

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

4,400

Open access books available

117,000

International authors and editors

130M

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)



# Electrochemical Cells with the Liquid Electrolyte in the Study of Semiconductor, Metallic and Oxide Systems

Valery Vassiliev<sup>1</sup> and Weiping Gong<sup>2</sup>

<sup>1</sup>*Chemistry Department, Lomonosov University, Moscow,*

<sup>2</sup>*Institute of Huizhou,*

<sup>1</sup>*Russia*

<sup>2</sup>*China*

## 1. Introduction

The first publications devoted to a study of the thermodynamic properties of metallic alloys, using electrochemical cells (EMF method) was known since 1936 year (Strikler & Seltz, 1936). This was the groundwork for all the next studies.

Co-workers from Moscow State University (Geyderih et al., 1969) have considered some questions about this experimental method.

A new attempt to generalize the electrochemical methods on thermodynamic studies of metallic systems was made again in the book (Moratchevsky, 1987). The general aspects of the thermodynamics of nonstoichiometric compounds were presented there and the methods for experimental studies of the thermodynamic properties of molten metal and salt systems were discussed.

The different types of electrochemical cells with solid and liquid electrolytes and dynamic EMF methods were examined in the recent book (Moratchevsky et al., 2003). A separate chapter of this book deals with methods of treatment and presentation of experimental data. In recent decades the important step of qualitative development of EMF method had been made and it was not considered in this book.

In the present chapter we focus on those experimental techniques that help to increase significantly the experimental result precision.

The knowledge of thermodynamic properties and phase diagrams of binary, ternary and multi component systems is necessary for solving materials science problems and for designing new products and technologies fitted to actual needs. A rational study of equilibria among phases and of the given system thermodynamic properties not only leads to the discovery of unknown phases but also to the determination of phase thermodynamic stability, to homogeneity domain boundaries, and finally to the elaboration of analytical description of the system by using thermodynamic models which are based on the dependence of phase Gibbs energies on such parameters as temperature, concentration and pressure.

Experimental studies are the primary information sources for thermodynamic properties and phase diagrams of all systems. The method of electromotive force (EMF) is one of the most important methods of the physicochemical analysis. One peculiarity of the EMF is its proportionality to the chemical potential:

$\Delta\mu_i = n \cdot F \cdot E$  of one of the system components,

where  $n$  is a charge of the ion responsible for the potential,

$F=96485.34$  C/mol is the constant of Faraday,

$E$  is electromotive force.

Improving the accuracy and reproducibility of measurements leads to the increase of the quality and quantity of information about the system. Values of  $\Delta\mu_i$  ( $T, x_i$ ) versus temperature ( $T$ ) and atomic fraction ( $x_i$ ) obtained with uncertainties of  $\pm 500$  J/mol (especially in a narrow temperature range) give only rough estimates of partial entropy and enthalpy of the components.

An accuracy improvement in determining of the chemical potential ( $\Delta\mu_i(T, x_i)$  versus temperature ( $T$ ) and atomic fraction ( $x_i$ ) from  $\pm 10$  to  $50$  J/mol not only leads to the various thermodynamic properties of the system (partial entropies ( $\Delta_f \bar{S}_i$ ) and enthalpies ( $\Delta_f \bar{H}_i$ ) of components, phase enthalpies of transformation ( $\Delta_f \bar{H}_{tr}$ ), partial enthalpies at infinite dilution ( $\Delta_f \bar{H}_i^\infty$ ), thermal capacities ( $C_p$ ), but also gives a possibility to study the phase diagram in detail (liquidus and solidus, miscibility gaps, invariant points, stoichiometry deviations, ordering, etc...)

## 2. Principals of the method

We perform measurements of the EMF or chemical potential across the electrochemical cells with liquid electrolyte, such as:



$x$  represents a molar fraction of component A in liquid or solid alloy  $A_x B_{(1-x)}$ . The component A (usually a pure metal) is the negative electrode, the alloy  $A_x B_{(1-x)}$  where the component B is more noble than A, is the positive electrode.

The chemical potential of pure metal A  $\mu_A^{(A)}$ , is always higher than its chemical potential in the alloy  $A_x B_{(1-x)}$  or ( $\mu_A^{(A)} > \mu_A^{(A_x B_{(1-x)})}$ )

$$\Delta\mu_A = RT \ln(a_A^{(A_x B_{(1-x)})} / a_A^{(A)}) = RT \ln a''/a' \quad (1)$$

If  $a_A^{(A)} = 1$ , we can simplify the equation (1) and we have the equation (2).

$$\Delta\mu_A = RT \ln(a_A^{(A_x B_{(1-x)})}) \quad (2)$$

$\mu_A^{(A)}$  is the change of the chemical potential of component A in its transition from a pure metal A into an alloy  $A_x B_{(1-x)}$  in reference conditions. The measurement of EMF as a function of temperature leads to partial thermodynamic functions.

$$\Delta\mu_A = \Delta\bar{H}_A - T \cdot \Delta\bar{S}_A \quad (3)$$

$$\Delta\mu_A = -n \cdot F \cdot E \quad (4)$$

$$\Delta\bar{H}_A = -n \cdot F \cdot a \quad (5)$$

$$\Delta\bar{S}_A = n \cdot F \cdot b \quad (6)$$

$$\Delta\bar{S}_A = -(\partial\Delta\mu_A / \partial T)_p = nF(\partial E / \partial T)_p \quad (7)$$

where  $b$  is  $\text{tg}(\alpha)$  (see Fig.1)

$$\Delta\bar{H}_A = \Delta\mu_A + T\Delta\bar{S}_A = nF[T(\partial E / \partial T)_p - E] \quad (8)$$

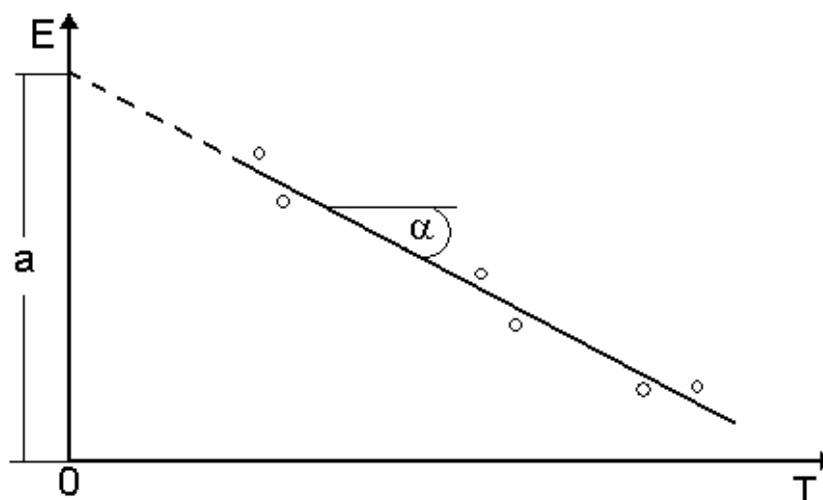


Fig. 1. Graphical relation of measured values  $E(T)$  with partial thermodynamic functions  $a = -\Delta\bar{H}_A$  and  $b = \Delta\bar{S}_A$ .

The integral thermodynamic functions can be calculated with help of Gibbs-Duhem or Gibbs-Duhem- Margules equations:

Gibbs-Duhem equation for the two-component system AB is:

$$\Delta\Phi = x_1\Delta\bar{\Phi}_1 + (1-x_1)\Delta\bar{\Phi}_2 \quad (9)$$

The Margules equation is generalized by Gibbs-Duhem equation:

$$\Delta\Phi = (1-x_i) \int_0^{x_1/1-x_1} \Delta\bar{\Phi}_A d\left(\frac{x_1}{1-x_1}\right) \quad (10)$$

The partial and integral thermodynamic values are presented by the terms  $\Delta\bar{\Phi}_i$  and  $\Delta\Phi$ , respectively.

If we can ignore the homogeneity regions of the intermediate phases of certain binary phase diagram, we can calculate the integral properties of these phases by combining equations.

For example, the system lutetium-indium in the region 0-50 at % Lu has two intermediate phases of 1:2.5 and 1:1. Calculation of the thermodynamic integral properties is easily carried out, if we have in our possession, the partial thermodynamic properties of these phases:

$\text{Lu} + 2.5\text{In} \rightarrow \text{LuIn}_{2.5}$   $\Delta_f \bar{\Phi}'_{\text{Lu}}$  is partial thermodynamic value of formation  $\text{LuIn}_{2.5}$  for one mole of lutetium

$\text{Lu} + 0.667 \text{LuIn}_{2.5} \rightarrow \Delta_f \bar{\Phi}''_{\text{Lu}}$  is partial thermodynamic value of formation  $\text{LuIn}$  for one mole of lutetium.

Combining these equations permits to determine the integral properties of  $\text{LuIn}$  phase.

$$0.667 | \text{Lu} + 2.5 \text{In} \rightarrow \text{LuIn}_{2.5} \Delta_f \bar{\Phi}'_{\text{Lu}} \equiv \Delta \Phi(\text{LuIn}_{2.5})$$

$$| \text{Lu} + 0.667 \text{LuIn}_{2.5} \rightarrow 1.667 \text{LuIn} \Delta_f \bar{\Phi}''_{\text{Lu}}$$

$$1.667 \text{Lu} + 1.667 \text{In} \rightarrow 1.667 \text{LuIn} \Delta_f \bar{\Phi}'_{\text{Lu}} + \Delta_f \bar{\Phi}''_{\text{Lu}}$$

The integral functions of  $\text{Lu}_2\text{In}_5$  and  $\text{LuIn}$  phases are equal for one mole-atom:

$$\Delta_f \Phi'(\text{Lu}_2\text{In}_5) = 2 \Delta_f \bar{\Phi}'_{\text{Lu}} / 7$$

$$\Delta_f \Phi''(\text{LuIn}) = (0.667 \Delta_f \bar{\Phi}'_{\text{Lu}} + \Delta_f \bar{\Phi}''_{\text{Lu}}) / 1.667 \cdot 2$$

### 3. Main experimental steps

Here are the main experimental steps of the EMF method:

- synthesis of alloys and preparation of the electrodes,
- dehydration of salt mixture and preparation of the electrolyte,
- different types of electrochemical cell and its assembly.

#### 3.1 Synthesis of alloys and preparation of the electrodes

The alloy preparation techniques are different and depend on the work objectives. A study of the systems in the liquid state does not require such special treatment as annealing, while a study of alloys in solid state requires annealing for several days. And then it is necessary to avoid working with alloy ingots. As a rule we use the pellets fabricated from powdered alloys. For this reason the dismountable mold is best suited. For this reason it is necessary to use the dismountable mold (Fig.2). The internal party of this mold consists of dismountable block cylinder from high strength tempered steel of four sections (Fig.3). To fabricate a pellet we introduce the tungsten wire (diameter 0.5 mm) throughout special groove of support. Then we introduce the powdered alloys and press the pellet by punch, using the hydrolic press. The contact between the pellet and the tungsten wire must be well secured.

If the alloy is sufficiently plastic, it can be drilled with a hole a little larger than the diameter the conductor wire and compress with the vise. Sometimes, the reference electrodes or measuring one are extremely fragile, and it is impossible to ensure good contact between the wire and the sample. In this case, we prepare the mechanic mixture of powder studied alloys with powder or filling of a more plastic inert metal and then we press the pellets. This added inert plastic metal serves as a matrix of the studied material. For this reason tantalum fillings are mixed in proportion 1:1. We used this procedure in forming the reference manganese electrodes (Vassiliev et al., 1993). It is better to work with the pellets (Vassiliev et al., 1968). Sometimes using the samples in the form of ingot leads to distortion of the measurement results of the EMF, especially if these measurements are made lower of solidus temperature (Terpilowski et al., 1965). If the study of alloys is carried out over a wide temperature range, from liquid homogeneous state to mixed solid-liquid and then to solid states, the EMF measurements are reliable if they are carried out at the complete solide state (of the studied phases) but the temperature should not be more than 100-150 K below the solidus line.



Fig. 2. The four-part dismantlable mold is shown in this picture: 1-punch, 2-four-section dismantlable block cylinder from high strength tempered steel, 3 - constricting clamp with two tightening bolts, 4 - support with groove for tungsten wire.

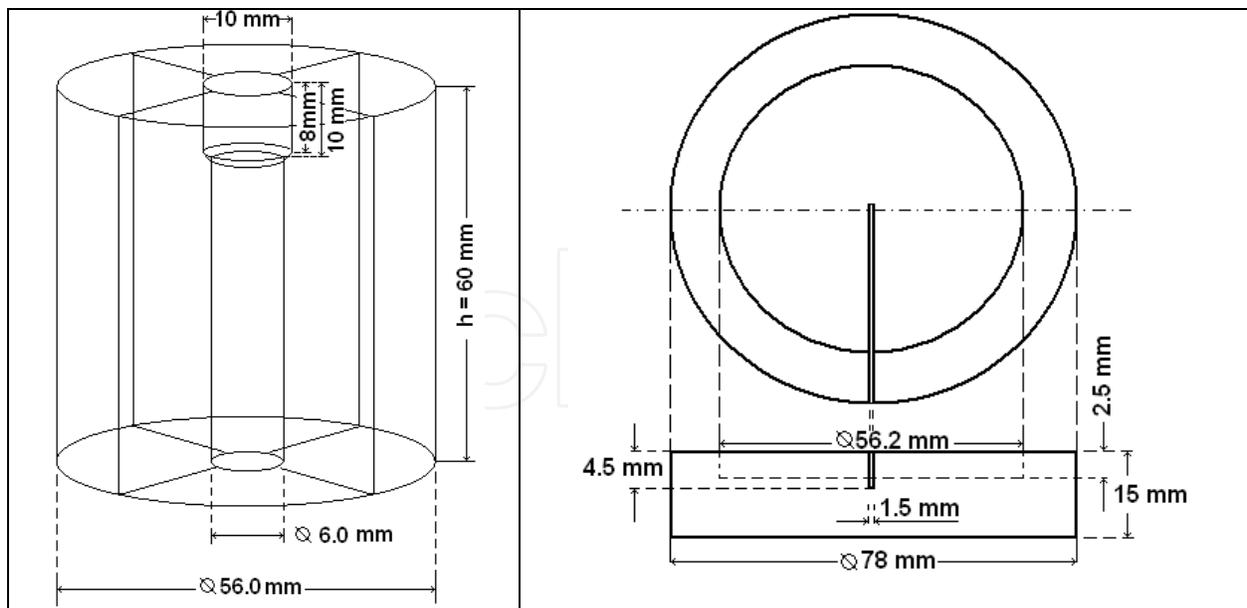
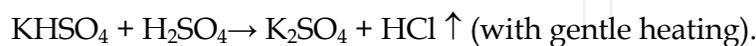
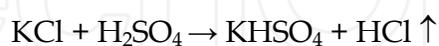


Fig. 3. Internal four-section dismantlable block cylinder of mold (2) and support with groove (4).

### 3.2 Salt mixture dehydration and preparation of the electrolyte

It is necessary to pay special attention to the preparation of salts of the electrolyte. They must be dried very carefully. It applies especially to Li, Ca, Zn and Al halides. These salts are extremely hygroscopic, and their melting without special dehydration leads to the formation oxyhalogenides which presence must be avoided. The used electrolyte in the liquid state must be completely transparent and shows no disorder or heterogeneity. The ingots of electrolyte can be stored in sealed Pyrex ampoules. Upon introduction of the electrolyte in a cell, contact with air should be minimal (no more than 10 seconds). Dehydration salts (eg LiCl + RbCl) must pass under pumping with a slowly increasing heating for 5 days to prevent formation of hydroxides. Then the dehydrated salt mixture is transferred to a silica beaker preheated to 500°C in an electrical furnace. To remove oxychlorides, the molten salts are treated with dry hydrochloride gas (HCl). Hydrogen chloride can easily be synthesized by reacting potassium chloride (KCl) or sodium chloride (NaCl) by reaction of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (Fig.4):



Hydrogen chloride must be dried using zeolites loaded into a U-tube. The gas is bubbled through the melt until there are no suspended particles (about 1h). The melt prepared in this way is poured into Pyrex ampoules with a neck, which are sealed then. The electrolyte can be stored indefinitely in sealed Pyrex ampoules and may be used as required. In practice, it is possible to use the different eutectic mixtures of halides (See Table 1).

The study of some systems such as chalcogenides of zinc, cadmium, mercury, thallium, bismuth, etc. (binary or multicomponent) can be achieved in "low temperature" cell. In this case the calcium chloride (CaCl<sub>2</sub>) is dissolved in glycerol between 40 and 180°C. Calcium

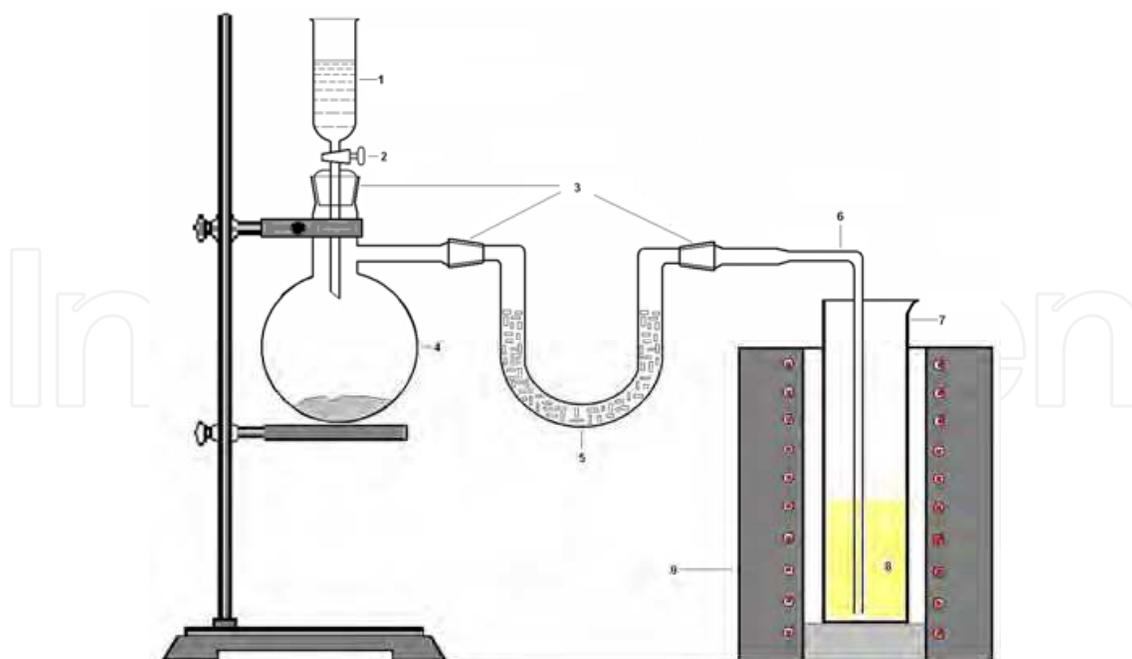


Fig. 4. Device for obteing of gazeous hydrogen chloride: 1- Container of concentrated sulfuric acide, 2- Tap, 3- Glass grandings, 4- Vial for potassium chloride, 5- U-shaped tube for zeolites, 6- Quartz tube, 7- Quartz beaker with a spout, 8- Molten electrolyte, 9- Furnace.

Mixtures of salts	$T_m$ °C
55.5 NaI - 44.5 KI	585
38.0 NaCl - 62.0 CaCl <sub>2</sub>	500
32.9 LiCl - 34.8 NaCl - 32.3 KCl	357
46.0 LiCl - 54.0 KCl	352
48. LiBr - 52.0 KBr	348
29.75 LiCl - 64.77 KCl - 5.48 CaCl <sub>2</sub>	320
30.3 LiCl - 69.7 RbCl	312
28.97 LiCl - 4.42 NaCl - 66.61 CsCl	299
45.0 LiBr - 55.0 RbBr	270
52.7 LiI - 47.3 KI	260
54.0 CH <sub>3</sub> COOH - 46.0 CH <sub>3</sub> COONa	233
70.0 ZnCl <sub>2</sub> - 18 KCl - 12 NaCl	206
69.5 AlCl <sub>3</sub> - 30.5 NaCl	152
<i>Solution of CaCl<sub>2</sub> in the glycerole</i>	<i>40 - 180</i>

Table 1. Eutectic mixtures of halides (weight percent) used for preparation of electrolyte.

chloride (dried under vacuum at temperature of 200°C) is used as a water absorbent for glycerol and also for creating an ionic conductivity of the electrolyte with chloride (AlCl<sub>x</sub>) (Vassiliev et al., 1968).

### 3.3 Different types of electrochemical cells and their assembly

There are many examples of construction of electrochemical cells, proposed in the literature (Morachevski et al. 2003).

We have tested the different types of alloys with three types of cells from 'Pyrex' glass, which had been made by ourselves. One of three cell works well up to 200°C (Vassiliev et al., 1968, 1971) using the salts solution of glicerine as electrolyte. We can also use the same types of cells at the high temperature to 1000°C (Vassiliev et al., 1998a) if we use the refractory material as quartz or alumina glasses. The other two types of cell are operated at high temperatures to softening up 'Pyrex' glass (800-900 K) (Vassiliev et al., 1980, 1993, 1995, 1998b, 2001). When we experiment with a liquid electrolyte, we can use the various electrochemical cells. One of them represents a double H-shaped vessel is suspended on a central tube of 6-8 mm in diameter, fitted with hooks, and which also is served as a cover for the thermocouple. This construction is incorporated inside a protective glass cylinder which is equipped with ground-in cap and two vacuum valves on the sides. This valves permit to control the vacuum and the pression of inert gas inside of the cell. The tungsten current leads with electrodes are soldered in inlet tubes 8 mm in diameter. Height and diameter of the protective cylinder depend on the internal diameter and depth of a using electric furnace. Described construction of the cell is convenient for working with glycerine electrolyte (Pyrex material) and for salt melts (quartz material) (See Fig.5).

Figure 6 shows a scheme of the isothermal Pyrex cell. The lower part of the cell (below the dashed line) is 54 - 60 mm in diameter and about 90 mm in height. The tungsten current leads and the electrodes attached to them are soldered in inlet tubes 8 mm in diameter. The bottom of the cell has cruciblelike holes, which are enable to study both solid and liquid alloys, with no risk of accidental mixing. A calibrated Pt/Pt-10% Rh thermocouple is introduced into the casing, which is soldered in the centre of the cell at the level of the electrodes. Such cells can operate indefinitely between the solidification temperature of the eutectic melt and the onset of softening of Pyrex glass (about 900 K). The offtake of the cell is about 400 mm in length and 25 mm in diameter is fitted with a ground-glass joint. It is served as a container for the electrolyte. The time needed to withdraw the ingot from the storage ampoule, to introduce into the container, and to connect it to the vacuum system does not exceed ten seconds. At the first we pump the cell ( $10^{-3}$  to  $10^{-4}$  Pa) for a day, then we flush with purified argon, and then the ingot is melted under dynamic vacuum using a portable gas torch. The melt drains down into the lower part of the cell, which is introduced into a microfurnace heated from 50 to 100°C above the melting point of the eutectic mixture. Next, the cell is sealed off at the neck under vacuum and transferred to a preheated working furnace. The electrochemical cell in running order is presented in Fig.7.

The third type of cell (Fig. 8) is a modification of the previous. The bottom of that cell is the same as the previous one. The difference concerns a technic of the electrolyte charging into the cell. For certain systems, such as chalcogenides, it is necessary to avoid the vacuum heating of the bottom part of cell that causes an evaporation of volatile metals such as Hg (Vassiliev et al., 1990) or chalcogens (Vassiliev et al., 1980). To put the electrolyte in the vessel we should proceed in this way. An ingot of electrolyte, sealed in a Pyrex ampoule, and a massive porcelain mortar were warmed previously in an oven to 200°C. The ingot was removed gently from the ampoule with a special knife and a Pyrex glass stick as follows. One end of the stick was heated up to temperature of softening with help of the torch. After we have applied this part of stick on the stripe traced with a knife on the ampoule. The ampoule was broken easily and the ingot became free. Then the ingot was grounded into small pieces in a mortar and as soon as possible the pieces were loaded in a small offtake flask and it was connected with cell and vacuum. This flask was heated gradually in a

microfurnace under vacuum (0.1 Pa) up to 200 ° C for 24 hours. Then the cell was rinsed by purified argon and the electrolyte was poured out at the bottom by turn of the flask. Vacuum-sealed cells can be preserved for a long time and can be used reasonably. This cells permit to obtain the reproducible results of measurements during many months.

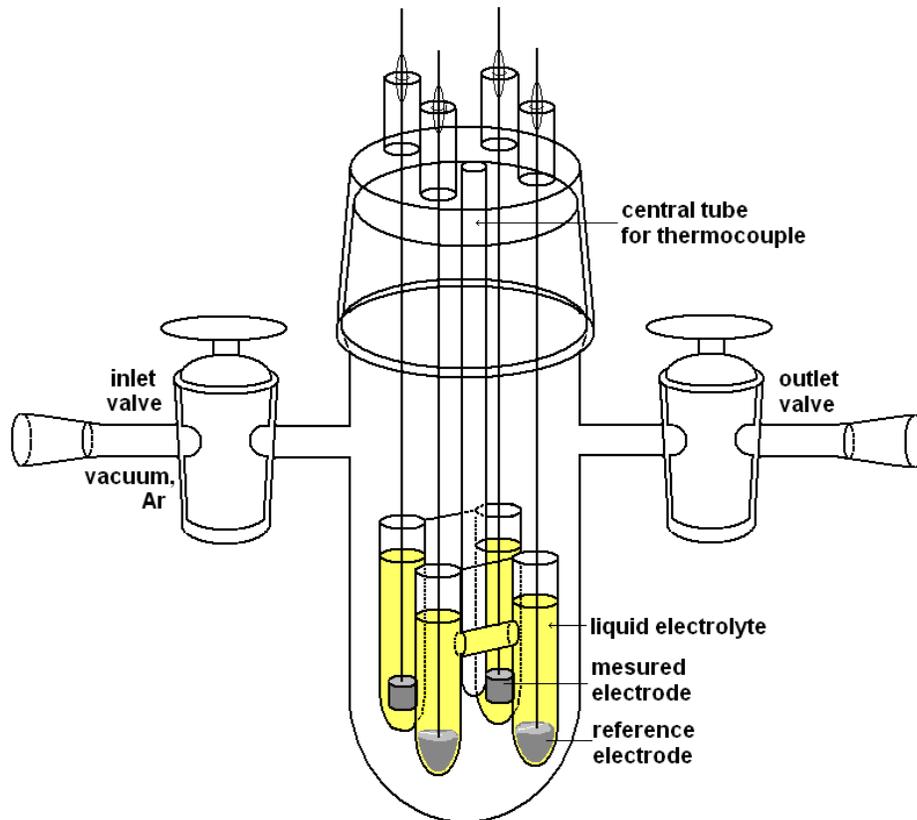


Fig. 5. Cell with control of vacuum and inert gas pressure inside.

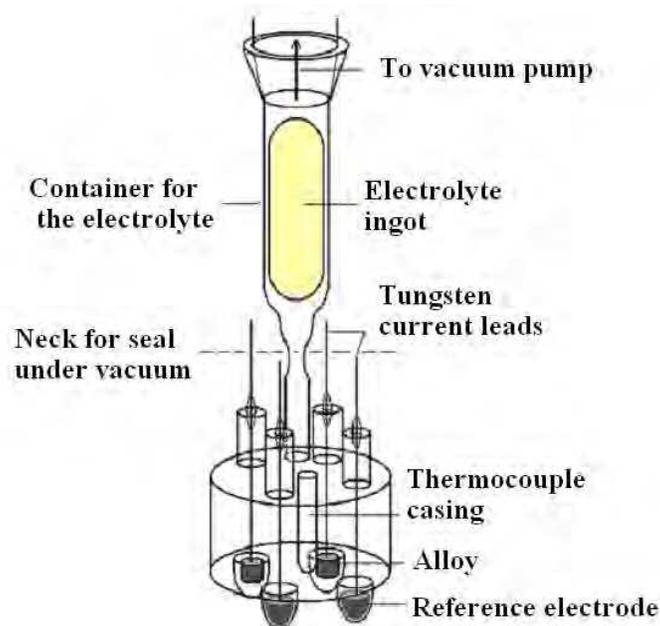


Fig. 6. Vacuum isothermic cell (first variant).

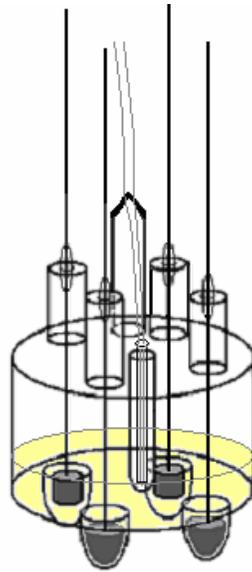


Fig. 7. Electrochemical cell in running order.

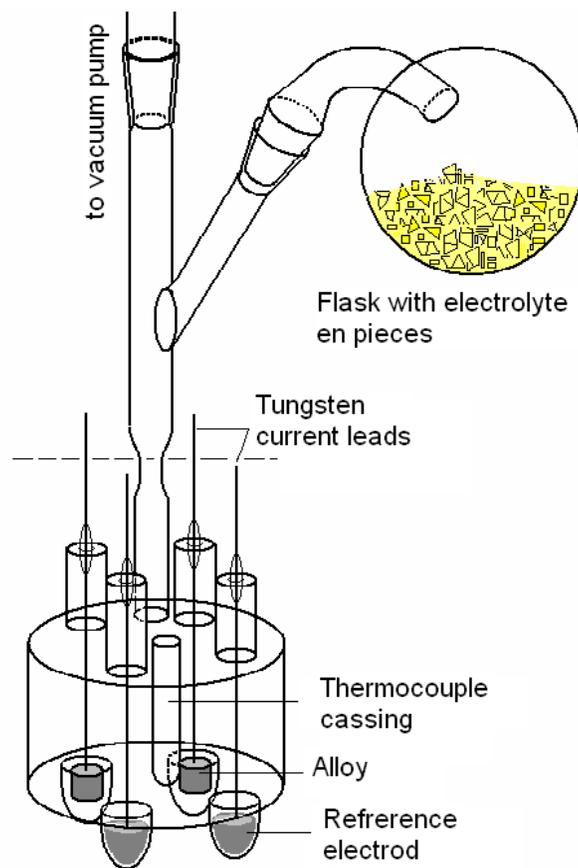


Fig. 8. Vacuum isothermic cell (second variant).

### 3.4 Cell with diaphragm

In some cases the decrease in activity of metal A does not lead to expected results. This concerns to the metals such as titanium, zirconium, hafnium, uranium, and beryllium ...



M1 is more electronegative than Me2 in a series of electrode potentials.

$$[Me_1^{m+}]^0, [Me_1^{n+}]^0, [Me_2^{z+}]^0, [Me_2^{p+}]^0$$

- equilibrium concentration in the ion mole fraction

$$E_1 = \varphi_{\text{all.}} - \varphi_{\text{Me1}}; E_2 = \varphi_{\text{Me2}} - \varphi_{\text{all.}}$$

One compare  $E_1 + E_2$  with  $E_3$  ( $E_1 + E_2 = E_3$ ) to verify the accuracy of the electromotive forces of the chain.

#### 4. Required apparatus and materials

In this paragraph we cite the main required apparatus and materials:

Simple vacuum post is presented in Fig.10.

- Electric furnaces with precise control of temperature. To speed up the work it is desirable to use several furnaces.
- Microfurnaces. Microfurnace presents a porcelain tube with an inner diameter of 65-70 mm and a length of 100-120 mm. This microfurnace can be easily made in the laboratory.
- Laboratory transformers.
- Primary and secondary vacuum pumps or turbomolecular one.
- Gauge (Vacuummeter)
- Vacuum baker.
- Digital millivoltmeter at high impedance.
- Hand or automatic commutation.
- Computer in case of automatic measurement system.
- Manuel or automatic press.
- Thermostat for cold ends of the thermocouples or Dewor bottle.
- Analytic balance.
- Vacuum post with multiple outputs.
- Vacuum comb for making of alloys.
- Hard steel mold of the four sections.
- Pyrex cells. In perspective, using the intermediate glass between Pyrex and quartz is possible for applying the electrochemical cells up to 1200-1300K. The coefficient of expansion of this type of glass must be as closer to the tungsten.
- Electrode leak detector
- Pt/Pt-10% Rh thermocouples.
- Oxygen and propane cylinders.
- Portable gas torch.
- Tungsten wire 0.5 mm. Simple vacuum post is presented in Fig.10.

Trap with liquid nitrogen (Fig.11) serves to catch aggressive substances vapors and it can be used as the sorption pump. In the second case it is recommended to use the zeolytes annealed at 300°C.

Sorption column serves to purificate the argon against the traces of oxigen and moisture. Sorbtion is performed by the activated copper deposited on silicagel at 170°C (Brauer, 1954).

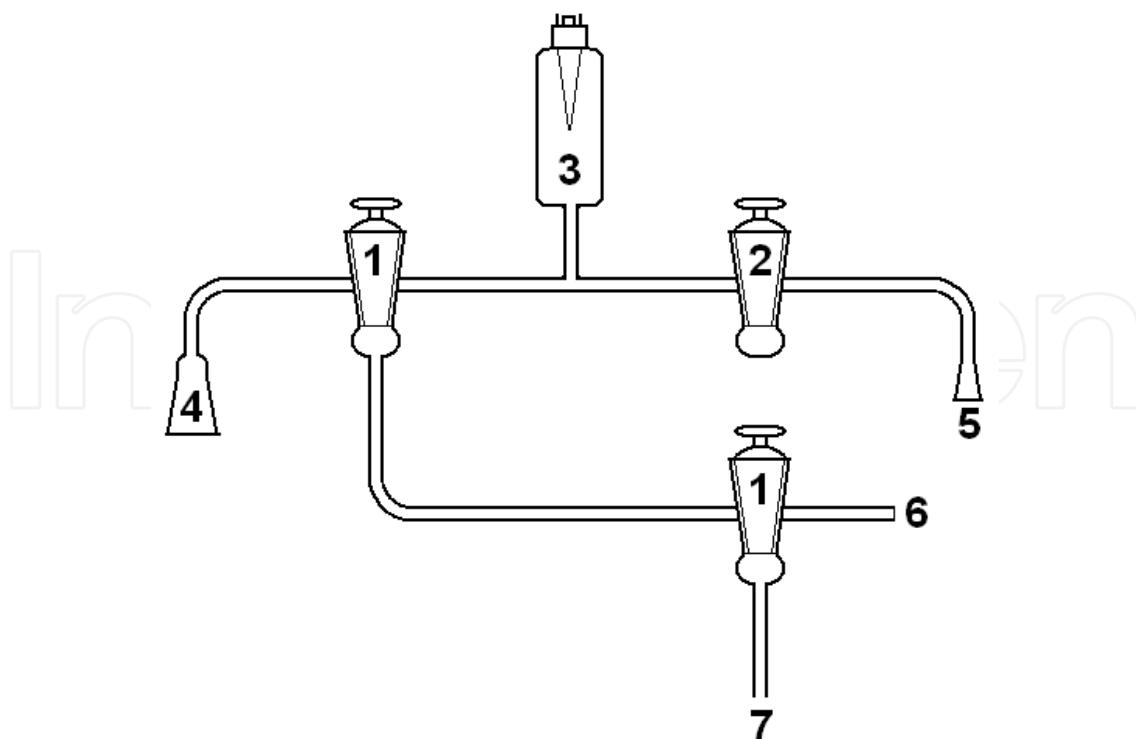


Fig. 10. Simple vacuum post: 1- three-way valve (T=valve), 2- two way valve, 3- gauge, 4- cell sleeve 5- ampule sleeve, 6- to air, 7- to pump.

Vacuum comb permits to accelerate the preparation of alloys (Fig.12). The block-scheme of the EMF measuring is presented in the Fig.13. The configuration of the vacuum post and related details may be changed by the experimenter (Fig.10).

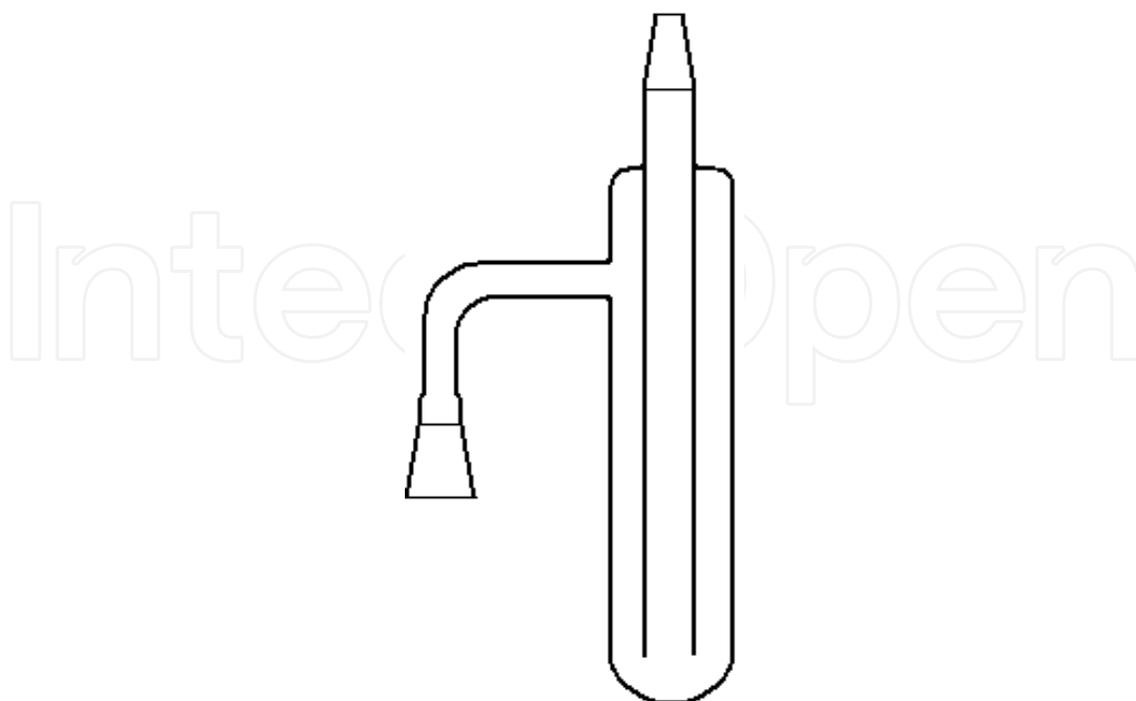


Fig. 11. Liquid-nitrogen trap.

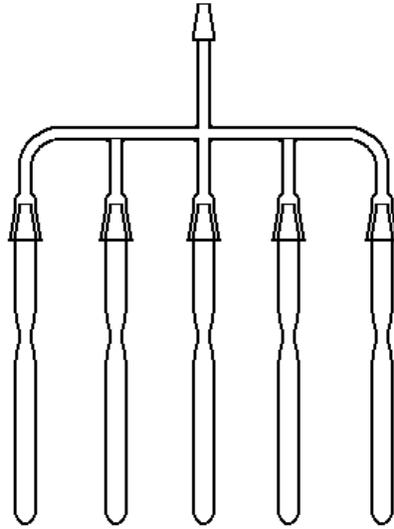


Fig. 12. Vacuum comb for alloy preparation.

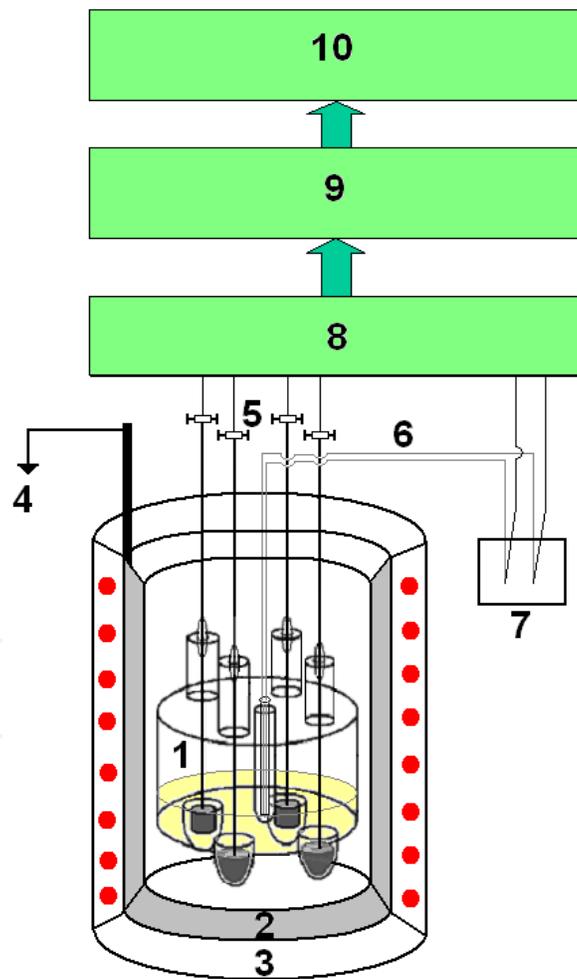


Fig. 13. Block-scheme of the measuring assembly: 1- cell, 2- stainless steel protector nozzle, 3- furnace, 4- ground, 5 - clamp of current leads, 6-thermocouple, 7- thermostat for cold ends of the thermocouples, 8- hand or automatic commutation, 9- digital millivoltmeter at high impedance, 10- computer.

## 5. Methodological problems most frequently encountered in EMF method

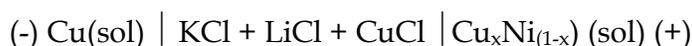
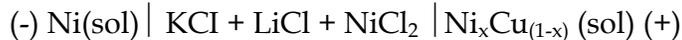
On the difficult path of the experimental study we overcame the various methodological problems that had significantly and successfully improved the method of the EMF. Let us consider these main methodological problems of the EMF method, having a significant influence on the potentiometric measurements:

1. Exchange reaction between electrodes caused by a small difference of electrode potentials components of the alloy in the given electrolyte (Hladik, 1972).
2. Spontaneous reactions due to a large chemical potential difference between measured electrodes and reference.
3. Presence of multiple oxidation states of ions involved in redox reaction generating the EMF of the cell.
4. Liquation (or phase separation) of liquid alloys.
5. Evaporation of element and the temperature of the experiment.

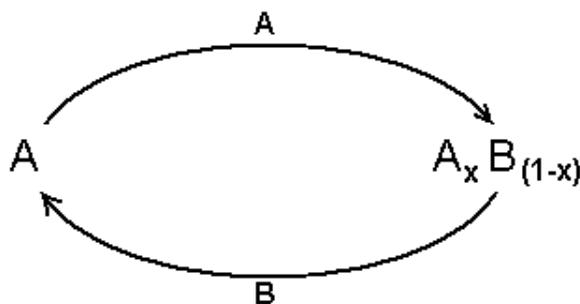
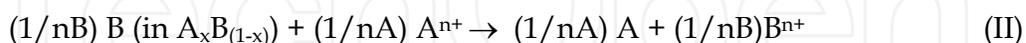
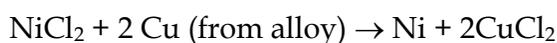
### 5.1 Choice of different types of halides as the electrolyte

It is possible to use different types of halides as the electrolyte: chlorides, bromides and iodides. All these salts are hygroscopic and their treatment by the corresponding hydrogen halide (HCl, HBr, HI) is necessary to avoid water marks. If one type of halide unsuitable due to the exchange reaction, it can be replaced by another.

For the study of the Ni-Cu (Geyderih et al. 1969), measurements of EMF were made from two reference electrodes



In both cases there is a reduction of the second metal; the electrodes of pure metals are covered with crystals of the second metal. So, there are two oxidoreduction reactions:



The replacement of the chloride on iodide electrolyte permits to determine the thermodynamics of the Cu-Ni system.

(-) Cu(sol.) | KI + NaI + CuI | Cu<sub>x</sub>Ni<sub>1-x</sub> (sol.) (+) This experiment have made possible to formulate an empiric rule:

By working with electrochemical cells without separation of electrodes, enthalpy of formation ( $\Delta_f H$ ) salt of the metal B must not exceed 75% of enthalpy of formation of metal salt A (Geyderih et al. 1969).

As the equilibrium constant of the reaction  $K_p$  (II) has a finite value, there will be always an exchange reaction, even partial, between the salt ions  $A^{n+}$  and alloy  $A_xB_{(1-x)}$ . The authors have attempted to assess the relative error in determining the activity of the less noble metal by the EMF method based on constant exchange reaction (II) (Wagner & Werner, 1963). Simplified equation, admitting a relative error, expressed by the expression:

$$\textcircled{R} = (n_B/n_A) (Y^\circ/Y_A) (n_A/n_B) (1/x) (1 + (n_A/n_B)) (D^\circ/D)^{1/2} (V'_m/V''_m) \exp(-(n_B E^\circ F)/RT) \quad (12)$$

where  $Y_A$  is the coefficient activity of component A, and  $Y^\circ$  is the molar salt fraction of component A in the melt.

$D^\circ$  and  $D$  are the diffusion coefficients of salt  $BX_n$  in the electrolyte and the component A in the alloy respectively,

$E^\circ$  is difference of the reference potentials of the components,

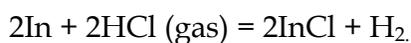
$V'_m$  and  $V''_m$  molar volumes of alloy and electrolyte.

In the formula (12) we can see:

1. that the error is maximum for the minimum concentration of component A,
2. that the higher is potential difference of the electrodes the smaller is the relative error,
3. that increasing of the salt concentration  $AX_n$  causes the increase of error  $\textcircled{R}$ , nevertheless, too small concentration may give a relative error greater than the reaction (II). The optimal concentration of salt in the molten electrolyte  $AX_n$ , according to Wagner, is 1 - 3%

In concordance to our experience, the concentration of  $AX_n$  salt in liquid electrolytes must not exceed 0.1%. In some cases, this concentration can be reduced if the salt  $AX_n$  is slightly soluble in the electrolyte.

If there is a problem of chemical stability or hygroscopicity  $AX_n$  of certain salts (e.g. as the indium chloride or zinc chloride) we can do forming potential without salt. Synthesis of indium monochloride (InCl) is carried out inside the cell by the interaction of hydrogen chloride absorbed by the electrolyte, with metallic indium:



Contact of indium monochloride (InCl) with moist air provokes the formation of indium ions with different valence states:  $\text{InCl} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{In(OH)Cl}_2 + \text{In(OH)}_2\text{Cl} + \text{In(OH)Cl} + \text{InOCl} + \dots$ ,

that leads to the exchange reaction between the electrodes of electrochemical cell.

## 5.2 Exchange reactions

The interaction between the electrodes via the electrolyte is one of the most important problems. In the electrolyte, the A and B elements are characterized by different potentials against a reference electrode (Hladik, 1972). We must choose an electrolyte which causes a potential difference of A and B as large as possible. The more the difference is between of the electrode potentials, the smaller is the exchange reaction between the component B and the  $A^{n+}$  ions in the melted electrolyte. Information about a possible exchange reaction between electrodes can be found from the electrode potentials for different halide melts (Hladik, 1972). This set of the chemical potentials characterizes activity of metals against each other for the system in study for giving electrolyte. The more metal is electronegative the more it is chemically active. In particular, in the set of the electrochemical potentials each metal replaces in an electrolyte all metals with lower potential. And, in turn, it will be replaced in the same electrolyte by metals with greater potential. So, the metal with the most negative potential, in the given electrolyte, replaces all those with more positive potentials. If we study the binary system Zn-Sb or In-Sb by the potentiometric method we do not see any problem of exchange reactions. So we can note that if the difference of the electrochemical potential reaches 0.4 V, the exchange reactions do not exist. And opposite, this problem appears for the systems Zn-In and In-Sn if the difference of the electrochemical potential is 0.19 V.

If we study the cells of the type:



the exchange reactions take place easily when the concentration of the second element has reached 90%. The continuous drop of the EMF of the cells with alloys  $x \leq 0.1$  is observed if the duration of the experiment is over several weeks (Vassiliev et al., 1998b; Mozer, 1972). The rate of the exchange reaction increases with increasing temperature especially in liquid systems. The speed of the exchange reaction depends on:

1. the difference of electrochemical potentials of the elements,
2. the difference in alloy composition,
3. the presence of metal ions of different charges ( $A^{(n+)}$  et  $A^{(m+)}$  ;  $m+ > n+$ ) in the electrolyte,
4. the temperature in the cell.

This set of electrochemical potentials characterizes the chemical activity of metals against each other under consideration system and a given electrolyte. The more metal is electronegative the more this metal is chemically active. Especially, in the set of the electrochemical potentials each metal replaces in the electrolytes of all metals with inferior potential. In turn, it was replaced in the same electrolyte by metals with superior potential. If the data for the electrode potentials are incomplete, it is possible to judge about the relative chemical activity of two elements by comparing the Gibbs energies or enthalpy of formation of salts  $AX_n$  and  $BX_n$  (X being the corresponding a salt anion). See Table 4 bottom. We will consider some binary systems based on elements of Table 2 and 3.

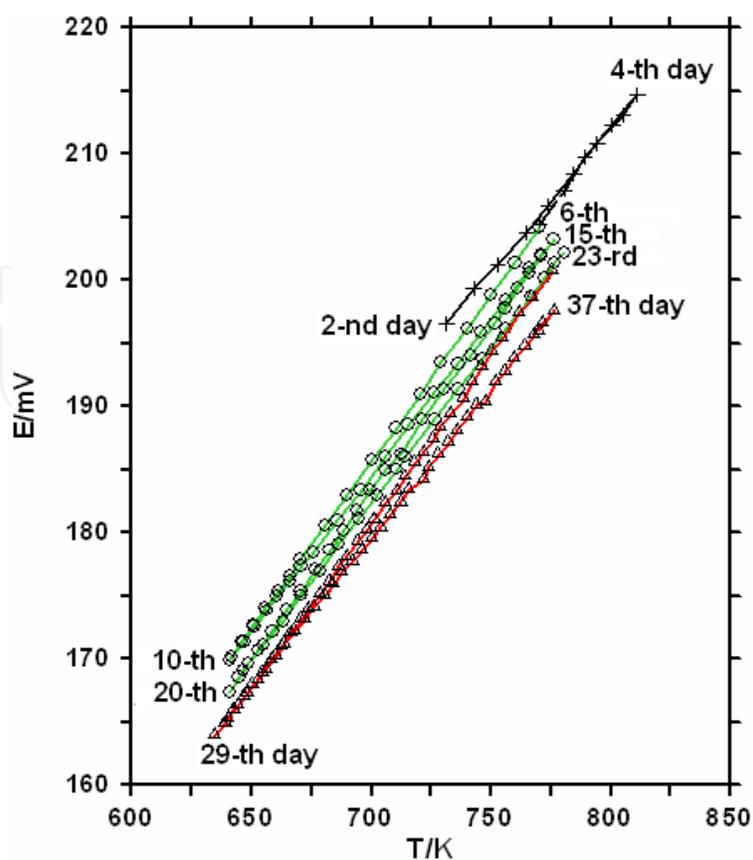


Fig. 14. Effect of exchange reaction between pure indium and its alloy  $\text{In}_{0.05}\text{Sn}_{0.95}$  on the EMF measures as a function of temperature and time experience in the cell  $(-) \text{In} | \text{In}^+$  in electrolyte  $| \text{In}_x\text{Sn}_{1-x}$  (+) (- o -) - used points (-+- and -Δ-) - unused points.

Electrochemical system		$\phi / \text{V}$			
		450°C	700°C	800°C	1000°C
$\text{Li}^+$	Li	- 3.684	- 3.514	- 3.457	- 3.352
$\text{Na}^+$	Na	- 3.566	- 3.332	- 3.250	- 3.019
$\text{La}^{3+}$	La	- 3.241	- 3.016	- 2.997	- 2.876
$\text{Ce}^{3+}$	Ce	- 3.193	- 3.014	- 2.945	- 2.821
$\text{Nd}^{3+}$	Nd	- 3.103	-	- 2.856	- 2.736
$\text{Gd}^{3+}$	Gd	- 3.013	-	- 2.807	- 2.709
$\text{Mg}^{2+}$	Mg	- 2.720	- 2.536	- 2.460	- 2.346
$\text{Sc}^{3+}$	Sc	- 2.621	- 2.455	- 2.375	- 2.264
$\text{U}^{3+}$	U	- 2.530	- 2.350	- 2.280	- 2.162
$\text{Be}^{2+}$	Be	- 2.167	-	-	-
$\text{Al}^{3+}$	Al	- 2.018	-	-	-
$\text{Mn}^{2+}$	Mn	- 1.999	- 1.854	- 1.807	- 1.725
$\text{V}^{2+}$	V	- 1.794	- 1.794	- 1.636	- 1.441
$\text{Zn}^{2+}$	Zn	- 1.629	- 1.512	- 1.476	
$\text{Tl}^+$	Tl	- 1.629	- 1.512	- 1.473	
$\text{Cd}^{2+}$	Cd	- 1.442	- 1.262	- 1.193	- 1.002
$\text{In}^+$	In	- 1.43	-	-	-
$\text{Cr}^{3+}$	Cr	- 1.374	-	- 1.113	- 1.006
$\text{Sn}^{2+}$	Sn	- 1.34	- 1.264	- 1.259	

Electrochemical system		$\phi/V$			
		450°C	700°C	800°C	1000°C
Pb <sup>2+</sup>	Pb	-1.30	-1.163	-1.112	-1.039
Fe <sup>2+</sup>	Fe	-1.297	-	-1.118	-1.050
Co <sup>2+</sup>	Co	-1.171	-1.028	-0.977	-0.900
Ni <sup>2+</sup>	Ni	-1.104	-0.939	-0.875	-0.763
Sb <sup>3+</sup>	Sb	-1.019 (300°C)	-	-	-
Cu <sup>+</sup>	Cu	-1.035	-0.987	-0.970	-0.943
Ag <sup>+</sup>	Ag	-0.911	-0.848	-0.826	-0.784
Bi <sup>3+</sup>	Bi	-0.844	-0.817	-	-
Pd <sup>2+</sup>	Pd	-0.487	-0.487	-0.340	-0.285
Pt <sup>2+</sup>	Pt	-0.299	-0.180	-	-
Au <sup>+</sup>	Au	+0.223	-	-	-

Table 2. Calculated electrochemical potential ( $\phi_{Cl_2/Cl^-}$ ) in individual molten chlorides, calculated from thermodynamic data.

Electrochemical system		$\phi/V$ for the anions in Volt			
		F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>
Ba <sup>2+</sup>	Ba	-1.31	-2.59	-2.62	
K <sup>+</sup>	K	-0.62	-2.50	-2.53	-1.98
Sr <sup>2+</sup>	Sr	-1.16	-2.51	-2.41	-1.94
Li <sup>+</sup>	Li	-0.08	-2.39	-2.40	-1.95
Na <sup>+</sup>	Na	-1.84	-2.36	-2.35	-1.81
Ca <sup>2+</sup>	Ca	-1.13	-2.35	-2.25	-1.53
Mg <sup>2+</sup>	Mg	-0.28	-1.58	-1.58	-1.01
Mn <sup>2+</sup>	Mn	-0.17	-0.85	-0.83	-0.44
Zn <sup>2+</sup>	Zn	-1.09	-0.40	-0.50	-0.27
Cd <sup>2+</sup>	Cd	-0.91	-0.25	-0.46	-0.19
Tl <sup>+</sup>	Tl		-0.44	-0.29	-0.41
<b>Sn<sup>2+</sup></b>	<b>Sn</b>	-	<b>-1.270</b>	-0.981	<b>-0.462</b>
<b>Pb<sup>2+</sup></b>	<b>Pb</b>	-	<b>-1.215</b>	-0.976	<b>-0.620</b>
Cu <sup>+</sup>	Cu	+1.37	+0.29	-0.06	-0.17
Co <sup>2+</sup>	Co	+0.52	+0.06	-0.05	+0.43
2H <sup>+</sup>	H <sub>2</sub>	0	0	0	0
Bi <sup>3+</sup>	Bi	-0.14	+0.39	+1.19	+0.33

Table 3. Electrochemical potential of metals in molten liquid halides at the temperature 700°C compared with reference electrode  $\phi_{H_2}$ .

Electrochemical system		$\phi/V$	
		T=300°C	T=500°C
Zn <sup>2+</sup>	Zn	1.706	1.603
In <sup>+</sup>	In	1.520	1.414
Sn <sup>2+</sup>	Sn	1.428	1.320
Pb <sup>2+</sup>	Pb	1.420	1.271
Sb <sup>3+</sup>	Sb	1.019	-

Table 4. Comparison of certain electrochemical potentials of metals in molten liquid chloride.

So, if we study the electrochemical cell of the type:



the exchange reactions occur readily in these systems if the concentration of the second element has reached 90% (Fig.14). We observed a continuous fall of the EMF for alloys with  $x \leq 0.1$  when the duration of the experiment was a few weeks (Vassiliev et al., 1998b; Mozer, 1972). The rate of the exchange reaction was augmented with increasing temperature, especially in the case of liquid systems.

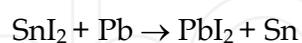
### 5.3 Influence of a third component on the exchange reaction

Exchange reactions occur not only between a pure A metal and alloy  $A_xB_{(1-x)}$  but also between alloys of different compositions, if the activities  $a_A$  of them are very different. This phenomenon is very pronounced in the liquid ternary system In-Sn-Sb (Vassiliev, 1998). Table 4 shows that the attraction between atoms In and Sb is greater than between In and Sn or between Sn and Sb. Accordingly, the tin atoms of the ternary alloy are very free, and exchange reactions between electrodes of different compositions of alloys, with indium, occur easily.

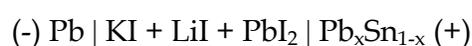
### 5.4 Selection of different types of halides such as electrolytes

It is possible to use different halides such as electrolytes: chlorides, bromides and iodides. All these salts are hygroscopic and their treatment by the corresponding hydrogen halide (HCl, HBr, HI) is needed to avoid water marks. If some halogenade is not appropriate due to an exchange reaction it is replaced by another.

The choice of the electrolyte is determined by its melting temperature and by the need to minimize the exchange reaction. The study of Sn-Pb system is not possible in molten chlorides (the difference of potential electrodes is 0.05 V at 500°C ; Table 4). The substitution of chloride by iodide significantly increases this difference to 0.168 V (see Tabl.3) and decreases the exchange reactions:



Although it is impossible to eliminate their influence completely, especially for tin-rich alloys, the electrochemical chain:



can be studied.

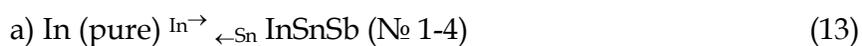
### 5.5 Effect of exchange reaction on the EMF measurements in ternary system In-Sn-Sb

Let us consider the example of spontaneous exchange reaction in the cell that contains the series of four alloys with low indium content, number 1-4, ( $x_{\text{In}}$  from 0.05 to 0.11), and one indium-rich alloy № 5 ( $x_{\text{In}}=0.5$ ) at presence of two electrodes of pure indium. (See Table 5)

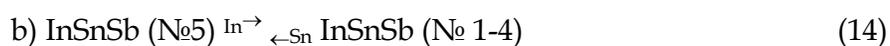
No	$x_{In}$	$x_{Sn}$	$x_{Sb}$
1	0.0500	0.4751	0.4749
2	0.0503	0.4497	0.5000
3	0.1002	0.3996	0.5003
4	0.1112	0.4444	0.4444
5	0.5000	0.2499	0.2501

Table 5. Composition of In-Sn-Sb alloys used for detection of kinetic of spontaneous exchange reaction in the electrochemical cell.

We can state that the measured values  $E(T, x_{In})$  for alloys with number 1-4, and slightly for number 5, are exposed to such reactions. So, we used only the first points of the measurements  $E(T, x_{In})$ , which were less susceptible to this influence. Exchange reaction is more pronounced for alloy 1 and 2. Dynamics of a regular drift of EMF values for alloys № 2 and 5 versus time and temperature were shown in Fig. 15 and Fig. 16. Experimental points are divided into two series. The gap of EMF values between two series is connected with the study of other phases at lower temperatures are not indicated in Fig. 15 and 16. We took in consideration only the black dots. The different stages of the experiment are marked in time. Fig. 15 and 16 show that the exchange reaction depends on the time and temperature. Two main types of exchange reactions (*a* and *b*) take place in cell:



$$a_{In}=1 \quad a'_{In}<1$$



$$a''_{In} > a'_{In}$$

Reactions *a* and *b* lead to a decrease of the EMF values for alloys (№№ 1-4) and the reaction of *b* increases the EMF values of the alloy number 5 in relation to the reference electrode made of pure indium. The rate of exchange reaction prevails over the reaction (13) and (14). Kinetics of exchange reactions is shown in Fig. 17 and Fig.18 in accordance with 4 passes at the same temperature 755K versus the time. We did not observe exchange reactions for alloys with  $x_{In} > 0.1$ , although the duration of the experiment exceeded more than two months, the maximum temperature reached 822K.

### 5.6 Issues are related to the valence of $A^{n+}$ ion

To obtain good experimental results, it is necessary to know rigorously the ion charge that is responsible for the EMF in cell of type (I). However, the difference in activities of pure metal A and alloy  $A_xB_{(1-x)}$  can lead to different charges of the  $A^{n+}$  ion in the vicinity of the electrodes A and  $A_xB_{(1-x)}$ . In this case, even in open circuit, a spontaneous transfer of component A to alloys  $A_xB_{(1-x)}$  is possible and a constant drift of the EMF occurs over time.

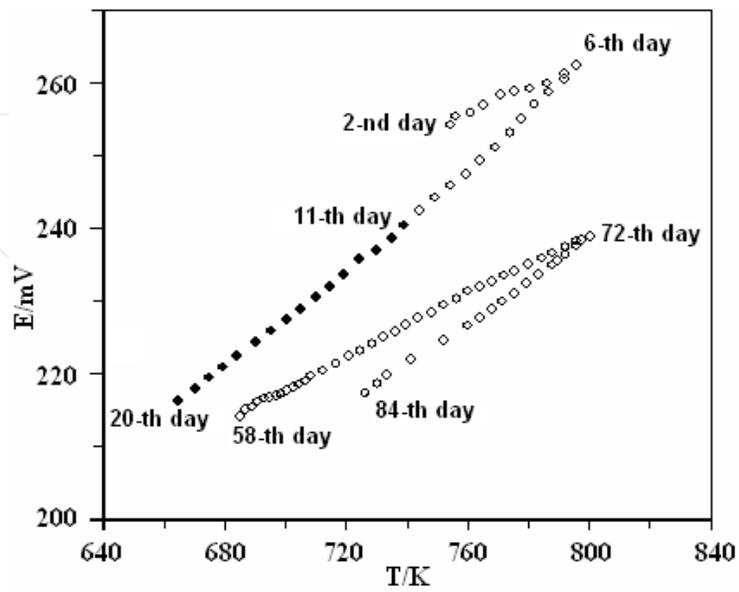


Fig. 15. EMF of alloy number 2 versus temperature and time.

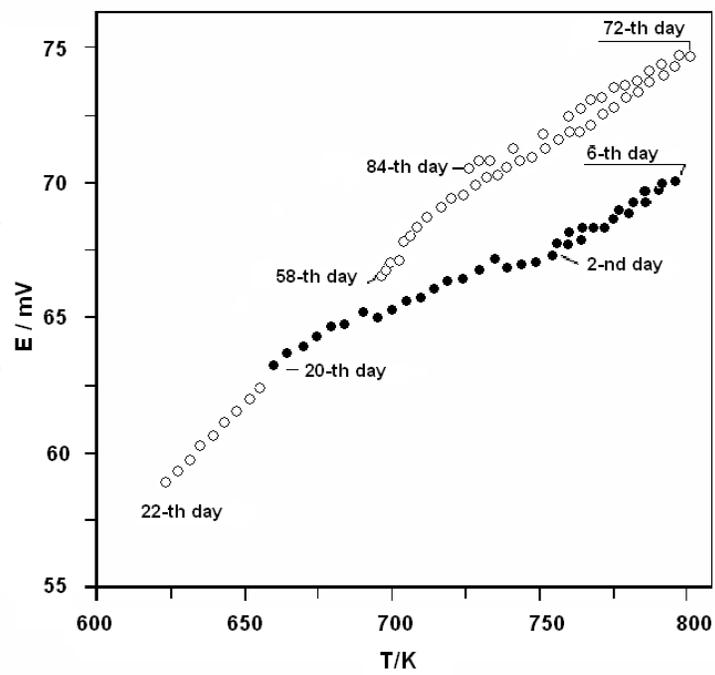


Fig. 16. EMF of alloy number 5 versus temperature and time.

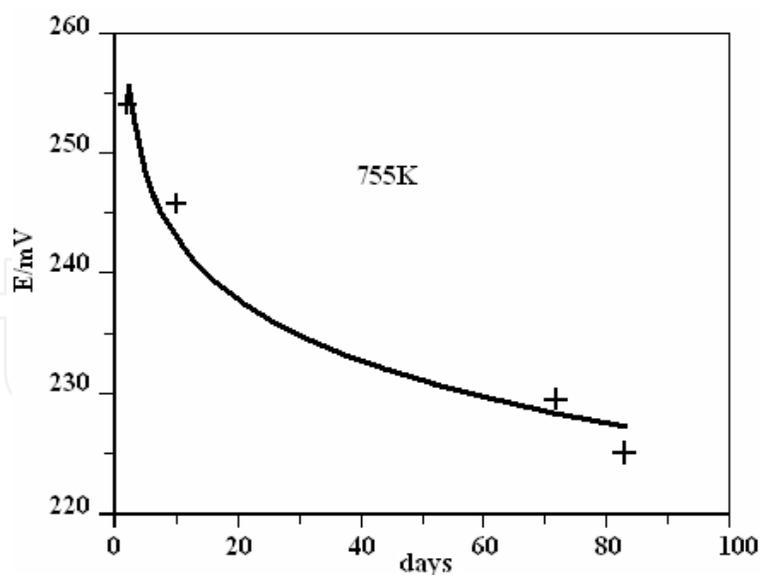


Fig. 17. Kinetics of the exchange reaction of the alloy number 2 at the T=755K.

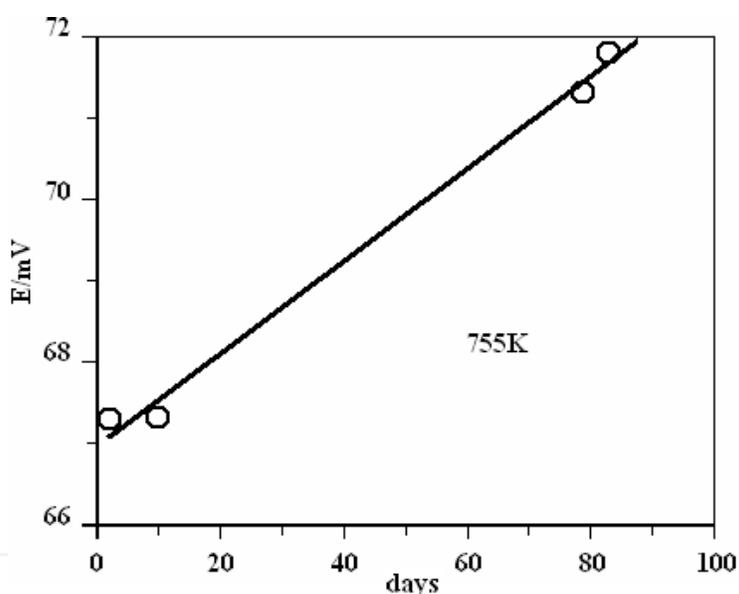


Fig. 18. Kinetics of the exchange reaction of the alloy number 5 at T=755K.

This relates to the ions of metal that may have the different charges of ions ( $m > n$ ) in different parts of cell in electrolyte:



So, in the case of open circuit, there is a transfer of component A from pure metal to its alloy  $A_xB_{(1-x)}$ . Near the cathode, the fraction of charged ions ( $n+$ ) will be greater and near anode around of the alloy  $A_xB_{(1-x)}$  will be smaller. In another words, there is dissolution of pure metal and deposit on the surface of alloy  $A_xB_{(1-x)}$ . The transfer is even faster than the temperature T and the concentration of  $A^{m+}$  ions is higher and the distance between electrodes is smaller. A metal is transferred through an electrolyte by ions of lower charge.

If an activity of component A in the cell of type (I) is reduced, it is possible to determine the thermodynamic properties even in cases of spontaneous transfer of the component A. In this case, it is necessary to take as reference electrode some electrode binary alloy  $A_xC_{(1-x)}$ , which the thermodynamic properties are well known, and it can substitute the pure metal A.

Then we have

$$\Delta\mu_A = RT \cdot \ln ( a'' / a' ) \quad (15)$$

In this case the activity ( $a'$ ) is less than 1. The difference of the chemical potential of component A between electrodes, and hence, the electromotive force will be smaller.

This problem is encountered when the system Ln -Te (Ln = lanthanide) was studied with the cell:



$$\Delta\mu_A = RT \cdot \ln \left( a_A^{A_xB_{(1-x)}} / a_A^{A_xC_{(1-x)}} \right)$$

Alloys, rich in metal B (in this case by tellurium) generate an electromotive force E near 1.5 V. The substitution of the lanthanide by one of its alloys of Ln-In system (Vassiliev et al., 2009), allows to make the measurements with the following electrochemical cell:

$$a_A^{A_xC_{(1-x)}} < a_A^{(A)} = 1$$



The electromotive force of the cell is as twice as smaller and spontaneous transfer becomes negligible.

### 5.7 Problem of liquation (or phase separation) of liquid alloys

If the metal liquid system does not contain any components that provoke the exchange reactions in an electrochemical cell, the EMF method is well suited for such a system. The problem of liquation (or phase separation) is less serious, but the big difference of the specific density of alloying effects on the rate of establishment of thermodynamic equilibrium and distorts the potentiometric measurements.

Element	Specific density (g/cm <sup>3</sup> )	Element	Specific density (g/cm <sup>3</sup> )
Al	2.7	Cu	8.94
Sn	5.85	Bi	9.80
Zn	7.13	Ag	10.50
In	7.31	Pb	11.34

Table 6. Specific density (g/cm<sup>3</sup>) of some metals.

The more the difference of the specific density of elements and their chemical interaction are weaker, the liquation influence is greater. As a consequence, the EMF measurements do not

correspond to thermodynamic equilibrium, because the surface of alloy is depleted by the elements of the smaller density. Especially it should be taken into account that the metallic systems with a miscibility gap. Table 6 shows the specific density of some metals. The liquation problem was noted by us in the investigation of systems based on ternary zinc-lead alloys (Zn-Pb-Sn, Zn-Pb-In) (David et al., 2004) and In-Sn-Ag and In-Bi-Ag (Vassiliev et al., 1998c). We observed hysteresis loops during heating and cooling of the cells in a wide temperature range for a number of alloys. In the case of the hysteresis loop, it is necessary to choose measurement results only when the temperature is lowered, starting from the homogeneous liquid region. The isothermal cell is also well suited for the thermodynamic study of metals with high vapor pressure (mercury, zinc, etc.) (Vassiliev et al., 1990; David et al., 2004). We did not observe any evaporation of zinc, even though long-term measurements (more than two months and the temperature to 780 K) were taken.

In the systems based on zinc, the latter serves as the reference electrode and the part of both the internal calibration of the thermocouple in the cell, because the measured values  $E(T)$  give a clear kink at the melting point of zinc. The kinetic curve of solidification or melting of the metal also exhibits a characteristic jump EMF at the melting point. Such curve is easily obtained by continuous measurement of the EMF of the cell at the phase transition  $\text{sol} \rightleftharpoons \text{liq}$ . The zinc chloride must not be added to electrolyte previously. We found that the ions, forming the potential, appeared in a few hours inside the cell after the experiment began. We used the metals of 99.999% and chlorides of lithium and potassium 99.99% purity. The type of electrochemical cell for EMF measuring has been used:



Temperature range of research is limited on one hand by the crystallization of the electrolyte, and on the other hand by the softening Pyrex glass. Control of the state reference electrodes of pure zinc in the course of the experiment was carried out by measuring the difference of EMF between such electrodes. If the cell functions normally, this difference is about 5  $\mu\text{V}$ . Temperature correction is performed by the melting point of zinc, located in the cell.

### 5.8 How to study the systems with closely spaced electrode potentials. The EMF measurements of ternary Pb-Sn-Sb system

EMF measurements of the ternary system Pb-Sn-Sb (Vassiliev et al., 1995) were carried out for five alloys along the isopleth (Pb-Sn<sub>0.5</sub>Sb<sub>0.5</sub>) with  $x_{\text{Pb}} = 0.15, 0.20, 0.25, 0.30, 0.333$  at temperatures 690 - 820K. Alloy Sn<sub>0.5</sub>Sb<sub>0.5</sub> has been used as a reference electrode. Scheme for EMF measuring and the definition of excess functions of mixing in the ternary system Pb-Sn-Sb are shown in Fig. 19 and 20. To measure the EMF we can not use the alloys of the ternary Pb-Sn-Sb system as reference electrodes from pure metals. The using of tin or lead in a cell with undivided space is impossible, because their electrode potentials are almost equal and the exchange reactions take place. Cell with a diaphragm (Shourov, 1974, 1984) allows solving this problem, but the experiment is very laborious. In order to avoid the exchange reaction, we choose an alloy of tin and antimony with a component ratio 1:1 (Sn<sub>0.5</sub>Sb<sub>0.5</sub>) as the reference electrode, which chemical potential we studied in this paper using an isothermal cell without diaphragm. Activity of tin  $a_{\text{Sn}}$  in the Sn<sub>0.5</sub>Sb<sub>0.5</sub> alloy at 900K is equal 0.41, that is much less than its activity in pure tin ( $a_{\text{Sn}}=1$ ). So, the activity of lead becomes comparable with the activity of tin when we study the ternary alloys (Sn<sub>0.5</sub>Sb<sub>0.5</sub>)<sub>1-x</sub>Pb<sub>x</sub>. Thus,

we have practically eliminated the exchange reaction between the electrodes with different contents of tin and lead. The choice of electrode  $\text{Sn}_{0.5}\text{Sb}_{0.5}$  allowed us to obtain stable and reproducible results  $E(T)$  (Fig.21).

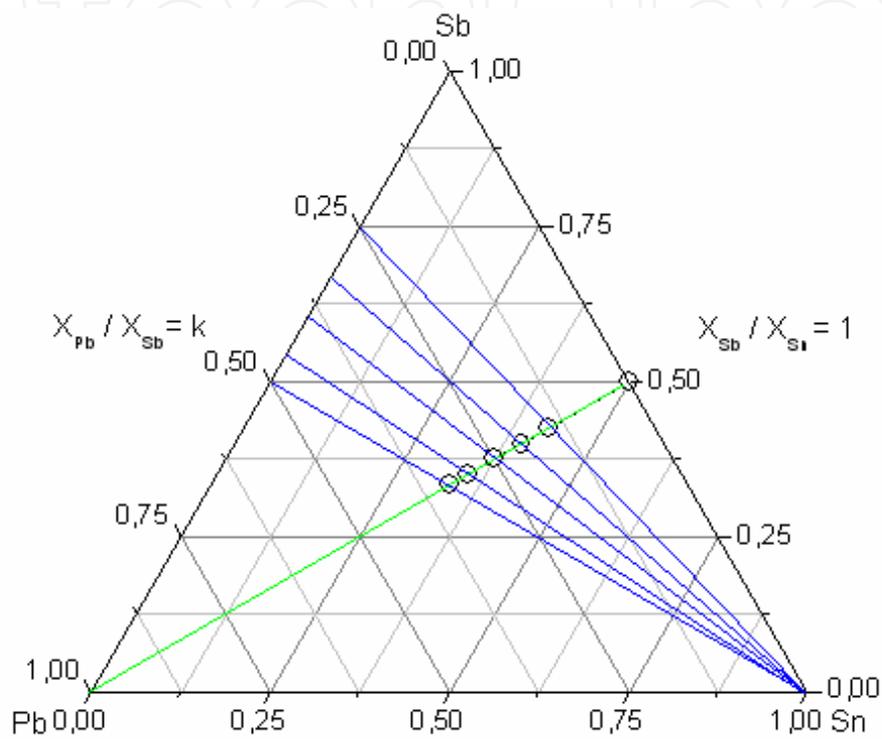


Fig. 19. Measurements of EMF ( $\mu_{\text{Sn}}^E$ ) in the ternary Pb-Sn-Sb system.

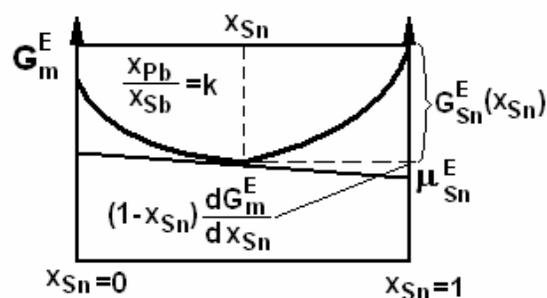


Fig. 20. Scheme for determining the excess functions of mixing of the ternary Pb-Sn-Sb system.

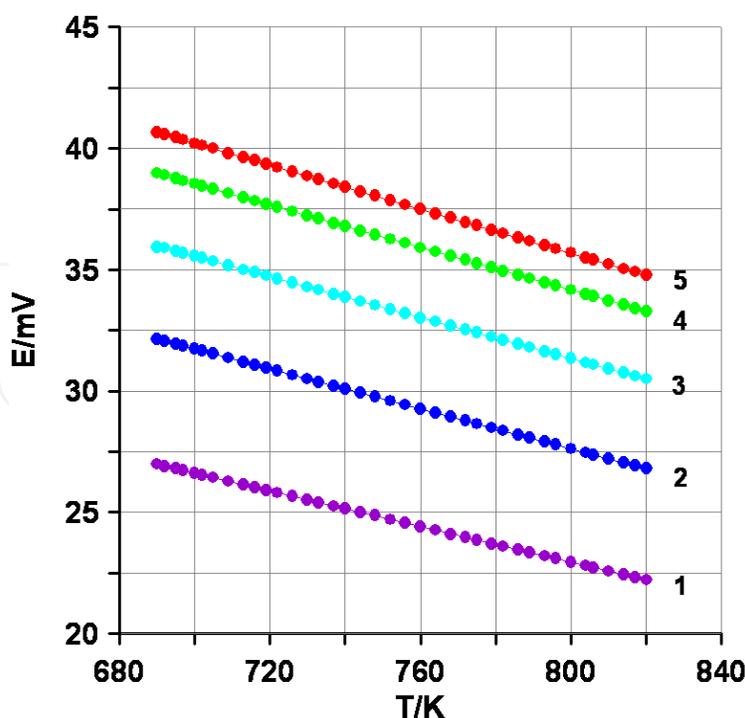


Fig. 21. Dependence  $E(T)$  cell and compositions of alloys  $(-)Sn_{0.5}Sb_{0.5} | KCl+LiCl+Sn^{2+} | (Sn_{0.5}Sb_{0.5})_{1-x}Pb_x(+)$  1- $(Sn_{0.5}Sb_{0.5})_{0.666}Pb_{0.333}$ , 2-  $(Sn_{0.5}Sb_{0.5})_{0.70}Pb_{0.30}$ , 3-  $(Sn_{0.5}Sb_{0.5})_{0.75}Pb_{0.25}$ , 4-  $(Sn_{0.5}Sb_{0.5})_{0.80}Pb_{0.20}$ , 5-  $(Sn_{0.5}Sb_{0.5})_{0.85}Pb_{0.15}$

There were obtained 39 experimental points  $E(T)$  for each ternary alloy with a maximum error  $\pm 0.1$  mV. The coefficients of linear equations  $E_1(T)$  of ternary alloys (1-5) was obtained with respect to the reference electrode  $Sn_{0.5}Sb_{0.5}$ . The correction was performed using the ratio (16) to find the chemical potential of ternary alloys relatively to pure tin:

$$\mu_{Sn} = E_1(T) + E_2(T) \quad (16)$$

Where the dependence  $E_2(T)$  ( $E_2/mV = 10.52 + 26.5 \cdot 10^{-3} \cdot T$ ) was obtained between the liquid alloy  $Sn_{0.5}Sb_{0.5}$  and the reference electrode from pure tin.

### 5.9 Pb-Pd system

Finally, let us consider an example of the Pb-Pd phase diagram that has several intermediate phases Fig.22 (Vassiliev et al., 1998a). We have established a narrow region of homogeneity of the phases  $Pb_2Pd$  and  $Pb_9Pd_{13}$ , and the deviation from stoichiometry of  $PbPd$  phase. We have determined also the coordinates of the gamma phase, and refined the melting point of  $Pb_2Pd$  phase and the coordinates of the eutectic point.

General trend of experimental EMF results versus temperature and composition for the Pb-Pd system is shown in the Fig.23. The points at the right of curves L2-L6 correspond to the homogeneous liquid alloys with  $x_{Pd}$  from 0.10 to 0.60). The curves L2-L6 correspond to the heterogeneous alloys (liquid and solid states). The lines at the left of the curves L<sub>2</sub>-L<sub>6</sub> correspond to the heterogeneous solid alloys from S<sub>2</sub> to S<sub>8</sub> (see, please, Fig.23). Monophasic supercooled liquid alloys are on the left of lines L<sub>2</sub>-L<sub>4</sub> with  $x_{Pd}$  from 0.25 to 0.40. Points of intersections of the lines S<sub>5</sub> and S<sub>8</sub>, S<sub>2</sub> and S<sub>7</sub>, S<sub>4</sub> and S<sub>6</sub> correspond to the phase

transformations in solid state. Line S'1 corresponds to solid solution on the base of  $Pb_2Pd$  phase. Points of intersections of the lines  $S_i$  with curves  $L_i$  correspond to the eutectic or peritectic transformations. Points of intersections of the  $E(T)$  for liquid homogeneous region with curves  $L_2-L_6$  correspond to the points of liquidus. Invariants points ( $T_e = 721K$  and  $T_m(Pb_2Pd) = 725K$ ) were shown in the Fig.22 and 23.

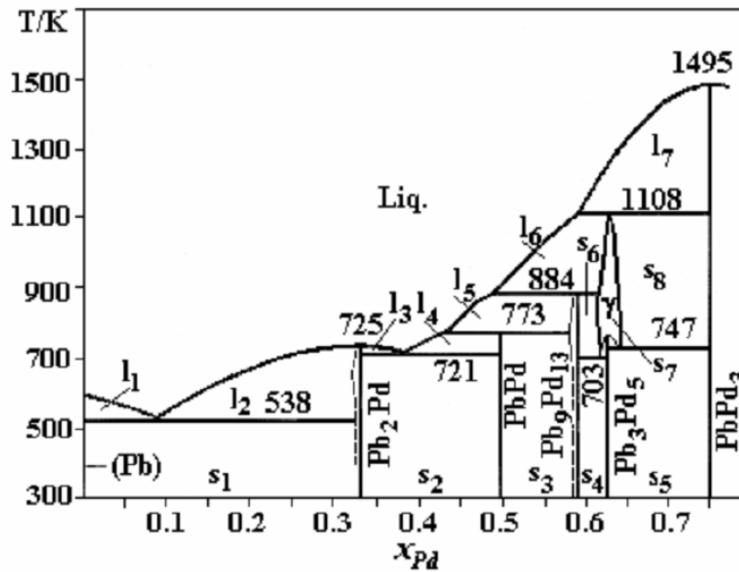


Fig. 22. Equilibrium phase diagram of the palladium-lead with our corrections.

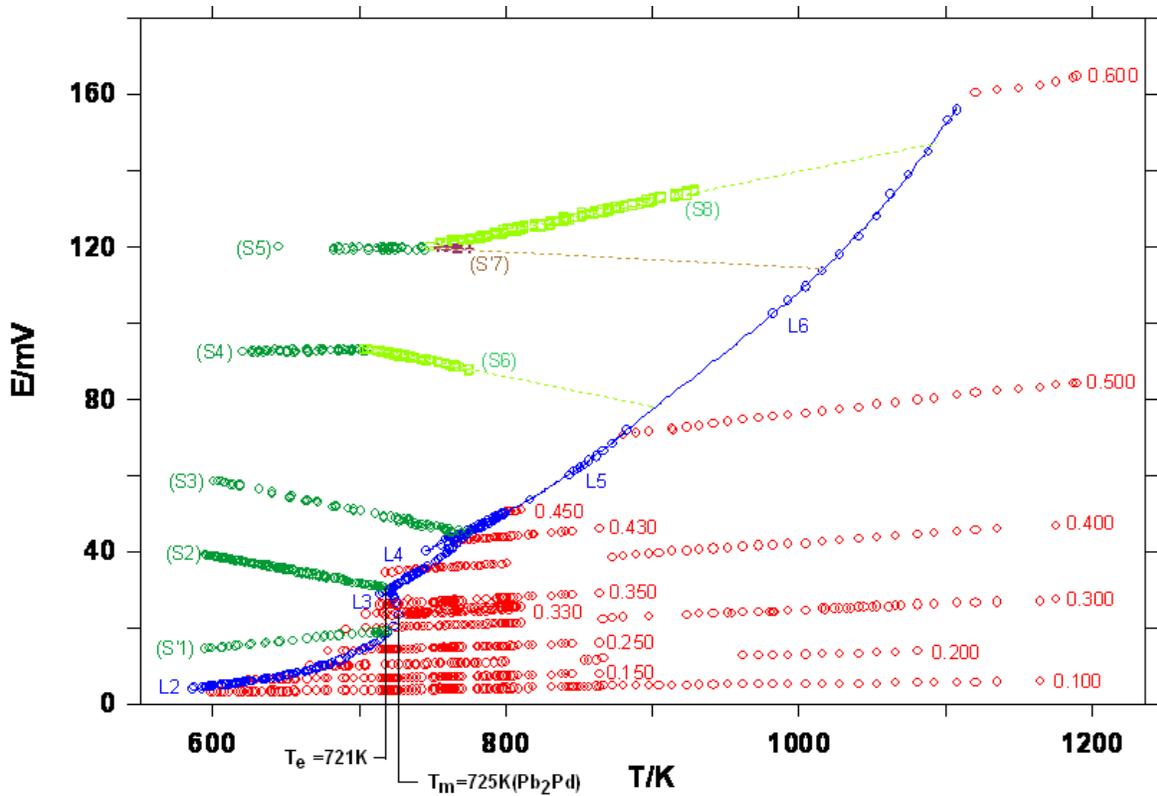


Fig. 23. General trend of experimental EMF results versus temperature and composition for the Pb-Pd system.

We applied successfully the described technique for different binary, ternary and quaternary systems:

Tl-S (Vassiliev et al., 1971,1973a, 1973b, 2008), Tl-Se (Vassiliev et al., 1967,1969,1971), Tl-Te (Vassiliev et al., 1968); Cd-Te (Vassiliev et al., 1990); **Pb-Pd** (Vassiliev et al., 1998a); In-P (Vassiliev & Gachon, 2006); In-As (Abbasov et al., 1964); In-Sb (Vassiliev, 2004); In-Sn (Vassiliev et al., 1998b); Ga-As (Abbasov et al., 1964); Ga-Sb (Abbasov et al., 1964); Sn-Sb (Vassiliev 1997, 2005); Bi-Se (Vassiliev et al., 1968); Ga-Te (Abbasov et al., 1964); Mn-Te (Vassiliev et al., 1993); Rare Earth Metals (REM) with In (Vassiliev et al., 2009), Sb (Gorjacheva et al.,1981), Pb (Vassiliev et al., 1993), Te (Vassiliev et al., 1980); Cd-Hg-Te (Vassiliev et al., 1990,2004); In-Sn-Sb (Vassiliev et al., 2001); **Pb-Sn-Sb** (Vassiliev et al., 1995); Pb-Sn-Zn (David et al., 2004) In-Bi-Ag (Vassiliev et al., 1998c); In-Ni-Sb (Vassiliev et al., 2003); Pb-Cu-Zn; Pb-In-Zn; Pb-In-Zn-Sn (Hertz et al., 1998). As well as, this technic can be applied for the oxide systems also.

## 6. Conclusion

The accuracy of the proposed experimental technique does not yield the best calorimetric measurements and completeness of the information obtained by the EMF exceeds the calorimetric methods in some case. So, the proposed variant of the EMF can be called as universal and self-sufficient, and the cost of equipment used in the EMF method is much lower than the calorimetric one. EMF remains one of the most important methods in metallurgical thermodynamics. The method of electromotive force (EMF) with proposed electrochemical cells is a powerful tool to study the thermodynamic properties of metallic, semiconductor and oxide systems. It permits to identify a set of values of the chemical potentials of one of the component of the different phases. The final result of this work consist of the thermodynamic optimization of the studied system.

## 7. Acknowledgements

This work was financially supported by the Russian Foundation for Basic Research, project **11-08-01154** as well as the Talents Project of Guangdong Province, Guangdong, P.R. China. We would like to thank Dr. S. Kulinich for helpful discussion.

## 8. References

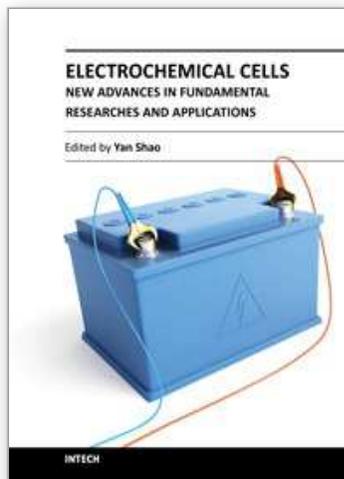
- Abbasov A.S., Nikoliskaja A.V., Gerassimov Ja.I., Vassiliev V.P. (1964) The thermodynamic properties of gallium antimonide investigated by the electromotive force method. Dokl. AN SSSR, Vol.156, No.6, pp.1399-1402. (in Russian)
- Abbasov A.S., Nikoliskaja A.V., Gerassimov Ja.I., Vassiliev V.P. (1964) The thermodynamic properties of indium arsenide investigated by the electromotive force method. Dokl. AN SSSR, Vol.156, No.1, p.118-121. (in Russian)
- Abbasov A.S., Nikoliskaja A.V., Gerassimov Ja.I., Vassiliev V.P. (1964) The thermodynamic properties of gallium tellurides investigated by the electromotive force method. Dokl. AN SSSR, Vol.156, No.5, pp.1140-1143. (in Russian)

- Abbasov A.S., Mamedov K.N., Nikoliskaja A.V., Gerassimov Ja.I., Vassiliev V.P. (1966) The thermodynamic properties of gallium arsenide investigated by means of electromotive forces. Dokl. AN SSSR, Vol.170, No.5, pp.1110-1113. (in Russian)
- Brauer G. (1954) Handbuch der Präparativchemie Anorganischen Chemie. Ferdinand Enke Chemie. Stuttgart.
- Chourov N.I. (1984) Institut of Electrochemistry, Science Center of Ural "Modification of electromotive forces method by the determination of thermodynamic properties in case of exchange reacton". Deposited document VINITI № 2422-84. (in Russian).
- David N., Vassiliev V., Hertz J., Fiorani J.M., Vilasi M. (2004) Measurements EMF and thermodynamic description of Pb-Sn-Zn liquid phase, Z. Metallkunde, Vol.95B, pp.1-8.
- Geyderih V.A., Nikolskaya A.V., Vasilyeva I.A., (1969) in book *Coedineniya peremennogo sostava»* pod red. Ormonta B.F., Izdatelstvo Himiya.-Leningrad, glava 4, 210-261. *Nonstoichiometric Compounds*, Edited by B.F. Ormont, Publishing House Chemistry, Leningrad, chapter 4, pp.210-261. (in Russian)
- Goryacheva V.I., Gerassimov Ja.I., Vassiliev V.P. (1981) Thermodynamic study of monoantimonides of holmium and erbium by EMF method. Vol.55, No.4, pp.1080-1083. (in Russian)
- Hertz J., Naguet Ch., Bourkba A., Fiorani J.M., Vassiliev V., Sauvanaud J. (1998) A strategy to establish an industrial thermodynamic data bank. The ternary (Pb, Sn, Zn) liquid phase in the zinc purification process. Extension to quaternary system (M, Pb, Sn, Zn). *Thermochim. Acta*, Vol.314, No.1-2, pp.55-68.
- Hladik J. (1972) *Physics of Electrolytes. Thermodynamics and Electrode Processing in Solid State Electrolytes*, Vol.2, Academic Press, London.
- Morachevsky A.G. (1987) *Thermodynamics of Molten Metal and Salt Systems*. Publisher "Metallurgy" Moscow. 1987. 240 C (in Russian)
- Morachevsky A.G., Voronin G.F., Geyderih V.A., Kutsenok I.B. (2003) "Electrochemical methods in the thermodynamics of metallic systems", Edition "Akademkniga", 334 p. (in Russian)
- Mozer Z. (1972) Thermodynamic studies of liquid Zn-In solution. *Metal. Transaction*, Vol.2, pp.2175-2183.
- Shourov N.I. (1974). Ph. Diss. Thesis in Physical Sciences "Potentiometric method for the study of thermodynamic properties of alloys whose components are electrochemically very close to each other. Sverdlovsk.
- Strikler H.S., Seltz H.A. (1936) Thermodynamic Study of the Lead-Bismuth System, Vol.58, pp.2084-2090.
- Terpilowski J., Zaleska E., Gawel W. (1965) Charakterystyka termodynamiczna układu stalego tal-tellur *Roczniki Chemii*. Vol.39, pp. 1367-1375.
- Vasil'ev V. P. (2004) Thermodynamic properties of alloys and phase equilibria in the In-Sb system. *Inorganic Materials* Vol.40, No.5, pp.524-529.
- Vasil'ev V.P. and Gachon J. C. (2006) Thermodynamic properties of InP. *Inorganic Materials*. Vol.42, No.11, pp.1171-1175.
- Vasil'ev V.P. (2005) A complex study of the phase diagram of Sn-Sb system *Rus.J Phys.Chem*. Vol.79, No.1, pp.26-35.

- Vassiliev V. P., Mamontov M. N., Bykov M. A. (1990). Thermodynamic properties and stability of solid solutions CdTe-HgTe-Te system, *Vestnik Moskovskogo Universiteta, serie2, Chemistry*, Vol. 31, No.3, pp. 211-218. (in Russian)
- Vassiliev V., Borzone G., Gambino M., Bros J.P. (2003) Thermodynamic properties of ternary system InSb-NiSb-Sb in the temperature range 640-860K. *Intermetallics*, Vol.11, pp.1211-1215.
- Vassiliev V., Lelaurain M., Hertz J. (1997) A new proposal for binary (Sn, Sb) phase diagram and its thermodynamic properties based on a new e.m.f. study. *J. Alloys Comp.*, Vol.247, p.223-233.
- Vassiliev V., Alaoui-Elbelgeti M., Zrineh A., Gambino M., Bros J.P. (1998) Thermodynamic of Ag-Bi-In system with  $0 < x_{Ag} < 0.5$ ) *J. Alloys Comp.*, Vol.265, pp.160-170.
- Vassiliev V., Azzaoui M., Hertz J. (1995) EMF study of ternary (Pb, Sn, Sb) liquid phase Z. *Metallkunde*, Vol. 86, pp.545-551.
- Vassiliev V., Bykov M., Gambino M., Bros J.P. (1993). Thermodynamic properties of the intermetallic compounds MnTe and MnTe<sub>2</sub>. *Z. Metallkunde*, Vol. 84, pp. 461-468.
- Vassiliev V., Feutelais Y., Sghaier M., Legendre B. (1998). Liquid State Electrochemical Study of the System Indium-Tin *Thermochim. Acta*, Vol.315, pp.129-134.
- Vassiliev V., Feutelais Y., Sghaier M., Legendre B., (2001) Thermodynamic Investigation in In-Sb, Sn-Sb and In-Sn-Sb liquid systems *J. Alloys Comp.*, Vol. 314, pp.197-205.
- Vassiliev V., Gambino M., Bros J.P., Borzone G., Cacciamani G., Ferro R. (1993) Thermodynamic investigation and optimisation of the Y-Pb alloys system. *J. Phase Equilibria*. Vol.14, No.2, pp.142-149.
- Vassiliev V., Voronin G.F., Borzone G., Mathon M., Gambino M., Bros J.P. (1998) Thermodynamics of the Pb-Pd system. *J. Alloys Comp.*, Vol. 269, Vol.123-132.
- Vassiliev V.P., Goryatcheva V.I., Gerassimov Ja.I. (1980) The phase equilibria and thermodynamic properties of solid alloys of erbium with tellurium. *Vestnik Moskovskogo Universiteta, serie 2, chimie*, 21, No 4, pp. 339-345. (in Russian)
- Vassiliev V.P., Goryacheva V.I., Gerassimov Ja.I., Lazareva T.S. (1980) A study of phase equilibrium and thermodynamic properties of solid alloys of erbium with tellurium. *Vest. Mosk. Univ. Ser.2. Chim.*, Vol.21, No.4, pp.339-345. (in Russian)
- Vassiliev V.P., Minaev V.S. (2008) Tl-S phase diagram, structure and thermodynamic properties. *J. Optoelectronics Advanced Materials*. Vol.10. No.6. pp.1299-1305
- Vassiliev V.P., Nikoliskaja A.V., Chernyshov V.Y., Gerassimov Ja.I. (1973) Thermodynamic properties of thallium sulphides. *Izv.AN SSSR, Neorg. Material.*, Vol.9, No.6, pp.900-904. (in Russian)
- Vassiliev V.P., Nikoliskaja A.V., Bachinskaja A.G., Gerassimov Ja.I. (1967). The thermodynamic properties of thallium monoselenide. *Dokl.AN SSSR*, Vol.176, No.6, pp.1335-1338. (in Russian)
- Vassiliev V.P., Nikoliskaja A.V., Gerassimov Ja.I. (1969) The thermodynamic properties of the lowest thallium selenide (Tl<sub>2</sub>Se), *Dokl. AN SSSR*. Vol.188, No 6, pp. 1318-1321 (in Russian)
- Vassiliev V.P., Nikoliskaja A.V., Gerassimov Ja.I. (1971) Thermodynamic investigation of thallium-selenium system by the electromotive force method. *J. Phys. Chem.*, (russ), Vol.45, No.8, pp.2061-2064. (in Russian)

- Vassiliev V.P., Nikoliskaja A.V., Gerassimov Ja.I. (1971), Thermodynamic characteristics of higher thallium sulfides, and certain correlation for IIIB subgroups of monochalcogenides Docl.AN SSSR. Vol.199, Vol.5, pp.1094-1098. (in Russian)
- Vassiliev V.P., Nikoliskaja A.V., Gerassimov Ja.I. (1973) Phase equilibriums of thallium-sulphur system in the solid state. Izv.AN SSSR, Neorg. Material., Vol.9, No.4, pp.553-557. (in Russian)
- Vassiliev V.P., Nikoliskaja A.V., Gerassimov Ja.I., Kuznestov A.F. (1968), Thermodynamic study of thallium tellurides by electromotive forces Izv. AN SSSR, Neorg. Material. Vol.4, No 7, pp. 1040-1046. (in Russian)
- Vassiliev V.P., Pentine I.V., Voronine G.F. (2004) Conditions de stabilité thermodynamique de la solution solide du système CdTe-HgTe. J.Phys. IV, France. Vol.113,. pp. 97-100.
- Vassiliev V.P., Somov A.P., Nikoliskaja A.V., Gerassimov Ja.I. (1968) Investigation of the thermodynamic properties of bismuth selenide by the electromotive force method. J. Phys.Chem., Vol.42, No.3, pp.675-678. (in russian)
- Vassiliev V.P., Taldrik A.F., Legendre B., Thermodynamics analysis of the rare earth solid metals and their alloys REIn<sub>3</sub>. XXXV JEEP (Journées d'Etude des Equilibres entre Phases), 1-3 avril 2009, Annecy. France, pp.103-107.
- Wagner C., Werner A. (1963) The role of displacement reaction in the determination of activities in alloys with the aid of galvanic cells J.Electrochem.Soc. Vol.110, No 4, pp.326-332.

IntechOpen



## **Electrochemical Cells - New Advances in Fundamental Researches and Applications**

Edited by Dr. Yan Shao

ISBN 978-953-51-0032-4

Hard cover, 240 pages

**Publisher** InTech

**Published online** 07, March, 2012

**Published in print edition** March, 2012

Currently the research field of electrochemical cells is a hotspot for scientists and engineers working in advanced frontlines of micro-, nano- and bio-technologies, especially for improving our systems of energy generation and conversation, health care, and environmental protection. With the efforts from the authors and readers, the theoretical and practical development will continue to be advanced and expanded.

### **How to reference**

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

Valery Vassiliev and Weiping Gong (2012). Electrochemical Cells with the Liquid Electrolyte in the Study of Semiconductor, Metallic and Oxide Systems, *Electrochemical Cells - New Advances in Fundamental Researches and Applications*, Dr. Yan Shao (Ed.), ISBN: 978-953-51-0032-4, InTech, Available from: <http://www.intechopen.com/books/electrochemical-cells-new-advances-in-fundamental-researches-and-applications/the-method-of-electromotive-force-emf-with-liquid-electrolyte->

**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

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen