediate phases in the ternary heterogeneous systems from PTF of one of components by using of the phase diagram and thermodynamic functions of some boundary binary phases and elementary components. The EMF method with liquid electrolyte has been realized on an example over 30 systems of Thallium-Metal-Chalcogen and have been obtained complexes interconsistency thermodynamic data for the many ternary chalcogenides of thallium [M.Babanly et.al, 1992].

However, it is known, that using a classical variant of EMF method with liquid electrolyte has a number of the restrictions due to with percolation of collateral processes [M.Babanly et.al, 1992; Morachevskii et.al., 2003; Wagner, 1952]. In the works [M.Babanly, 2001, 2009, N.Babanly, 2009, 2010] it is shown, that one of effective ways of expansion of possibilities of EMF method is connected with use solid cationconducting superionic conductors as electrolyte. Advantage of solid electrolytes in comparison with the liquid consists that in them conductivity is carried out by means of ions of one element, and strictly certain charge. It is, firstly, provides a constancy and stability of a charge potential forming ion which is in equilibrium with electrodes of a concentration chains, secondly, solid electrolytes plays a role of the original membrane dividing two electrode spaces and by that prevents many collateral processes due to interaction between electrolyte and electrodes, as well as through electrolyte - between electrodes.

In this chapter is short considered specific features of application of EMF method to heterogeneous systems and results of thermodynamic study of ternary chalcogenides of copper and silver by EMF method with solid electrolytes  $\text{Cu}_4\text{RbCl}_3\text{I}_2$  and  $\text{Ag}_4\text{RbI}_5$  are presented. A part of these thermodynamic data are published earlier, and some are presented for the first time.

## 2. Some features of application of EMF method to heterogeneous systems

Investigation of thermodynamic properties in homogeneous (liquid or solid state) system A-B usually consists in measurement EMF of concentration chains of type [Wagner, 1952]



Potential definition process of such elements served reversible electrochemical transfer at constant temperature of a component A from a condition with the big chemical potential (on the left electrode) in a condition with smaller (on the right electrode). Measured EMF (E) at temperature T is directly connected with partial Gibbs energy of a component A in an alloy relative pure element A as standard condition:

$$\Delta \bar{G}_A = \Delta \bar{H}_A - T \Delta \bar{S}_A = -zFE, \quad (2)$$

where z-charge of potentialforming ions, F - Faraday number, E - EMF value.

The relative partial molar entropy of component A in  $\text{A}_x\text{B}_{1-x}$  phase composition can be calculate on temperature coefficient of EMF chains (1), as

$$\left( \frac{\partial \Delta \bar{G}_A}{\partial T} \right)_P = -\Delta \bar{S}_A \quad (3)$$

Substitute (2) in (3), we receive:

$$\Delta \bar{S}_A = zF \left( \frac{\partial E}{\partial T} \right)_P \quad (4)$$

The relative partial molar enthalpy can be calculated, substituting the equations (2) and (4) in Gibbs-Helmholtz equation:

$$\Delta \bar{H}_A = \Delta \bar{G} + T \Delta \bar{S}_A$$

$$\Delta \bar{H}_A = -zFE + zFE \left( \frac{\partial E}{\partial T} \right)_p = -zF \left[ E + T \left( \frac{\partial T}{\partial T} \right) \right] \quad (5)$$

Thus, measuring equilibrium values of EMF of concentration chains of type (1) in a wide temperature range for various compositions of the right electrodes, it is possible to calculate relative partial molar free energy and entropy of A component in solid solution  $A_xB_{1-x}$  at any concentration.

Application of EMF method to heterogeneous systems has some features essentially unlike from homogeneous systems. In the given chapter are shortly considered these features which have allowed to planning experiments correctly at studying of heterogeneous systems what are the overwhelming majority of binary and multicomponent metal and semi-conductor alloys

At investigation of solid-state alloys of binary or more difficult metal and semi-conductor systems by EMF methods should deal with the phase diagrams characterized by various combination homogeneous and heterogeneous areas. In most cases for thermodynamic investigation of phases in such systems, it is necessary to change measurements EMF of chains of type (1) in heterogeneous phase areas. However as shown in [M.Babanly et.al, 1992], despite wide application of EMF method to binary heterogeneous systems, using of EMF measurements results in heterogeneous areas at thermodynamic calculations is not always correctly proved.

If in the homogeneous system A-B the temperature coefficient of EMF of concentration chains of type (1) has physical meaning relative partial molar entropy of A component in alloy, in heterogeneous A-B mix it also reflects change of their compositions with temperature along curves two-phase equilibrium on T-x diagram. By using the results of EMF measurements in two-phase area on T-x diagram is limited to that, unlike relative free energy, relative partial molar entropy and enthalpy discontinuous changes on the border of one- and two-phase areas.

Hence, use of results of EMF measurements of concentration chains in heterogeneous phase areas required the special analysis. Such analysis was carried out in works of [M.Babanly et.al, 1985a, 1992]. We will consider some features of application EMF method to binary heterogeneous systems.

The partial heterogeneous functions (PHF) method offered by G.F.Voronin [Voronin, 1976] for thermodynamic investigation of binary heterogeneous systems, allows to apply to heterogeneous mixes all mathematical apparatus of thermodynamics of solutions, keeping the form of the corresponding thermodynamic equations. Hence, having experimental data on relative partial molar functions of one of components of binary system in all composition field, including homogeneous and heterogeneous phase areas, integration of Gibbs-Duhem equation it is possible to calculate integral thermodynamic functions of separately phases and heterogeneous mixes without any out of thermodynamic assumptions.

Possibility of application of EMF method to binary heterogeneous systems is reduced in definition conditions at which results of EMF measurements of concentration chains of type (1) in heterogeneous areas can be used for calculation partial thermodynamic functions of A component and developing of other calculation procedures of integral thermodynamic functions when direct use of these experimental results is impossible [M.Babanly et.al, 1985a].

Let's see the A-B binary system with the limited solid solutions ( $\alpha$  - and  $\beta$ -phases) based on both components. At certain constant temperature  $T_1$  with increasing concentration of B in alloy A-B partial free Gibbs energy of A component continuously decreases in homogeneity area of  $\alpha$ -phases, remains constant in two-phase area of  $\alpha+\beta$  ( $\Delta\overline{G}_A$ ) and again continuously decreases in single-phase area of  $\beta$  (fig. 1). According to a condition of chemical equilibrium, at the given temperature

$$(\Delta\overline{G}_A) = \Delta\overline{G}_A(x') + \Delta\overline{G}_A(x'') \tag{6}$$

For partial enthalpy and entropy (6) type equality do not follow from the general conditions phase equilibriums. It means rupture of functions  $\Delta\overline{H}_A$  and  $\Delta\overline{S}_A$  on borders of homogeneity areas of  $\alpha$  - and  $\beta$ -phases.

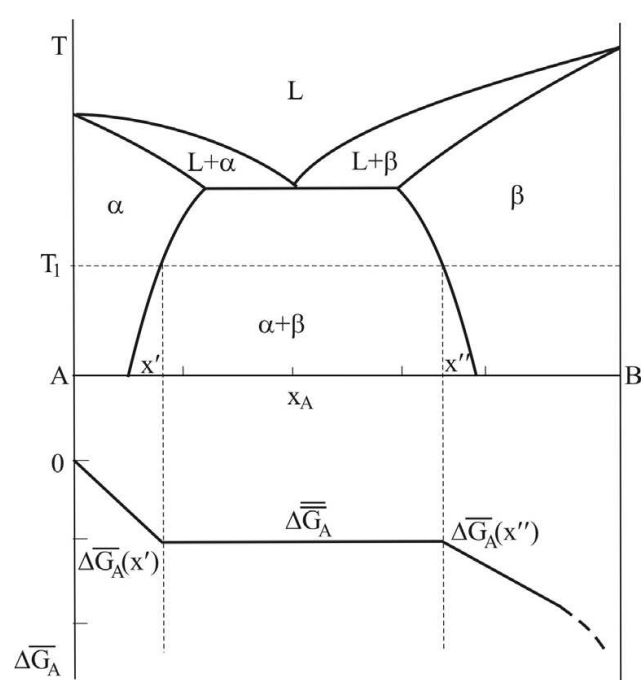


Fig.1. T-x diagram of binary system with limited solid solutions and changes of partial free Gibbs energy with composition.

Compositions of co-existing phases in two-phase area of  $\alpha+\beta$  are function temperature and are defined by the conjugate curves of disintegration (fig. 1). Therefore, differentiating equality (6) on temperature for boundary concentration of  $\alpha$ -phases ( $x'$ ) , we will receive

$$\frac{d}{dT} \Delta\overline{G}_A = \left( \frac{\partial \Delta\overline{G}_A}{\partial T} \right)_{x'} + \left( \frac{\partial \Delta\overline{G}_A}{\partial x'} \right)_T \left( \frac{dx'}{dT} \right) \tag{7}$$

From this expression taking into account Gibbs-Helmholtz equation

$$\Delta G = \Delta H - T \Delta S \tag{8}$$

follows, that

$$\Delta \bar{S}_A = \Delta \bar{S}_A(x') - \left( \frac{\partial \Delta \bar{G}_A}{\partial x'} \right)_T \left( \frac{dx'}{dT} \right) \quad (9)$$

and

$$\Delta \bar{H}_A = \Delta \bar{H}_A(x') - T \left( \frac{\partial \Delta \bar{G}_A}{\partial x'} \right)_T \left( \frac{dx'}{dT} \right) \quad (10)$$

The similar equations can be received also for boundary concentration of  $\beta$ -phases ( $x''$ ).

The analysis of the equations (9) and (10) leads to a following important conclusion: at practically vertical borders ( $dx'/dT = 0$  и  $dx''/dT = 0$ ) considered two-phase area on T-x to the diagram

$$\Delta \bar{S}_A = \Delta \bar{S}_A(x') = \Delta \bar{S}_A(x'') \quad (11)$$

$$\Delta \bar{H}_A = \Delta \bar{H}_A(x') = \Delta \bar{H}_A(x'') \quad (12)$$

It is show, that in heterogeneous  $\alpha+\beta$  mixes and co-existing phases the partial entropy and enthalpy of A component are equal between themselves, i.e. on borders between single-phase and two-phase areas discontinuously changes are not observed

EMF values of concentration chains of type (1) and constants of linear equation  $E=a+bT$  are connected with PHF equations (2), (4) and (5). Then, for two-phase alloys fairly equality

$$\Delta \bar{G}_A = \Delta \bar{G}_A(x') = \Delta \bar{G}_A(x'') = -zFE \quad (13)$$

At observation of conditions (11) and (12) for two-phase alloys the equalities are carried out also

$$\Delta \bar{S}_A = \Delta \bar{S}_A(x') = \Delta \bar{S}_A(x'') = zFb \quad (14)$$

$$\Delta \bar{H}_A = \Delta \bar{H}_A(x') = \Delta \bar{H}_A(x'') = -zF \left[ E + \left( T \frac{\partial E}{\partial T} \right)_P \right] = -zFa \quad (15)$$

At non-observation of conditions (11) and (12) values a and b in  $E = a + bT$  equation do not satisfy the equalities (14), (15) and cannot be used for calculation partial thermodynamic functions of A component.

[M.Babanly et.al, 1992] were carried out the similar analysis of behavior partial heterogeneous functions (PHF) in ternary heterogeneous systems and they found, that under condition of vertical position of section borders of phase areas for two-phase equilibrium are fair equalities (11) and (12), and for three-phase area  $\alpha+\beta+\gamma$  - equalities

$$\Delta \bar{G}_A = \Delta \bar{G}_A(\alpha') = \Delta \bar{G}_A(\beta') = \Delta \bar{G}_A(\gamma') \quad (16)$$

$$\Delta \bar{S}_A = \Delta \bar{S}_A(\alpha') = \Delta \bar{S}_A(\beta') = \Delta \bar{S}_A(\gamma') \quad (17)$$



$$\overline{\overline{\Delta H}}_A = \overline{\Delta H}_A(\alpha') = \overline{\Delta H}_A(\beta') = \overline{\Delta H}_A(\gamma') \quad (18)$$

where  $\alpha', \beta', \gamma'$  - limiting compositions of  $\alpha$ -,  $\beta$ - and  $\gamma$ -phases, in the three-phase equilibrium. Thus, at studying of heterogeneous systems by EMF method measurement it is necessary to conduct in intervals of temperatures in which limits of border of section of phase areas are practically vertical. It is a necessary condition for a calculation substantiation partial thermodynamic enthalpy and entropy from EMF measurements in heterogeneous phase areas [M.Babanly et.al, 1985b, 1992]. In the majority of ternary metal and semi-conductor systems in solid state, at temperatures considerably below temperatures melting this condition it is carried out and at correct drawing up is reversible working in the specified temperatures area of an electrochemical chain it is possible to receive experimental data on relative partial molar functions ( $\Delta\overline{G}$ ,  $\Delta\overline{H}$ ,  $\Delta\overline{S}$ ) of one of components.

[M.Babanly et.al, 1992] detailed considered schemes of calculations of integral thermodynamic functions (ITF) from corresponding partial molar value of one of components for various diagram types of a condition ternary systems under condition of vertical position of borders of section of phase areas.

Considering the accepted condition about constancy of coordinates of borders of phase areas independently from temperature in a temperature interval of EMF measurements, various isothermal sections T-x-y diagrams at the specified temperatures ranges should be absolutely identical and quantitatively reflect an arrangement of phase areas on Gibbs triangle. Therefore a basis for an exact choice of limits of integration at calculations is the phase diagram.

Having precisely constructed isothermal section of the phase diagram and the full information about partial molar free energy, entropy and enthalpy for calculation ITF of formation of ternary phases of any compositions, in principle, can be using all methods of thermodynamic calculations applied in thermodynamics of solutions.

Nowadays, for the majority of binary semiconductor phases have reliable data on thermodynamic functions of formation, therefore the most rational way of calculations is integration of Gibbs-Duhem equation on beam sections of type A-ByC<sub>1-y</sub> (where A - component which used in concentration chain as the left electrode for which are known values relative partial molar thermodynamic functions in homogeneous and heterogeneous areas) [M.Babanly et.al, 1985b, 1992]. Thus the bottom limit of integration, unlike the binary systems, is not one of pure components, two-component alloy of B<sub>y</sub>C<sub>1-y</sub> (homogeneous or two-phase) of boundary system B-C:

$$\Delta Z_{A_x(B_yC_{1-y})_{1-x}} = (1-x) \int_0^x \frac{\Delta \overline{Z}_A}{(1-x)^2} dx + \Delta Z_{B_yC_{1-y}}^* \quad (19)$$

where,  $\Delta \overline{Z}_A$  - relative partial function of A component on isothermal section of phase diagram,  $\Delta Z_{B_yC_{1-y}}^*$  - integral thermodynamic function of formation of homogeneous and heterogeneous alloys B<sub>y</sub>C<sub>1-y</sub>.

The similar approach to calculation of integrated thermodynamic properties of ternary homogeneous systems is offered by Elliott and Chipman [Morachevskii, et.al., 2003].

Advantage of this way of calculation ITF consists is that, all alloys irrespective of their phase composition, are considered as independent investigation objects as in case of a two-

component solution, with the partial and integral thermodynamic characteristics. It gives the chance make up integration of Gibbs-Duhem equation in the necessary direction, to be exact, in a direction of composition change in the potentialforming process. In case of binary system this direction from noble component to less noble, and in ternary –from any way chosen  $B_yC_{1-y}$  composition of boundary binary system B-C to a A component on corresponding beam section. In other words, possible variants of changes of compositions of various phases in the ternary system in the process of reversible carrying over A in the alloy are formally reduced to composition change on the section  $A-B_yC_{1-y}$ , that in the equation (19) variable reflects quantitatively X-mol part of A

In three-phase area composition of co-existing phases and, accordingly, partial molar functions of A component remain constants irrespective of total composition of alloys, and in two-phase (in cases when the direction of beam line  $A-B_yC_{1-y}$  does not coincide with connod lines) and single-phase areas is composition functions.

On fig. 2 various types of isothermal phase diagram which reflect all possible variants of alternations of phase areas on the phase diagram are presented:

- the homogeneity fields of ternary ( $ABC_2$ ) and binary compounds degenerated in points, and two-phase areas - in direct lines (fig. 2a);
- on the base of binary compound BC there is a limited homogeneity field ( $\beta$ ) on certain section of ternary system A-B-C. It leads to formation of a wide field of two-phase equilibrium ( $\beta+C$ ) (fig. 2b);
- there are homogeneity field on a base both initial binary ( $\beta$ ), and intermediate ternary ( $\gamma$ ) compounds (fig. 2c).

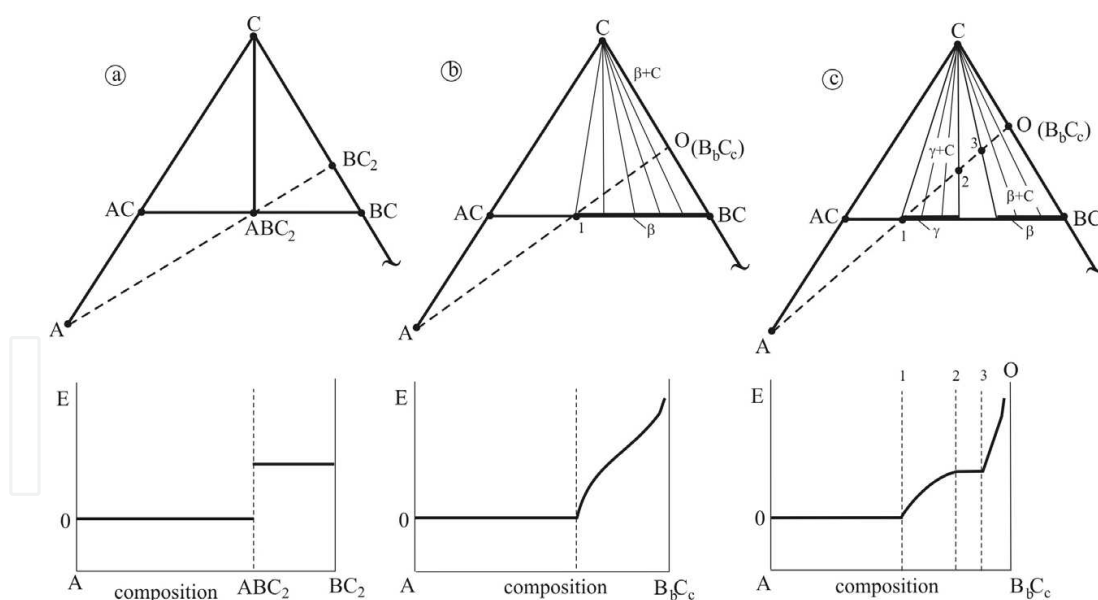


Fig. 2. Some types of phase equilibria in ternary systems and corresponding dependences of E-x on beam sections of type  $A-B_yC_{1-y}$  (dot lines on phase diagram) [M.Babany et.al, 1992]

Apparently from fig. 2, concentration dependences of EMF on beam sections (dot lines) on character coincide with dependences for certain types of diagrams of the phase diagram of binary systems:

- with binary system with one intermediate compound and imperceptible areas of solid solutions;



- b. with binary system with the limited solubility based on more noble initial component;
- c. with the binary system, characterized by presence of limited solid solutions based on more noble component and intermediate phase of variable compositions;

Application of the (19) equation to fig. 2 formally differs from binary systems that at  $x=0$ ,  $\Delta Z_{B_y C_{1-y}}^* \neq 0$ . At calculations value of last function can be borrowed from the literature.

In works of [M.Babanly et.al, 1992] in detail considers calculation procedures ITF for each types of phase given in fig.2

### 3. Solid-state superion conductors with $\text{Ag}^+$ and $\text{Cu}^+$ conductivity

Solid electrolytes - materials possessing high ionic conductivity in a solid state, - are object of comprehensive investigation in various areas of physics and chemistry. From the end of 60<sup>th</sup> years of the last century interest to this unique class of compounds invariably extended. Solid superionic conductors are the major functional materials of a modern materials science and technology. They are used with the big success as electrochemical sensor controls, electrodes or electrolytes materials in devices of electrochemical transformation energy - in solid-state batteries, displays, high-temperature fuel elements, etc. [Gurevich & Kharkats, 1992; Hagenmuller & Gool, 1978; Ivanov-Shits & Murin 2000; West, 1981]. Discovery of solid electrolytes with pure ionic conductivity also has given a new impulse to thermodynamic investigations by electromotive forces method (EMF) and has allowed to extending considerably number of systems studied by this method [M.Babanly et.al, 1992].

Classical example for solid cationconducting electrolytes is high-temperature modification silver iodide  $\alpha\text{-AgI}$ , existing at temperature above 146°C. High electroconductivity ( $\sim 1 \text{ Om}^{-1} \cdot \text{sm}^{-1}$ ) the given phase which on 4 order exceeds that for low-temperature modification  $\beta\text{-AgI}$  have found out in 1914 year by Tubandt and Lorentz. In the range of temperatures from 146 to melting temperature 555°C ionic conductivity of  $\alpha\text{-AgI}$  monotonously increases, and even in a melting point a little bit decreases [West, 1981].

Silver iodide has appeared good basic compound for synthesis new solid electrolytes possessing high ionic ( $\text{Ag}^+$ ) conductivity at room and lower temperatures. It is usually reached by addition to it of the ions which stabilizing cubic structure and interfering its transformation at low temperatures in hexagonal, close-packed on anions. So unipolar solid electrolytes with high ionic conductivity have been synthesized at a room temperature:  $\text{Ag}_8\text{SI}$ ,  $\text{Ag}_8\text{SBr}$ , a solid solution  $0,78\text{AgI} \cdot 0,22\text{Ag}_2\text{SO}_4$ ,  $\text{Ag}_7\text{I}_4\text{PO}_4$ ,  $\text{Ag}_{19}\text{I}_{15}\text{P}_2\text{O}_7$ ,  $\text{Ag}_6\text{I}_4\text{WO}_4$ , and also the gained greatest distribution group of compounds with general formula  $\text{Ag}_4\text{MI}_5$ , where  $\text{M}=\text{Rb}$ ,  $\text{K}$ ,  $\text{NH}_4$ ,  $\text{Cs}_{1/2}$ ,  $\text{K}_{1/2}$ . Electrolytes with general formula  $\text{Ag}_4\text{MI}_5$  have one of the highest values of ionic conductivity at a room temperature ( $\sim 0.2 \text{ Om}^{-1} \cdot \text{sm}^{-1}$ ) among which it is necessary to allocate so-called "rubidic" electrolyte  $\text{Ag}_4\text{RbI}_5$  electroconductivity which is long time was record-breaking high ( $0,25 \text{ Om}^{-1} \cdot \text{sm}^{-1}$ ). This compound has superionic conductivity at extremely low temperature - 151°C which there is a phase transition [Ivanov-Shits & Murin, 2000; West, 1981]. At 64°C  $\text{Ag}_4\text{RbI}_5$  undergoes second sort phase transition, however for this reason electroconductivity changes continuously.

The  $\text{Ag}_4\text{RbI}_5$  melts at 503K with decompose on peritectic reaction, and below 300 K it decomposes on solid state reaction [Ivanov-Shits & Murin, 2000]. However, last process kinetically is strongly broken and at observance of certain care (absence of a moisture and iodine vapor)  $\text{Ag}_4\text{RbI}_5$  can be cooled easily without decomposition below a room temperature and to use as solid electrolyte.

In the beginning of 70th years of last century have been synthesized the  $\text{Cu}^+$  conducting superionic conductors which mainly halides of copper. In 1979 the Japanese and independently American chemists have been synthesized related "rubidic" electrolyte the solid electrolyte  $\text{Cu}_4\text{RbCl}_3\text{I}_2$  possessing at a room temperature record-breaking high ( $0,5 \text{ } \Omega^{-1}\cdot\text{cm}^{-1}$ ) ionic conductivity on  $\text{Cu}^+$  cations [Gurevich & Kharkats 1992; Ivanov-Shits & Murin, 2000].

The discovery of solid-state electrolytes with pure  $\text{Cu}^+$  and  $\text{Ag}^+$  conductivity was stimulate to thermodynamic investigation of systems based on copper and silver by EMF method.

The electrochemical cell in the EMF method with solid cationconducting electrolyte like:

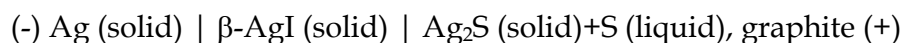


Where the left electrode has pure A component, and right - a homogeneous or heterogeneous alloy of multicomponent system.

As solid electrolytes, basically, superionic conductors with pure ionic conductivity are used, as only in this case there is unique dependence between EMF value (E) and Gibbs energy of potentialforming reactions, in condition of constants charge of the ion causing electroconductivity. Presence of electronic making conductivity leads to decrease of EMF value of cells in comparison with its thermodynamic value as active electrons cause short circuit electrolytic chains through internal resistance of electrolyte. As a result of it in cells with the mixed conductors is not reached the equilibrium condition [M.Babanly et.al, 1992].

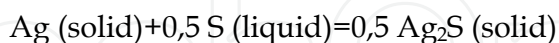
The solid electrolytes divides two electrode spaces and the last can contain solid phases, liquids or gaseous substances of the identical or various chemical natures. For example, on both side of solid electrolyte there can be gaseous oxygen at two kinds of various partial pressures.

For the first time the electrochemical cell of type (20) has been used for thermodynamic research of two-component system of Ag-S, where as solid electrolyte served  $\beta\text{-AgI}$  [West, 1981]. For this purpose it was measured of EMF of concentration chain



at the 450-550 K temperature range.

Considering, that in system Ag-S is formed only one binary compound  $\text{Ag}_2\text{S}$  with narrow homogeneity area, and solubility of  $\text{Ag}_2\text{S}$  in liquid sulphur in the specified temperatures range is insignificant, potentialforming reaction can be given as:



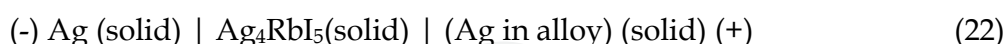
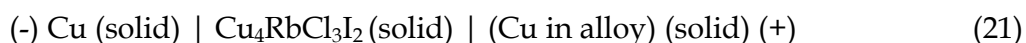
From experiments have received temperature dependence of EMF and authors have calculated,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of  $\text{Ag}_2\text{S}$

#### 4. Thermodynamic investigation of the ternary chalcogenides based on copper and silver by EMF method with solid-state electrolytes

Chalcogenides of copper and silver with p<sup>1</sup>-p<sup>3</sup> elements [Max Plank Institute, 1992-1995; M.Babanly et.al, 1993; Shevelkov, 2008] have the practical interest as functional materials of electronic techniques (photoelectric, thermoelectric and magnetic semiconductors, superconductors, superionic conductors etc.).

Phase equilibriums in the specified systems are studied in the many works which are results are periodically systematized and critically analyzed in a number of handbooks and monographies [Max Plank Institute, Stuttgart, 1992-1995; M.Babanly et.al, 1993].

For investigation solid-phase equilibria in the systems A-B-X (A-Cu, Ag; B-elements of subgroups of gallium, germanium, arsenic; X-S, Se, Te) and thermodynamic properties of ternary compounds formed in them we had been made concentration chains of types:



The equilibrium alloys from various phase areas of the above-mentioned systems served as the right electrodes.

The compound  $\text{Cu}_4\text{RbCl}_3\text{I}_2$  synthesized by melting stoichiometric amounts of chemically pure, anhydrous CuCl, CuI and RbCl in evacuated ( $\sim 10^{-2}$  Pa) quartz ampoule at 900 K with the cooling to 450K and annealed at this temperature for 100 h.  $\text{Ag}_4\text{RbI}_5$  synthesized from chemically pure RbI and AgI by a technique [West, 1981]: stoichiometric mix initial iodides have co-melted in evacuated quartz ampoule ( $\sim 10^{-2}$ Pa) and then quickly cooled to a room temperature. At cooling melt crystallizes in fine-grained and microscopic homogeneous state and then annealed at 400K for 200 h. Obtained cylindrical ingots in diameter  $\sim 8$ mm cuts like pellets in the thickness of 4-6 mm which used as solid electrolyte in chains of types (21) and (22).

The elementary copper and silver served as left electrodes and the right electrodes –pre-synthesized and annealed alloys of investigated systems from various phase areas. Compositions of alloys have been chosen from data on phase equilibrium. For preparation of the right electrodes annealed alloys grinded as powder, and then pressed as pellet in weight of 0,5-1 gram. The electrochemical cell of type in fig. 3 has filled with argon and has placed in the tube furnace, where it held at  $\sim 380$ K for 40-50 hours. Cell temperature measured by chromel-alumel thermocouples and mercury thermometers with accuracy  $\pm 0,5^\circ\text{C}$ .

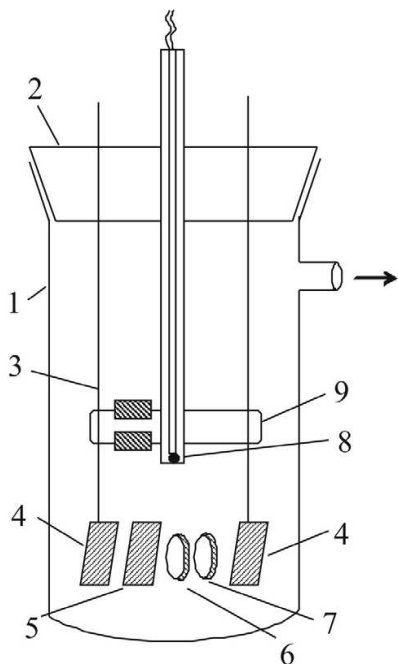


Fig. 3. The electrochemical cell for EMF measurement of chains of type (4.1) and (4.2). 1-glass block; 2-cover; 3-platinum wires; 4-platinum plates; 5-copper (silver) plate; 6-solid electrolytes; 7-investigated alloy (the right electrode); 8-thermocouple, 9-clip [M.Babanly, et.al. 2009].

EMF measured by the compensation method by means of high-resistance digital voltmeters B7-34A. Measurements were carried out in each 3 hours after an establishment of certain temperature. Equilibrium considered those values of EMF which at repeatedly measurement at the given temperature differed from each other not more than on 0,5 mV irrespective from direction of temperature change. In order to of occurrence elimination thermo-e.m.f. contacts of all leads with copper wires had identical temperature.

EMF measurements of alloys of selenium and tellurium containing systems are carried out in the range temperatures of 300÷420K, and sulphur containing 300÷380 K. Maximum limits of temperature intervals of EMF measurements are chosen to exclude melting and transition in a metastable state of alloys of the right electrodes.

**Processing of the EMF measurements results.** For the thermodynamic calculations the results of the experiments were used, which are satisfying to criteria of the reversible work of a chain. Results of EMF measurements for alloys with different compositions within one heterogeneous area were processed in common.

Measured equilibrium values of EMF put on  $E=f(T)$  diagram. Appreciable deviations from linear dependence of EMF were not observed. It is indirectly confirms a constancy of compositions of existing phases in heterogeneous areas of the investigated systems, that, as shown above, is a necessary condition for carrying out of thermodynamic calculations according to the EMF measurements of chains of type (21) and (22). Considering this, results of EMF measurements processed by the least squares method [Gordon, 1976]. Temperature dependence is expressed by the linear equation

$$E = a + bT \equiv \bar{E} + b(T - \bar{T}) . \quad (23)$$

Here  $\bar{E} = \frac{\sum E_i}{n}$ ,  $\bar{T} = \frac{\sum T_i}{n}$ ,  $b = \frac{\sum (E_i - \bar{E})(T_i - \bar{T})}{\sum (T_i - \bar{T})^2}$ , where,  $E_i$ -experimental values of EMF at

temperature  $T_i$ ;  $n$  - number of experimental points (both values  $E$  and  $T$ ),  $a = \bar{E} - b\bar{T}$ .

The statistical estimation of error of measurements consisted in calculation of dispersions of individual measurements of EMF ( $\delta_E^2$ ), average EMF values ( $\delta_{\bar{E}}^2$ ), and also coefficients  $a$  ( $\delta_a^2$ ) and  $b$  ( $\delta_b^2$ ) on relations

$$\delta_E^2(T) = \frac{\delta_E^2}{n} + \delta_b^2(T - \bar{T})^2$$

$$\delta_{\bar{E}}^2 = \frac{\sum (E_i - \bar{E})^2}{n - 2}$$

$$\delta_a^2(T) = \frac{\delta_E^2}{n} + \frac{\delta_{\bar{E}}^2 \bar{T}^2}{\sum (T_i - \bar{T})^2}$$

$$\delta_b^2(T) = \frac{\delta_{\bar{E}}^2}{\sum (T_i - \bar{T})^2}$$

$\bar{E}_i$  - EMF values, calculated by (23) equation at temperature  $T_i$ . Errors ( $\Delta_i$ ) corresponding values calculated by the relations

$$\Delta_i = t\delta_i$$

(t-Student's test,  $\delta_i$  -standard deflection). In the present work  $n \geq 20$ , that at confidential level of 95 % leads to  $t \approx 2$  [Gordon, 1976].

The accepted equations of temperature dependences of EMF according to the recommendation of [Kornilov et.al, 1972] are presented as:

$$E = a + bT \pm 2 \left[ \frac{\delta_E^2}{n} + \frac{\delta_E^2 (T - \bar{T})^2}{\sum (T_i - \bar{T})^2} \right]^{\frac{1}{2}} \quad (24)$$

From the accepted equations of type on relations (13) - (15) calculated relative partial molar free Gibbs energy, enthalpy and entropy of copper (silver) in alloys at 298K.

**The Cu-Tl-Te system** is studied by EMF measurement of concentration chains of type (21) in the  $\text{Ti}_2\text{Te}$ - $\text{Cu}_2\text{Te}$ -Te composition field and with taking into account literature data [Max Plank Institute, Stuttgart, 1992-1995; M.Babanly, 1993] the fragment of the solid phase equilibrium diagram (fig. 4) is constructed.

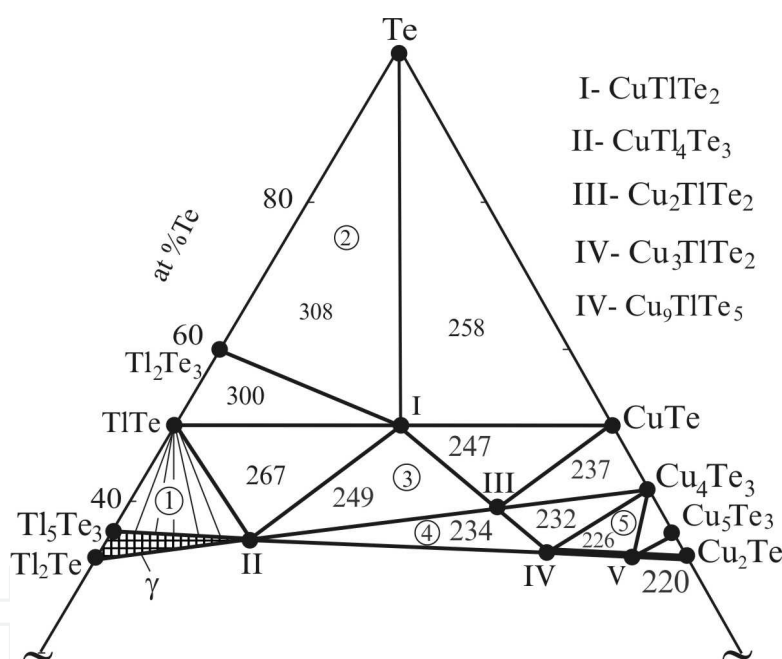


Fig. 4. The solid phase equilibrium diagram of the Cu-Tl-Te system. In some solid phase fields are given the EMF values (mV) of chains of type (5.1) at 300K.

In fig.4 we can see, that in the specified compositions fields five ternary compounds are formed. Compound  $\text{CuTl}_4\text{Te}_3$  forms continuous solid solutions ( $\gamma$ ) with  $\text{Tl}_5\text{Te}_3$ . Areas of homogeneity of other ternary and binary compounds of the system are insignificant.

The EMF measurements of chains of type (21) have shown that values of electromotive forces in each three-phase areas on fig. 4 are constant irrespective of total composition of alloys and in discontinuous change on their borders, and in two-phase area  $\text{TlTe} + \gamma$  and within homogeneity area  $\gamma$ -phases continuously change depending on composition of last.

Reproducibility of EMF measurements and conformity of sequence of their change in investigated system the thermodynamic conditions (impossibility of reducing of EMF values



in direction  $\text{Cu} \rightarrow \text{Tl}_x\text{Te}_{1-x}$ ) to specify possibility of use of these data for thermodynamic calculations.

For calculation of thermodynamic functions of ternary compounds and  $\gamma$ -phases of variable composition have been used data of measurements in phase areas №№ I-V on fig. 4 (table 1).

№	Phase area	$E, mV = a + bT \pm t \cdot S_E(T)$
1	$\text{TlTe} + \delta(\text{Cu}_{0,2}\text{Tl}_{4,8}\text{Te}_3)$	$317,4 + 0,138T \pm 2 \left[ \frac{0,7}{26} + 3,8 \cdot 10^{-5} (T - 351,2)^2 \right]^{1/2}$
2	$\text{TlTe} + \delta(\text{Cu}_{0,4}\text{Tl}_{4,6}\text{Te}_3)$	$296,8 + 0,086T \pm 2 \left[ \frac{0,6}{26} + 3,6 \cdot 10^{-5} (T - 351,2)^2 \right]^{1/2}$
3	$\text{TlTe} + \delta(\text{Cu}_{0,6}\text{Tl}_{4,4}\text{Te}_3)$	$290,1 + 0,032T \pm 2 \left[ \frac{1,3}{26} + 9,8 \cdot 10^{-5} (T - 351,2)^2 \right]^{1/2}$
4	$\text{TlTe} + \delta(\text{Cu}_{0,8}\text{Tl}_{4,2}\text{Te}_3)$	$279,3 + 0,009T \pm 2 \left[ \frac{1,8}{26} + 1,2 \cdot 10^{-4} (T - 351,2)^2 \right]^{1/2}$
5	$\delta(\text{CuTl}_4\text{Te}_3)$	$281,7 - 0,047T \pm 2 \left[ \frac{1,5}{26} + 1,1 \cdot 10^{-4} (T - 351,2)^2 \right]^{1/2}$
6	$\text{Tl}_2\text{Te}_3 + \text{CuTlTe}_2 + \text{Te}$	$286,3 + 0,073T \pm 2 \left[ \frac{3,2}{24} + 1,5 \cdot 10^{-4} (T - 353,7)^2 \right]^{1/2}$
7	$\text{CuTlTe}_2 + \text{Cu}_2\text{TlTe}_2$	$224,3 + 0,085T \pm 2 \left[ \frac{2,1}{24} + 1,2 \cdot 10^{-4} (T - 353,7)^2 \right]^{1/2}$
8	$\text{Cu}_2\text{TlTe}_2 + \text{Cu}_3\text{TlTe}_2$	$216,5 + 0,066T \pm 2 \left[ \frac{1,9}{24} + 8,9 \cdot 10^{-5} (T - 353,7)^2 \right]^{1/2}$
9	$\text{Cu}_3\text{TlTe}_2 + \text{Cu}_9\text{TlTe}_5 + \text{Cu}_4\text{Te}_3$	$200,4 + 0,091T \pm 2 \left[ \frac{2,6}{24} + 1,4 \cdot 10^{-4} (T - 353,7)^2 \right]^{1/2}$

Table 1. The temperature dependences of EMF of concentration chains of type (21) in some phase areas of the Cu-Tl-Te system ( $T=300\div 420\text{K}$ ).

From the accepted equations of temperature dependences of EMF (tab. 1) the relative partial thermodynamic functions of copper in alloys at 298K (tab. 2) are calculated.

Isotherms of partial thermodynamic functions of copper on the section  $\text{Tl}_5\text{Te}_3\text{-CuTl}_4\text{Te}_3$  (fig. 5) have continuous curves that specifies in formation of a continuous number of solid solutions between these compounds.



Phase area	$-\overline{\Delta G}_{Cu}$	$-\overline{\Delta H}_{Cu}$	$\overline{\Delta S}_{Cu}$ , J·K <sup>-1</sup> ·mole <sup>-1</sup>
	kJ·mole <sup>-1</sup>		
Tl <sub>2</sub> Te <sub>3</sub> +CuTlTe <sub>2</sub> +Te	29,723±0,142	27,62±084	7,04±2,36
CuTlTe <sub>2</sub> +Cu <sub>2</sub> TlTe <sub>2</sub>	24,086±0,123	21,64±0,74	8,20±2,11
Cu <sub>2</sub> TlTe <sub>2</sub> + Cu <sub>3</sub> TlTe <sub>2</sub>	22,787±0,104	20,89±0,65	6,37±1,82
Cu <sub>3</sub> TlTe <sub>2</sub> +Cu <sub>9</sub> TlTe <sub>5</sub> +Cu <sub>4</sub> Te <sub>3</sub>	21,953,0,136	19,34±0,82	8,78±2,28
TlTe+δ(Cu <sub>0,2</sub> Tl <sub>4,8</sub> Te <sub>3</sub> )	34,593±0,071	30,59±0,42	13,32±1,19
TlTe+δ(Cu <sub>0,4</sub> Tl <sub>4,6</sub> Te <sub>3</sub> )	31,110±0,070	28,64±0,41	8,30±1,16
TlTe+δ(Cu <sub>0,6</sub> Tl <sub>4,4</sub> Te <sub>3</sub> )	28,911±0,110	27,99±0,67	3,09±1,91
TlTe+δ(Cu <sub>0,8</sub> Tl <sub>4,2</sub> Te <sub>3</sub> )	27,208±0,123	26,95±0,74	0,86±2,11
δ(CuTl <sub>4</sub> Te <sub>3</sub> )	25,829±0,117	27,18±0,69	-4,53±2,02

Table 2. The relative partial thermodynamic functions of copper in Cu-Tl-Te alloys at 298 K.

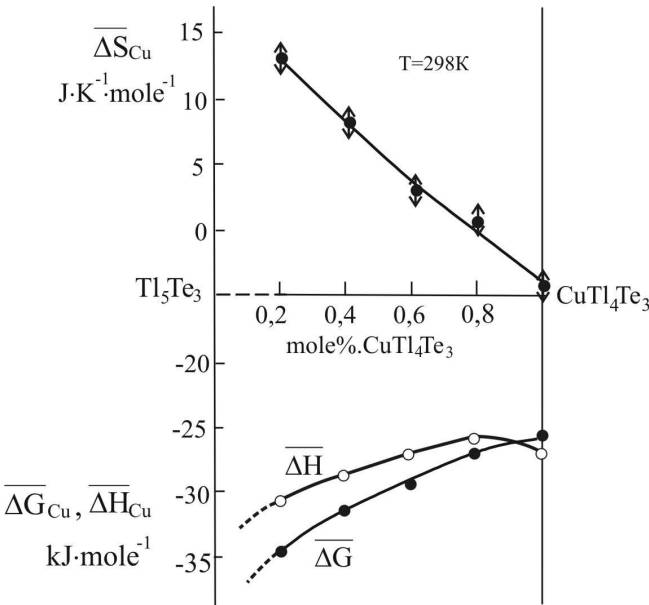


Fig. 5. Dependences of partial thermodynamic functions of copper with compositions on the Tl<sub>5</sub>Te<sub>3</sub>-CuTl<sub>4</sub>Te<sub>3</sub> section at 298K.

According to fig. 5, increasing of concentration of copper in solid solutions is accompanied by considerable decreasing of composition-sensitive function of  $\overline{\Delta S}_{Cu}$  that good agree with structural data of CuTl<sub>4</sub>Te<sub>3</sub> and  $\gamma$ -phases [M.Babanly et.al, 1993].

The standard thermodynamic function of formation of  $\gamma$ -phase and ternary compound CuTl<sub>4</sub>Te<sub>3</sub> are calculated by graphical integration of Gibbs-Duhem equation on the beam section of Cu-[Tl<sub>4</sub>Te<sub>3</sub>] (where, [Tl<sub>4</sub>Te<sub>3</sub>]-two-phase mix Tl<sub>5</sub>Te<sub>3</sub> и TlTe).

Insignificance of homogeneity areas of ternary compounds CuTlTe<sub>2</sub>, Cu<sub>2</sub>TlTe<sub>2</sub>, Cu<sub>3</sub>TlTe<sub>2</sub> and Cu<sub>9</sub>TlTe<sub>5</sub> and co-existing phases with them (Tl<sub>5</sub>Te<sub>3</sub>, Cu<sub>4</sub>Te<sub>3</sub> and Te) in three-phase areas NoNo II-V (fig. 4) allows calculate their standard thermodynamic functions of formation and standard entropy by method potentialforming reactions. According to fig. 4, the partial molar functions of copper in the specified phase areas are thermodynamic characteristics of following potentialforming reactions (all compounds in crystalline state):



Based on these reactions the thermodynamic functions of formation and standard entropy of corresponding ternary phases have been calculated.

At calculations besides experimental data (tab. 2) the corresponding thermodynamic data for compounds  $\text{Tl}_2\text{Te}_3$ ,  $\text{TlTe}$ ,  $\text{Tl}_5\text{Te}_3$  [M.Babanly et.al, 1993.] and  $\text{Cu}_4\text{Te}_3$  [Abbasov, 1981], also standard entropy of copper and tellurium [Yungman, 2006] were used. Errors calculated a method of accumulation of errors.

The obtained values of standard thermodynamic functions of formation and standard entropy of ternary compounds  $\text{Cu}_2\text{TlTe}_2$ ,  $\text{Cu}_3\text{TlTe}_2$  and  $\text{Cu}_9\text{TlTe}_5$  are well agree with the results [M.Babanly et.al, 2011] which is obtained from EMF measurements of concentration chains concerning a thallium electrode with liquid electrolit (tab. 3).

Compound	$-\Delta_f G^0(298\text{K})$	$-\Delta_f H^0(298\text{K})$	$S^0(298\text{K}),$
	kJ·mole <sup>-1</sup>		J·K <sup>-1</sup> ·mole <sup>-1</sup>
Tl <sub>5</sub> Te <sub>3</sub> [31]	213,6±1,7	216,7±2,0	458,6±6,7
δ(Cu <sub>0,2</sub> Tl <sub>4,8</sub> Te <sub>3</sub> )	210,2±1,7	213,0±2,2	454±7
δ(Cu <sub>0,4</sub> Tl <sub>4,6</sub> Te <sub>3</sub> )	207,8±1,6	210,5±2,3	449±7
δ(Cu <sub>0,6</sub> Tl <sub>4,4</sub> Te <sub>3</sub> )	205,3±1,6	207,6±2,4	444±8
δ(Cu <sub>0,8</sub> Tl <sub>4,2</sub> Te <sub>3</sub> )	203,8±1,5	206,0±2,5	438±8
CuTl <sub>4</sub> Te <sub>3</sub>	201,4±1,4	203,8±2,6	433±9

Table 3. The standard integral thermodynamic functions of solid solutions  $\text{Cu}_x\text{Tl}_{5-x}\text{Te}_3$  ( $0<x<1$ ).

From EMF measurements of concentration chains of types (21) and (22) the standard thermodynamic functions of formation and standard entropy of some ternary chalcogenides of copper (tab. 4) and silver (tab. 5) are calculated. Herein, some data are published for the first time, which are the sources do not show. In the tab.4 and 5 also presence the thermodynamic functions of thallium containing ternary compounds of copper and the silver which are obtained by EMF method with liquid electrolyte (Italic font). The data presented in tables strongly differ on errors. It is due to with different errors of thermodynamic functions of the binary compounds which are recommended in the handbooks [M.Babanly et.al, 1992; Kubaschewski, 1993; Mills, 1974, Yungman, 2006] which have been used at calculations.

Compound	$-\Delta_f G^0(298)$	$-\Delta_f H^0(298)$	$S^0(298)$	References
	kJ/mole		J·K <sup>-1</sup> ·mole <sup>-1</sup>	
CuIn <sub>3</sub> Se <sub>5</sub>	380,0±1,4	398,2±28,6	373±28	[Babanly, N.B., 2009]
CuInSe <sub>2</sub>	153,2±0,6	158,0±9,6	163±11	[Babanly, N.B., 2009]
CuTlS <sub>2</sub>	94,3±0,7	93,6±1,4	172,7±2,8	[Babanly, N.B., 2009]
	91,5±0,5	98,6±4,0		[Babanly, M.B., 1986]
CuTlS	90,3±0,7	88,3±2,1	132,4±6,2	[Babanly, N.B., 2009]
	84,1±1,5	82,1±4,9		[Babanly, M.B., 1986]
Cu <sub>3</sub> TlS <sub>2</sub>	163,8±2,6	159,2±9,8	251,8±5,8	[Babanly, N.B., 2009]
	152,7±1,8	145,8±12,3		[Babanly, M.B., 1986]
Cu <sub>9</sub> TlS <sub>5</sub>	373,8±3,9	371,8±21,4	529,0±19,0	[Babanly, N.B., 2009]
	354,6±4,5	339,7±30,8		[Babanly, M.B., 1986]
CuTlSe <sub>2</sub>	96,29±0,16	97,91±0,95	176,1±5,1	[Babanly, M.B., 1992]
	96,5±0,6	97,2±1,3		
CuTlSe	84,49±0,16	81,37±0,85	149,9±2,8	[Babanly, M.B., 1992]
	84,2±1,3	80,5±3,9		
Cu <sub>2</sub> TlSe <sub>2</sub>	119,06±0,27	118,61±1,54	216,2±6,8	
CuTlTe <sub>2</sub>	75,1±0,4	72,6±1,3	208±4	
Cu <sub>2</sub> TlTe <sub>2</sub>	99,2±0,5	94,3±2,1	249±6	[Babanly, M.B., 2010]
	94,8±0,9	92±7	237±3	
Cu <sub>3</sub> TlTe <sub>2</sub>	122,0±0,6	115,2±2,7	288±8	[Babanly, M.B., 2010]
	117,1±1,2	117±5	263±4	
Cu <sub>9</sub> TlTe <sub>5</sub>	264,3±2,6	253,8±9,8	637±15	[Babanly, M.B., 2010]
	244,0±2,4	2431±14	621±7	
CuTl <sub>4</sub> Te <sub>3</sub>	201,4±1,4	203,8±2,6	433±9	
Cu <sub>2</sub> GeS <sub>3</sub>	225±12	226±13	189±8	[Babanly, M.B. 2001]
Cu <sub>8</sub> GeS <sub>6</sub>	456±13	429±18	579±24	[Babanly, M.B. 2001]
Cu <sub>2</sub> GeS <sub>6</sub>	182±11	182±11	35	[Babanly, M.B. 2001]
CuGe <sub>3</sub> Se <sub>4</sub>	252±56	246±55	314,5±8,4	[Babanly, M.B. 2001]
CuGeSe <sub>2</sub>	131±21	129±21	154,9±7,0	[Babanly, M.B. 2001]
Cu <sub>2</sub> GeSe <sub>3</sub>	178,4±18,8	174,5±19,7	223,4±6,6	[Babanly, M.B. 2001]
Cu <sub>2</sub> GeTe <sub>3</sub>	89,6±13	92±14	236±12	[Babanly, M.B. 2001]
Cu <sub>2</sub> Sn <sub>4</sub> S <sub>9</sub>	659,9±4,3	650,9±29,7	560,3±74,7	[Babanly, M.B. 2001]
Cu <sub>2</sub> SnS <sub>3</sub>	239,6±1,5	242,6±12,0	196,3±21,9	[Babanly, M.B. 2001]
Cu <sub>4</sub> SnS <sub>4</sub>	316,4±2,4	327,7±18,8	266,5±28,2	[Babanly, M.B. 2001]
Cu <sub>2</sub> SnSe <sub>3</sub>	205,5±2,2	207,6±14	244±27,9	[Babanly, M.B. 2001]
Cu <sub>2</sub> SnTe <sub>3</sub>	124,3±1,9	118,7±11,6	278±15,9	[Babanly, M.B. 2001]
Cu <sub>3</sub> AsS <sub>4</sub>	179,2±0,6	172,2±2,6	278±8	
Cu <sub>6</sub> As <sub>4</sub> S <sub>9</sub>	429,4±1,2	419,5±8,2	673±23	
Cu <sub>4</sub> As <sub>2</sub> S <sub>5</sub>	257,8±0,8	249,8±4,6	395±13	
Cu <sub>3</sub> AsS <sub>3</sub>	170,2±0,6	163,9±2,7	254±8	
CuAsS	69,5±0,3	64,1±1,7	109±5	
Cu <sub>2</sub> As <sub>4</sub> Se <sub>7</sub>	206,7±1,6	208,1±10,6	501±17	

Compound	$-\Delta_f G^0(298)$	$-\Delta_f H^0(298)$	$S^0(298)$	References
	kJ/mole		J·K <sup>-1</sup> ·mole <sup>-1</sup>	
CuAsSe <sub>2</sub>	74,6±0,5	73,8±3,2	156±6	
Cu <sub>3</sub> AsSe <sub>4</sub>	163,5±1,1	157,2±5,6	325±12	
Cu <sub>4</sub> As <sub>2</sub> Se <sub>5</sub>	233,6±2,4	227,9±8,8	472±21	
Cu <sub>3</sub> AsSe <sub>3</sub>	158,0±1,3	151,5±5,3	296±13	
Cu <sub>3</sub> AsTe <sub>3</sub>	91,2±3,3	90,6±5,3	286±6	[Babanly, M.B. 2001]
Cu <sub>3</sub> SbS <sub>4</sub>	207,5±3,9	200±6,3	298±18	[Babanly, M.B. 2001]
CuSbS <sub>2</sub>	121,4±3,4	119±3,5	148±6,4	[Babanly, M.B. 2001]
Cu <sub>3</sub> SbS <sub>3</sub>	197,8±3,8	189,3±6,5	269,5±13,7	[Babanly, M.B. 2001]
Cu <sub>3</sub> SbSe <sub>4</sub>	191,6±2,5	178,6±5,4	358±18	[Babanly, M.B. 2001]
CuSbSe <sub>2</sub>	101,4±1,8	98,5±2,2	173±8	[Babanly, M.B. 2001]
Cu <sub>3</sub> SbSe <sub>3</sub>	175,6±2,5	164,0±5,3	311±15	[Babanly, M.B. 2001]
CuBiS <sub>2</sub>	138,6±4,0	138,2±2,9	156±12	[Babanly, M.B. 2001]
Cu <sub>3</sub> BiS <sub>3</sub>	213,0±4,4	209,9±5,2	264±21	[Babanly, M.B. 2001]
CuBi <sub>3</sub> Se <sub>5</sub>	248,7±1,9	248,6±5,8	421,9±7,8	[Babanly, M.B. 2001]
CuBiSe <sub>2</sub>	107,6±0,8	105,9±2,51	189,8±2,4	[Babanly, M.B. 2010]
Cu <sub>3</sub> BiSe <sub>3</sub>	162,5±1,2	155,9±5,7	315,0±8,5	[Babanly, M.B. 2010]
Cu <sub>9</sub> BiSe <sub>6</sub>	324,8±3,5	313,1±18,6	659±28	[Babanly, M.B. 2010]
CuBiTe <sub>2</sub>	64,2±1,0	61,3±1,0	200±7	[Babanly, N.B. 2007]

Table 4. Standard thermodynamic functions of formation and standard entropy of some ternary chalcogenides of copper.

Compound	$-\Delta_f G^0(298)$	$-\Delta_f H^0(298)$	$S^0(298)$	References
	kJ/mole		J·K <sup>-1</sup> ·mole <sup>-1</sup>	
AgGaS <sub>2</sub>	302,1±1,7	302,8±4,3	145,1±9,6	[Ibragimova G.I., 2006]
Ag <sub>9</sub> GaS <sub>6</sub>	447,5±2,4	393,9±12,4	786,8±27,8	[Ibragimova G.I., 2006]
Ag <sub>2</sub> Ga <sub>20</sub> S <sub>31</sub>	5131±21	5169±62	1772±87	[Ibragimova G.I., 2006]
AgGaSe <sub>2</sub>	237,0±3,4	239,4±5,6	159,6±11,2	[Ibragimova G.I., 2006]
Ag <sub>9</sub> GaSe <sub>6</sub>	433,0±4,1	413,1±10,9	742,9±32,5	[Ibragimova G.I., 2006]
AgGaTe <sub>2</sub>	120,8±4,6	119,6±3,1	186,8±6,9	[Ibragimova G.I., 2006]
Ag <sub>9</sub> GaTe <sub>6</sub>	276,8±11,5	233,4±11,0	867,0±30,7	[Ibragimova G.I., 2006]
Ag <sub>2</sub> GeS <sub>3</sub>	206±2,1	198±2,2	239,1±8,8	[Babanly, M.B., 1993]
Ag <sub>4</sub> GeS <sub>4</sub>	254±2,1	235±2,4	393,2±14,1	[Babanly, M.B., 1993]
Ag <sub>8</sub> GeS <sub>6</sub>	345±2,2	310±2,6	680,4±23,1	[Babanly, M.B., 1993]
Ag <sub>2</sub> GeSe <sub>3</sub>	145±2,1	139±2,2	262,2±10,4	[Babanly, M.B., 1993]
Ag <sub>8</sub> GeSe <sub>6</sub>	288±2,3	255±2,8	734,6±30,4	[Babanly, M.B., 1993]
Ag <sub>8</sub> GeTe <sub>6</sub>	268,0±1,0	245,0±7,0	745,8±17,1	[Babanly, M.B., 1993]
Ag <sub>2</sub> Sn <sub>2</sub> S <sub>5</sub>	358,8±2,3	339,5±12,6	397,9±16,3	[Babanly, M.B., 1993]
Ag <sub>2</sub> SnS <sub>3</sub>	213,3±1,6	202,7±8,8	260,7±16,8	[Babanly, M.B., 1993]
Ag <sub>8</sub> SnS <sub>6</sub>	351,7±2,6	328,9±18,0	652,9±16,3	[Babanly, M.B., 1993]
Ag <sub>8</sub> SnS <sub>5</sub>	355±3,2	330±3,8	628,43±23,6	[Babanly, M.B., 1993]

Compound	$-\Delta_f G^0(298)$	$-\Delta_f H^0(298)$	$S^0(298)$	References
	kJ/mole		J·K <sup>-1</sup> ·mole <sup>-1</sup>	
AgSnSe <sub>2</sub>	146,4±0,5	148±3	162±7,2	[Babanly, M.B., 1993]
Ag <sub>8</sub> SnSe <sub>6</sub>	350,3±1,8	320,4±8,1	736,6±23,8	[Babanly, M.B., 1993]
AgTlS	72,3±0,6	72,9±3,0	136,7±8,1	[Ibragimova G.I., 2001] [Babanly, M.B., 1993]
	71,7±0,7	73,3±3,2	133,3±5,9	
Ag <sub>7</sub> Tl <sub>3</sub> S <sub>5</sub>	320,2±2,6	351,9±15,7	544,2±36,5	[Ibragimova G.I., 2001] [Babanly, M.B., 1993]
	303,5±3,0	315,0±15,0	614,5±30,1	
Ag <sub>3</sub> TlS <sub>2</sub>	120,0±0,9	128,4±5,6	227,7±12,8	[Ibragimova G.I., 2001] [Babanly, M.B., 1993]
	114,3±1,2	118,0±6,0	243,8±23,1	
Ag <sub>8</sub> Tl <sub>2</sub> S <sub>5</sub>	278,0±2,4	287,5±14,6	597,0±32,3	[Ibragimova G.I., 2001] [Babanly, M.B., 1993]
	266,5±2,9	269,0±15,0	620,9±26,0	
Ag <sub>7</sub> TlS <sub>4</sub>	195,9±1,5	192,0±9,4	503,2±20,2	[Ibragimova G.I., 2001] [Babanly, M.B., 1993]
	189,2±2,8	184,0±13,0	507,1±27,1	
Ag <sub>7</sub> TlSe <sub>4</sub>	227,1±0,4	183,4±1,9	676,7±15,1	[Babanly, M.B., 1982]
	234,8±1,9	198,3±6,7	652,9±27,9	
Ag <sub>3</sub> TlSe <sub>2</sub>	130,8±0,2	113,5±1,1	333,9±12,8	[Babanly, M.B., 1982]
	133,3±0,9	116,8±3,2	292,2±14,1	
AgTlSe	80,4±0,2	74,3±1,2	173,9±5,9	[Babanly, M.B., 1982]
	82,4±0,5	75,8±1,8	176,9±7,7	
AgTlTe <sub>2</sub>	69,7±0,7	71,5±1,8	199,9±5,7	[Babanly, M.B., 1982]
	69,9±0,7	62,1±2,3	232,1±7,2	
Ag <sub>8</sub> Tl <sub>2</sub> Te <sub>5</sub>	273,4±2,0	253,3±6,8	784,1±21,6	[Babanly, M.B., 1982]
	267,9±3,3	234,4±6,9	829,7±19,7	
AgTlTe	67,3±0,5	63,6±1,2	168,8±5,9	[Babanly, M.B., 1982]
	69,3±0,6	62,8±2,0	178,7±6,0	
AgTl <sub>3</sub> Te <sub>2</sub>	151,5±1,2	149,1±1,9	342,1±7,2	[Babanly, M.B., 1982]
	153,5±0,9	147,3±3,1	355,3±9,5	
Ag <sub>9</sub> TlTe <sub>5</sub>	238,2±1,4	206,9±6,5	800,3±19,2	[Babanly, M.B., 1982]
	235,6±3,4	201,5±5,9	809,5±16,6	
AgAs <sub>3</sub> Se <sub>5</sub>	111,9±10,5	112,5±0,5	359,1±7,5	[Babanly, M.B., 2009]
AgAsSe <sub>2</sub>	55,6±3,6	54,4±3,5	167,0±3,8	[Babanly, M.B., 2009]
Ag <sub>7</sub> AsSe <sub>6</sub>	214±4,2	199,5±6,5	637±16	[Babanly, M.B., 2009]
Ag <sub>3</sub> AsSe <sub>3</sub>	107,8±3,8	101,8±4,6	310,7±7,7	[Babanly, M.B., 2009]
AgSbS <sub>2</sub>	110±5	103±5	175,1±6,9	[Babanly, M.B., 1993]
Ag <sub>3</sub> SbS <sub>3</sub>	153±5	141±7	309,2±13,3	[Babanly, M.B., 1993]
Ag <sub>7</sub> SbS <sub>6</sub>	233±7	218±12	595,3±28,1	[Babanly, M.B., 1993]
AgSbSe <sub>2</sub>	92,5±4,5	91,0±5	177,2±6	[Babanly, M.B., 1993]
AgSbTe <sub>2</sub>	49,6±1,5	44,5±1,3	204,6±5	[Babanly, M.B., 1993]
AgBi <sub>3</sub> S <sub>5</sub>	326,4±12,9	323,4±7,7	367,5±16,5	[Shykhyev Y.M. 1995]
AgBiS <sub>2</sub>	124,2±4,4	118,6±3,0	166,3±6,8	[Shykhyev Y.M. 1995]
AgBiSe <sub>2</sub>	100,5±0,8	94,1±2,3	205±10	[Shykhyev Y.M. 2003]

Table 5. Standard thermodynamic functions of formation and standard entropy of some ternary chalcogenides of silver.



## 5. Conclusion

The results of this chapter show that  $\text{Cu}^+$  and  $\text{Ag}^+$  conducting superionic conductors can be successfully applied as solid-state electrolyte in the thermodynamic studies and specification of solid-phase equilibria diagrams of ternary copper - and silver containing systems by EMF method. Unlike from classical variant of EMF method with liquid electrolyte they allow to investigate also the systems containing high electrochemical active component than copper or silver (in our case, thallium). It is due to that the solid-state electrolyte, unlike liquid, prevents percolation of collateral processes (interaction of electrodes with electrolyte and through electrolyte among themselves) and by that allows to obtain reproduced data for irreversible in classical understanding of concentration chains. The specified advantage solid-state cation-containing systems by EMF method of formation and standard entropy of some ternary chalcogenides of silver-ternary phases have been conducting electrolytes allows to essentially expanding a circle of the systems investigated by EMF method.

## 6. Acknowledgments

The authors would like to acknowledge to Dr. Samira Z. Imamaliyeva, Dr. Ziya S. Aliev and Leyla F. Mashadiyeva and for carrying out experiments and preparation of this chapter.

## 7. References

- Abbasov, A.S. (1981). *Thermodynamic Properties of Some Semiconductor Substances*, Elm, Baku
- Babanly, M.B., Kuliyevev A.A. (1982a). Phase Equilibria and Thermodynamic Properties of the Ag-Tl-Se System. *Russian Journal of Inorganic Chemistry*, Vol.27, No.9 (September), pp.1336-1340, ISSN 0036-0236
- Babanly, M.B., Kuliev A.A. (1982b). Phase Equilibria and Thermodynamic Properties of the Ag-Tl-Te System, *Russian Journal of Inorganic Chemistry*, Vol. 27, No.6 (June), pp.867-872.
- Babanly M.B., Kuliyevev A.A. (1985a), Thermodynamic investigation and refined the phase diagram of ternary chalcogenides systems by method EMF, In: *Mathematical Problems in Chemical Thermodynamics*, Novosibirsk, Nauka, Siberian Section, pp.192-201
- Babanly M.B. (1985b), Application of partial heterogeneous molar functions method in thermodynamic analysis of the ternary condensed systems, In: *Application of Mathematical Methods to studying Physico-Chemical Equilibria*, Vol.2, Novosibirsk p.202-204
- Babanly, M.B., Li Tai Un. & Kuliev, A.A. The Cu-Tl-S System (1986). *Russian Journal of Inorganic chemistry*, Vol. 32, No.7 (July), p.1837-1844, ISSN 0036-0236



- Babanly, M.B., Yusibov, Yu.A. & Abishov, V.T. (1992). *Method of Electromotive Forces in the Thermodynamics of Solid Semiconductor Substances*, Baku State University.
- Babanly, M.B., Yusibov, Yu.A. & Abishev, V.T. (1993). *Three-Component Chalcogenides on the Basis of Copper and Silver*, Baku, Baku State University.
- Babanly, M.B., Babanly, N.B., & Mashadiyeva, L.F. (2001). *Phase Diagrams and Thermodynamic Properties of the Cu-B<sup>IV</sup>(B<sup>V</sup>)-Chalcogen Systems*. Proceedings of VI International School-Conference "Phase Diagrams in Material Science», pp.5-6, Kiev, October, 14-20, 2001
- Babanly, M.B., Shykhiev, Yu.M. & Yusibov Yu.A. (2003). Thermodynamic investigation of ternary compounds of Ag-Tl-Te system by EMF method with solid-state electrolyte. *News of Baku University, natural science series*, No.1, pp. 30-35, ISSN 1609-0586
- Babanly, M.B., Mashadiyeva, L.F., & Imamaliyeva, S.Z. (2009) Thermodynamic Study of the Ag-As-Se and Ag-S-I Systems Using the EMF Method with a Solid Ag<sub>4</sub>RbI<sub>5</sub> Electrolyte. *Russian Journal of Electrochemistry*, Vol.45, No.4, (April 2009), pp.399-404, ISSN 1023-1935,
- Babanly, M.B., Salimov, Z.E., Babanly, N.B. & Imamaliyeva, S. Z. (2011). Thermodynamic properties of copper thallium tellurides. *Inorganic Materials*, Vol. 47, No.4 (April), pp.361-364, ISSN 0020-1685
- Babanly, N.B., Mokhtasebzadeh, Z; Aliyev, I.I. & Babanly, M.B. (2007) Phase equilibriums in the system Cu-Bi-Te and thermodynamic properties of CuBiTe<sub>2</sub> compound. *Reports of National Academi of Science of Azerbaijan*, Vol.63, No.1, pp.41-54,
- Babanly, N.B., Yusibov, Yu.A., Mirzoeva, R.J., Shykhiev, Yu.M. & Babanly, M.B. (2009). Cu<sub>4</sub>RbCl<sub>3</sub>I<sub>2</sub> Solid Superionic Conductor in Thermodynamic Study of Three-Component Copper Chalcogenides. *Russian Journal of Electrochemistry*, Vol. 45, No.4 (April), pp. 405-410, ISSN 1023-1935
- Babanly, N.B., Aliev, Z.S., Yusibov, Yu.A. & Babanly, M.B. (2010). A Thermodynamic Study of Cu-Tl-S System by EMF Method with Cu<sub>4</sub>RbCl<sub>3</sub>I<sub>2</sub> Solid Electrolyte. *Russian Journal of Electrochemistry*, Vol.46, No.3 (March), pp.371-375, ISSN 1023-1935
- Babanly, N.B., Yusibov, Yu.A., Aliev, Z.S. & Babanly, M.B. (2010). Phase Equilibria in the Cu-Bi-Se System and Thermodynamic Properties of Copper Selenobismuthites. *Russian Journal of Inorganic Chemistry*, Vol.55, No.9 (September), pp.1471-1481, ISSN 0036-0236
- Gordon, A; Ford, R. (1972). *The chemists Companion. A handbook of practical data techniques and references*. A Wiley-Interscience Publication. New-York-London-Sydney-Toronto
- Gurevich, Yu.Ya; Kharkats, Yu.I. (1992). *Superionic conductors*, Nauka, ISBN 5-02-014622-6, Moscow
- Hagenmuller, P., Gool, W.V. (1978) *Solid Electrolytes, General Principles, Characterization, Materials, Applications*, Acad. Press, ISBN 0-12-313360-2, New York, San Fransisco, London

- Ibragimova, G.I., Shikhiyev, Yu.M., & Babanly M.B. (2006). Solid Phase Equilibria in Ag-Ga-S (Se,Te) systems and thermodynamic properties of ternary phases. *Chemical Problems*, No.1, pp.23-28, ISBN 9952-8034-4-6
- Ibragimova, G.I., Babanly, M.B., & Shykhyev Yu.M. (2001). *Investigation of system  $\text{Ag}_2\text{Te}-\text{Ga}_2\text{Te}_3$  by EMF method*. Proceedings of VII National Science conference "Physico-chemical analyses and inorganic material science", pp.41-45, Baku State University, Baku, May 21-23, 2001
- Ibragimova, G.I., Shykhyev Yu.M. & Babanly, M.B. *Thermodynamic investigation of system  $\text{Ag}_2\text{S}-\text{Tl}_2\text{S}-\text{S}$* . Proceedings of VII National Science conference "Physico-chemical analyses and inorganic material science", pp.3-10, Baku State University, Baku, May 21-23, 2001/
- Ivanov-Shits, A.K. & Murin, I.V. (2000). *Solid-State Ionics*, Sankt-Peterburg State University, ISBN 5-288-02745-5, Sankt-Petersburg
- Kornilov, A.N. Stepina L.B., Sokolov V.A. (1972). The recommendation for the compact form of presents of experimental data at the publication of results of thermochemical and thermodynamic invstigations. *Russian Journal of Physical Chemistry*, Vol.46, No.11 (November), pp.2974-2980, ISSN 0036-0244
- Kubaschewski, O., Alcock, C.B., Spenser P.J. (1993). *Materials Thermochemistry*. Pergamon Press, INSB 0080418899
- Mills, K. (1974). *Termodinamic data for inorganic sulphids, selenides and tellurides*. Butterworths, ISBN 10 040870537X, London.
- Morachevskii, A.G., Voronin, G.F., & Kutsenok, I.B. (2003). *Electrochemical Research Methods in Thermodynamics of Metallic Systems*, ITsK "Akademkniga", ISBN 5-94628-064-3, Moscow:
- Shevelkov, A.V. (2008). Chemical aspects of the design of thermoelectric materials. *Russian Chemical Reviews*, Vol. 77, No.1 (January), pp.1-19, ISSN: 0036-021X
- Shykhyev, Yu.M., Yusibov, Yu.A., Popovkin, B.A., Babanly, M.B. (2003).The Ag-Bi-Se System. *Russian Journal of Inorganic Chemistry*, Vol. 48, No.12 (December), pp.1941-1948, ISSN 0036-0236
- Shykhyev, Yu.M., Yusibov, Yu.A., Babanly, M.B. (1995). Thermodynamic properties of system Ag-Bi-S. *News of Baku University, natural science series*, No.1, pp.93-98, ISSN 1609-0586
- Ternary Alloys. A Comprehensive Compendium of Evaluated Constitutional Data and Phase Diagrams. V.1-5, Max Plank In-t, Stuttgart, 1992-1995
- Yungman, V.S. (2006) Database of Thermal Constants of Compounds, Electronic Version, <http://www.chem.msu.su/cgi-bin/tkv>.
- Vasil'yev, V.P., Nikol'skaya, A.V., Gerasimov, Ya.I., Kuznetsov A.F. (1968). Thermodynamic investigation of thallium tellurides by method EMF. *Inorganic Materials*, Vol.4, No.7, pp. 1040-1046, ISSN 0020-1685.
- Voronin, G.A. (1976) Partial thermodynamic functions of heterogeneous alloys and their application in thermodynamics of alloys. In: *Modern problems of physical chemistry*, pp.29-48. Moscow State University, Moscow.
- Wagner, C. (1952). *Thermodynamics of Alloys*. Addison-Wesley Press, Cambridge.

West, A.R. (1987). *Solid State Chemistry and Its Applications*. Wiley, ISBN 978-0-471-90874-6, Camden, NY, U.S.A.

IntechOpen

IntechOpen



## **Electromotive Force and Measurement in Several Systems**

Edited by Prof. Sadik Kara

ISBN 978-953-307-728-4

Hard cover, 174 pages

**Publisher** InTech

**Published online** 21, November, 2011

**Published in print edition** November, 2011

This book is devoted to different sides of Electromotive Force theory and its applications in Engineering science and Industry. The covered topics include the Quantum Theory of Thermoelectric Power (Seebeck Coefficient), Electromotive forces in solar energy and photocatalysis (photo electromotive forces), Electromotive Force in Electrochemical Modification of Mudstone, The EMF method with solid-state electrolyte in the thermodynamic investigation of ternary copper and silver chalcogenides, Electromotive Force Measurements and Thermodynamic Modelling of Electrolyte in Mixed Solvents, Application of Electromotive Force Measurement in Nuclear Systems Using Lead Alloys, Electromotive Force Measurements in High-Temperature Systems and finally, Resonance Analysis of Induced EMF on Coils.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Mahammad Babanly, Yusif Yusibov and Nizameddin Babanly (2011). The EMF Method with Solid-State Electrolyte in the Thermodynamic Investigation of Ternary Copper and Silver Chalcogenides, Electromotive Force and Measurement in Several Systems, Prof. Sadik Kara (Ed.), ISBN: 978-953-307-728-4, InTech, Available from: <http://www.intechopen.com/books/electromotive-force-and-measurement-in-several-systems/the-emf-method-with-solid-state-electrolyte-in-the-thermodynamic-investigation-of-ternary-copper-and>

**INTECH**  
open science | open minds

### **InTech Europe**

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
[www.intechopen.com](http://www.intechopen.com)

### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen