

Thermodynamic properties of minerals and fluids

Korepanov Ya.I., Osadchii E.G. Modeling of a gold-silver-tellurium phase diagram by experimental thermodynamic data of phases and solid solutions. UDC 550.4.02.

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Abstract Based on the literature thermodynamic data for binary and ternary phases and our own data on the $\text{Ag}_x\text{Au}_{1-x}$ solid solution, isothermal sections of the Ag-Au-Te phase diagram were calculated. The simulation was carried out using the TERNAPI program (Voskov et al, 2015). For the ternary associations (paragenesis) of Ag_2Te - Ag_3AuTe_2 - AgAu , the compositions of the equilibrium alloy at temperatures of 323 and 373 K are given (table 2.). The temperature dependence of the composition of the alloy is about 2 at% Ag per 50 degrees.

Keywords: Ag, Au, Te, alloy, thermodynamics, metals and solid solution, EMF.

Introduction Gold and silver tellurides do not have such importance as native gold, despite the fact that the Ag-Au-Te mineral associations (Fig. 1) are present in many gold deposits and the study of their thermodynamic properties is an important task for understanding the geochemistry, transfer processes and the formation of gold deposits.

Based on the published papers and data being prepared for printing on the Ag-Au-Te system, the possibility of a theoretical study of the phase diagram was obtained using TERNAPI (Voskov et al, 2015). To simulate the Ag-Au-Te phase diagram, the following data were used (Table 1):

Table 1. Thermodynamic data used for modeling.

Mineral	Composition	Equation	Temperature range	References
Empressite	AgTe	$-15980-14.88T$	282-465 K	Voronin et. al. 2017
Stutzite	Ag_5Te_3	$-110900+523.9T-86.55T \ln(T)$	298-672 K	
No mineral	$\text{Ag}_{1.9}\text{Te}_3$	$-34990+112.9T-21.21T \ln(T)$	386-667 K	
Hessite	$\alpha\text{-Ag}_2\text{Te}$	$-43620+175.9T-28.85T \ln(T)$	298-424 K	
	$\beta\text{-Ag}_2\text{Te}$	$-37330+146.1T-26.37T \ln(T)$	424-667 K	
Calaverite	AuTe_2	$-48094+439.5T-57.7T \ln(T)$	298-424 K	Echmaeva 2009
Petzite	Ag_3AuTe_2	$-56080 - 49.84T$	298-400 K	
Sylvanite	AuAgTe_4	$-98596+847.4T-115.4T \ln(T)$	298-424 K	
Ag-Au alloy	$\text{Ag}_x\text{Au}_{1-x}$	$-10^{-3} \cdot 96484.56 \cdot (590 \cdot x^2/3 + 350 \cdot x + 200 + 0.1806 \cdot T) \cdot x(1-x)$ (J/mol)	273-723 K	Preparing for publication

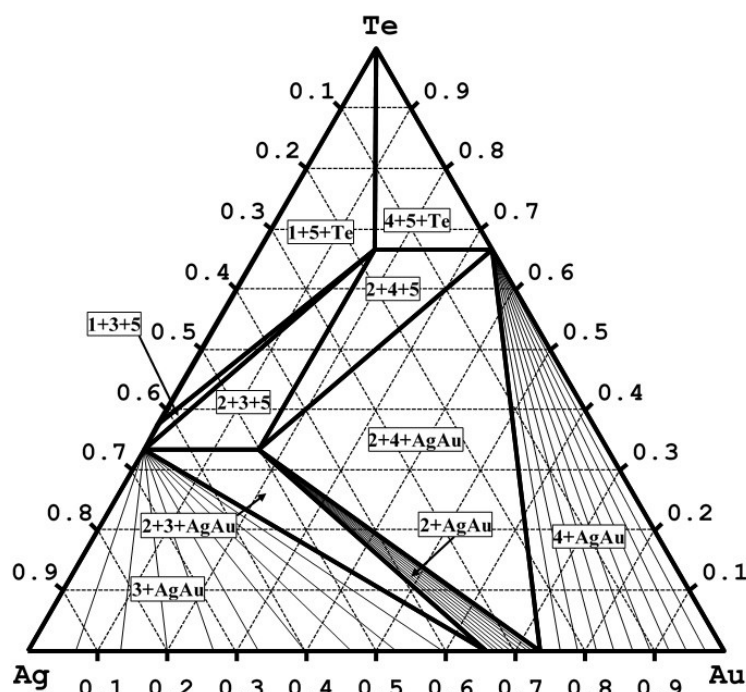


Fig.1. The ternary phase diagram of Ag-Au-Te, at a temperature 373 K, where 1 – Ag_5Te_3 , 2 – Ag_3AuTe_2 , 3 – Ag_2Te , 4- AuTe_2 , 5 – AgAuTe_4 , 6 - $(\text{Ag,Au})\text{Te}_2$, AgAu – solid solution $\text{Ag}_x\text{Au}_{1-x}$

It was found that the ratio of silver and gold in the mineral association Ag_2Te - Ag_3AuTe_2 - AgAu depends on the temperature of formation of parageneses. This fact can be used as a geothermometer.

Table 2. The composition of the alloy in field 2 (petzite) + 3 (hessite) + $\text{Ag}_x\text{Au}_{1-x}$ (native gold)

Temperature	Ag_2Te - Ag_3AuTe_2 - AgAu
323.15 K	$\text{Ag}_{0.329}\text{Au}_{0.671}$
373.15 K	$\text{Ag}_{0.343}\text{Au}_{0.657}$

Program Department of Earth Sciences RAS "Experimental study of mineral equilibria and isotopic ratios"

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Makarov V.P. Experimental study of natural fractionation of argon isotopes. UDC: 550.42:550.93

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Abstract. The field and experimental features of the isotope distributions in the triad (^{36}Ar , ^{39}Ar , ^{40}Ar), mainly in biotite, at high T were analyzed. It was established that in pairs ($^{40}\text{Ar}/^{36}\text{Ar}$) and ($^{39}\text{Ar}/^{36}\text{Ar}$) a linear relationship is observed with and not related to the isochron. The ^{40}Ar -T distribution is described by a parabolic equation, the total square of which has the form $\ln(^{40}\text{Ar}/^{36}\text{Ar}) \approx -A(1/T - 1/T_0)^2 + B$. Here $RTA = \Delta H_0$ is the enthalpy of sublimation (dissolution). Ar isotopes, i.e. the heat of dissolution of the impurity (Ar) in the mineral at the temperature T_0 (in Kelvin) of the mineral crystallization under natural conditions. They are related by the equation $\Delta H_0 = 22.51T_0 - 10545$.

Keywords: *sublimates, argon, temperature effects, parabolic equations, pressure of argon.*

The whole complex of geological observations on the behavior of the RGII (Radiogenic Isotopes and Isobar) in thermogradient fields indicates the possibility of fractioning them in natural conditions. The rare results of theoretical calculations available to us also speak of this possibility at high T. The purpose of the previously conducted experiments is to establish the degree of preservation of isotopic ratios under various thermodynamic conditions. At the same time, they have a number of common drawbacks: 1). They are not viewed from the position of isotope fractionation, but from the standpoint of the preservation of isotope ratios, which leads to ignoring the phenomenon of the equilibrium distribution of isotopes. 2). According to the theory of fractionation (TF), an analysis of the isotopic composition of the two compounds is necessary, but in experiments, as a rule, only one is studied. 3). All experimental studies ended with a qualitative statement of the results of changes in isotopic ratios without calculating the corresponding parameters: fractionation indicator, kinetic coefficients, etc.

Thus, if we rely on the theoretical and experimental materials on the fractionation of SILE (Stable Isotopes of Light Elements), then all experiments on the separation of the RGII were

performed methodologically at a low level. Below are the materials of the analysis of already conducted experiments on published data.

Argon in natural formations. These experiments are aimed at studying the features of migration and precipitation from the ^{40}Ar crystal lattice under the influence of high T in order to identify the influence of metamorphism of rocks on the results of determining the age of these rocks by the K-Ar method. In Russian Federation on a large scale, these studies were conducted primarily by E.K. Gerling and H.I. Amirkhanov. However, from the point of view of analyzing the influence of T, these studies have significant drawbacks, the main ones of which are as follows:

1) according to the TF SILE, the effect of T on fractionation is not reflected by a change in the absolute contents of isotopes, but by a change in the ratios of these contents. This means that temperature analysis requires the ratio of two isotopes of at least one element. However, in the works mentioned above, only the ^{40}Ar isotope was subjected to this analysis. True, recently, in connection with the advent of the age determination method by the ^{40}Ar – ^{39}Ar isotope ratio (Dalmeyr, 1984), the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio has been analyzed.

2) According to the theory of determining the age by the K-Ar method, the baseline for determining the age is the ratio $^{40}\text{Ar}/^{40}\text{K}$. However, in the presence of detailed studies on diffusion and loss of argon, there are practically no such studies for ^{40}K . The available data suggests a possibility of migration of ^{40}K at high T.

3) the inconsistency of the conditions of the experiments with Ar to the actual natural conditions and, therefore, the not completely correct interpretation of the phenomenon of "loss of argon" when heated. The fact is that when analyzing the temperature dependence of the amount of ^{40}Ar , all experiments are conducted in vacuum or other gas (air, etc.) medium. But these are environments in which gaseous Ar is freely released and it was they that were taken into account when forming the hypothesis about the "loss" of Ar at heating (Amirkhanov, 1960). On the other hand, there are experimental data on the artificial introduction of Ar into minerals (Gerling et al., 1965) under conditions of increased Ar pressure. These experiments are usually not related to each other in any way. At the same time, in natural conditions minerals are, as a rule, in close intergrowth with each other, having numerous borders of contact. therefore, when heated, Ar must overcome precisely these boundaries and stand out primarily not into a vacuum, but into the surrounding minerals. Thus, the combination of both experiments leads to the conclusion about the usual isotopic exchange between two minerals, which was observed earlier in other isotopic systems.

In other words, at high temperatures of heating of samples of rocks or minerals, we should, in the main, observe not the loss of Ar and K (through intergranular intervals), but the phenomenon of the usual isotopic (isobaric) exchange, or fractionation of Ar and K.

On the possibility of fractionation of isotopes of these elements speak and analysis of their distribution in natural minerals.

Recently, in connection with the advent of the new ^{40}Ar - ^{39}Ar age determination method, materials have appeared on the effect of T on the ratios of the $^{40}\text{Ar} / ^{36}\text{Ar}$, $^{39}\text{Ar} / ^{36}\text{Ar}$ and $^{40}\text{Ar} / ^{39}\text{Ar}$ isotopes.

Used (Dalmeyr, 1984, p.100) and the isochron method. In this case, the $^{40}\text{Ar} / ^{36}\text{Ar}$ and $^{39}\text{Ar} / ^{36}\text{Ar}$ ratios are calculated for each gas fraction with step heating, which are plotted on the isochronous diagram in similar coordinates.

Thus, we see here a complete analogy with the pyrochemical method for the isolation of Pb. Since ^{39}Ar reflects the distribution of ^{39}K , we can talk about different forms of ^{40}K in the mineral. This analogy with lead systems allows one to accept the same mechanism in explaining the patterns in the behavior of Ar isotopes.

Table 1. Calculation of fractionation indicators in the allocation of argon.

Isotope ratio	Temperature, °C				
	600	750	950	1025	1075
$\alpha(^{40}\text{Ar}/^{36}\text{Ar})$	0.2897	0.4026	0.3460	0.3265	0.3551
$\ln \alpha$	-1.2389	-0.9098	-1.0613	-1.1193	-1.0354
$\alpha(^{39}\text{Ar}/^{36}\text{Ar})$	0.2703	0.3884	0.3330	0.3128	0.3395
$\ln \alpha$	-1.3082	-0.9457	-1.0996	-1.1622	-1.0803
$\alpha(^{40}\text{Ar}/^{39}\text{Ar})$	1.0708	1.0365	1.0385	1.0438	1.0460
$\ln \alpha$	0.0684	0.0359	0.0378	0.0429	0.0450

Table 2. Calculation of the angular coefficient of the isotherm in the system

Parameter	Warming temperature, °C				
	600	750	950	1025	1075
$S = \text{tg} \gamma$	0.9470	0.9620	0.9652	0.9631	0.9584
γ°	43.44	43.89	43.99	43.92	43.78

Dependence of Ar isotope ratios on T. A diagram of the distribution of isotopic ratios from T based on materials (Dalmeyr, 1984), which was called isochronous, was constructed. As you can see, the dynamics of changes in the corresponding isotopic ratios show their clear dependence on T. This clearly indicates that the resulting diagram has no relation to the isochron, but is a temperature line showing the dependence of the isotopic ratios on T. The angular slope of this straight line is γ . The SIFE TF reflects the physicochemical conditions of the fractionation of Ar isotopes in the system $\text{Ar}_{\text{rock}} \rightleftharpoons \text{Ar}_{\text{vapor (gas)}}$.

Since, when Bi is heated, Ar is released up to the melting of the mineral, the total amount of selected argon in the first approximation characterizes all Ar present in the mineral. Comparison of the separated Ar with the remaining argon makes it possible to calculate the fractionation rate for the temperature effect on the mineral according to the formula $\alpha = (^{40}\text{Ar}/^{36}\text{Ar})_{\text{gas}} / (^{40}\text{Ar}/^{36}\text{Ar})_{\text{rock}}$, which are given in Table 1. Table 2 shows the calculation of the angular isotherm coefficient for the $^{39}\text{Ar} / ^{36}\text{Ar}$ — $^{40}\text{Ar} / ^{36}\text{Ar}$ system.

The fractionation of the ^{40}Ar and ^{39}Ar isotopes leads to the depletion of the gas phase with the ^{40}Ar and ^{39}Ar isotopes relative to the ^{36}Ar isotope, the

corresponding fractionation indicators being significantly less than 1.

In (Ashkinadze, 1980), data on the stepwise annealing of Bi from fenitized gneisses on contact with the Lake Varaka intrusion are described. Seeming ages - 1296-2027 million years. For the $^{40}\text{Ar} / ^{36}\text{Ar}$ and $^{39}\text{Ar} / ^{36}\text{Ar}$ ratio, it is bell-shaped, for $^{40}\text{Ar} / ^{39}\text{Ar}$ -approximately monotonously changing with a clearly pronounced sub-horizontal part, known as a "plateau" (Dalmeyr, 1984). On the general interval of 600-1200°C, two types of curves were revealed, on which the behavior of the same relations is opposite to each other.

Identified features in the nature of the behavior of isotopes with a change in T. If in one On the general interval of 600-1200 °C two types of curves were revealed, on which the behavior of some and the same relationship is opposite to each other.

Identified features in the nature of the behavior of isotopes with a change in T. If we can talk about the direct dependence of the magnitude of the relationship on T, then in the second, the inverse relationship for the same relations, and in the third, something intermediate. According to, TF (the theory of fractionation) SILE such a difference is due to an equilibrium compound with it. For example, in the case of pyrite, equilibrium with oxide compounds S, for example, with SO_4^{2-} , the isotopic composition S of pyrite sulfur is facilitated with the fall of T. In the case of equilibrium with reduced forms of S, for example, H_2S , the reverse occurs, i.e. with the fall of T, sulfur pyrite becomes heavier. It is possible that in cases with Ar isotopes this is also the case.

Table 3. Temperature dependence of Ar isotope ratios

Ratio	Warming temperature, °C								
	400	500	600	700	800	900	1000	1100	1200
$\ln(^{40}\text{Ar}/^{36}\text{Ar})$	8.35	9.19	10.69	10.99	10.30	10.02	9.57	7.07	8.392
$\ln(^{39}\text{Ar}/^{36}\text{Ar})$	0.51	0.98	2.433	1.893	1.884	1.716	1.263	-1.594	-2.753
$\ln(^{40}\text{Ar}/^{39}\text{Ar})$	7.85	8.21	8.257	8.353	8.305	8.303	8.309	8.660	6.392

Isotopes ^{40}Ar - ^{39}Ar . In modern geochronology, much attention is paid to the study of the so-called "plateau", i.e. that part of the diagram, which reflects the independence of this relation from T. However, this property has not been studied in detail. Analysis of materials reveals several types of properties of this "plateau". In some cases, this "plateau" is not detected at all. Such tests ~ 25%. The different quality of these "plateaus" has also been revealed: in some cases, the maximum values of the ratios ($^{40}\text{Ar}/^{36}\text{Ar}$) fall at low sublimation values T; in others, at high T values.

Isotopes ^{40}Ar - ^{36}Ar - ^{39}Ar . The graph of changes in these relations is approximated by a parabolic curve with the general equation $Y = AX^2 + Bx + C$, describing a parabola, whose branches can go either up or down. The presence of two forms of parabolas indicates the presence of two mechanisms for the formation of isotope ratios.

A full square in the form $y = A(x - x_0)^2 + C$, where $x = 1000/T$ K, which already allows for its genetic interpretation, is selected from this square trinomial.

Then the general distribution equation for both isotopic ratios is:

$$\ln(^{40}\text{Ar}/^{36}\text{Ar}) \approx -A(1/T - 1/T_0)^2 + B. \quad (1)$$

The interpretation of this equation is possible in two ways.

- Physical approach. According to the existing views, "parabolic type equations describe the processes of ... diffusion (the movement of medium particles, leading to the transfer of matter and leveling of concentrations) ..." (Chuprov, 1980). This approach is not very informative, so it is not considered.

- Thermodynamic approach. The closest to this situation is the fractionation equation for the isotopes of light elements (O, C, etc.). For example, for the distribution of oxygen isotopes between SiO_2 and water, this equation has the form (Kawabe, 1978)

$$\ln \alpha (\text{SiO}_2\text{-H}_2\text{O}) = 1.92 \cdot 10^6/T^2 + 8.58 \times 10^3/T - 18.98 \quad (2)$$

and is a typical polynomial (parabolic) second-order equation. In petrology, the type of distribution of impurities between the melt and the crystalline phase is known.

One of them is represented by the equation $\ln(N_i/N_c) = (-\Delta H_{\text{melting}}/R)(1/T - 1/T_{\text{melting}})$, where N_i and N_c are the molar fractions of the impurity in the molten

and crystalline phases, $\Delta H_{\text{melting}}$ and T_{melting} — warmth and the melting point of the solvent, T is the current temperature, R is the universal gas constant. This equation does not quite correspond to equation (2): the difference lies in the presence of T^2 in (2). Taking into account this data, as well as adherence to the principles of dimension, expression (1) is rewritten in the form

$$\ln(^{40}\text{Ar}/^{36}\text{Ar}) - \ln(^{40}\text{Ar}/^{36}\text{Ar})_0 \approx -[(\Delta H_i/R)^2 (1/T - 1/T_0)^2], \quad (3)$$

where ΔH_i is the enthalpy of sublimation (dissolution) of argon isotopes, i.e. the heat of dissolution of the impurity at the temperature T_0 (in kelvins) released as sublimate and determined in terms of [cal / mol]. The same can be said about the $^{39}\text{Ar}/^{36}\text{Ar}$ pair. In this equation, the parameters $(1/T_0)$ and $\ln(^{40}\text{Ar}/^{36}\text{Ar})_0$ are the coordinates of the "top" of the parabola. By analogy in equation (3), the parameters $(1/T_{\text{melting}})$ and $\ln N_0$ are also the coordinates of the crown of the parabola. Therefore, for one branch of a parabola, equation (3) is written as (4)

$$\ln(^{40}\text{Ar}/^{36}\text{Ar}) - \ln(^{40}\text{Ar}/^{36}\text{Ar})_0 \approx -(\Delta H_i/R)(1/T - 1/T_0), \quad (4)$$

This transformation facilitates the interpretation of argon temperature studies in Bi. The value of T_0 varies within 571–977 °C, corresponding to T crystallization of Bi in natural condition (Makarov, 2005). The value of ΔH varies within 3809–16160 cal/mol.

The T formation of Bi was compared with the isotope ratios used: TK (^{40}Ar) for the ratio

$(^{40}\text{Ar}/^{36}\text{Ar})$ and TK (^{39}Ar) - $(^{39}\text{Ar}/^{36}\text{Ar})$. These temperatures are clearly related by the equation $\text{TK} (^{39}\text{Ar}) = 1.137\text{TK} (^{40}\text{Ar}) - 127.7$. The angular coefficients are related by the equation $A (^{39}\text{Ar}) = 0.991A (^{40}\text{Ar}) - 43800$ ($R^2 = 0.995$). For the ^{40}Ar - ^{36}Ar system, a linear relationship between T and ΔH is revealed: $\Delta H_0 = 22.51T - 10545$ ($R^2 = 0.927$). For C (^{40}Ar) and C (^{39}Ar) - C (^{39}Ar) = $0.761C (^{40}\text{Ar}) - 3.531$ ($R^2 = 0.924$).

Isotopes $(^{40}\text{Ar}/^{36}\text{Ar})$ - $(^{39}\text{Ar}/^{36}\text{Ar})$. The distribution has a linear form, which we called the "temperature line". Its generalized form is $\ln(^{40}\text{Ar}/^{36}\text{Ar}) = A \ln(^{39}\text{Ar}/^{36}\text{Ar}) + B$. Such a dependence has been known for a long time; in (Dalmeyr, 1984), it is called the isochron, the angular coefficient reflects the age of Bi. In most cases, this is a straight line. According to these data, the angular coefficient A is close to unity.

In addition, this equation is a combination of two equations: $\ln(^{40}\text{Ar}/^{36}\text{Ar}) \approx -A(1/T - 1/T_{01})^2 + B$ and $\ln(^{39}\text{Ar}/^{36}\text{Ar}) \approx -C(1/T - 1/T_{02})^2 + D$. In the last

equations, it is assumed that $(1/T - 1/T_{01}) \approx (1/T - 1/T_{02})$. We write these equations in a more convenient form: $Y = aX^2 + A$; $Z = bX^2 + B$. The combination of these equations under the given conditions gives the final expression $Y \approx (a/b)Z + [A - (a/b)B]$. Next, the theoretical form of the temperature line is calculated, showing that this line is a combination of two parabolic equations and has no relation to geochronology. Associated with this is another property of the temperature line. So, in the pair $\ln(^{40}\text{Ar}/^{36}\text{Ar})$ and $\ln(^{39}\text{Ar}/^{36}\text{Ar})$ in the denominator of these fractions one component ^{36}Ar appears. In this regard, there is an assumption about the linear relationship between the components ^{40}Ar and ^{39}Ar , reflected by the equation $^{39}\text{Ar} = 0.039^{40}\text{Ar} + 0.021$ ($R^2 = 0,992$) and confirmed by calculations.

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Earlier studies (Makarov, 2013; Makarov, 2016) using correlation analysis showed a wide development in oils of linear dependence (up to 99% of objects) between the components of the oil composition, in particular, d - n - physical properties of oil, C-H (chemical composition of oil), C_m-H_n (molecular contents of elements), group composition parameters — Nf (naphthenes), Mn (methane components), Ap (aromatic components). In rare cases, a relationship was found that reflects the relationship between Nf and Ap and, being described by the equation $Ap = -1.4812(Nf)^2 + 4.1584(Nf) - 1.0284$, has the form of a polynomial or parabolic equation $y = Ax^2 + Bx + C$. This result indicates the possible distribution in nature of polynomial distributions of geological components.

Apparently for the first time, this fact was established when studying the distribution of isotopes in minerals. The closest to this situation is the fractionation equation for the isotopes of light elements (O, C, etc.). For example, for the distribution of oxygen isotopes between quartz and water, this equation has the form $\ln\alpha(\text{SiO}_2\text{-H}_2\text{O}^*) = 1.92 \cdot 10^6/T^2 + 8.58 \cdot 10^3/T - 18.98$ (Kawabe, 1978), representing typical polynomial (parabolic) second order equation. V.B. Polyakov also went the same way (Polyakov, 2007). In fig. 1A1 and 1A2 materials are also presented on other objects. There were more rare cases: in one sample of degassed oil (Brusilovsky, 2002) were fixed on two polynomials (Fig. 1B). In this regard, dependencies on T numbers of sublimates were studied from published data. The results of these studies are given in Table 1 ($X = 1000/T$ K, $Y = \ln(\text{Fr}/100)$; Fr - the amount of oil in the sublimation (in fraction) in%). In Table 1, sample analyzes are noted before the separation of the aromatics — the index is “da”, and after the separation of the aromatics — the index is “na”.

Makarov V.P. Oil. New properties: sublimates and polynomial equations.

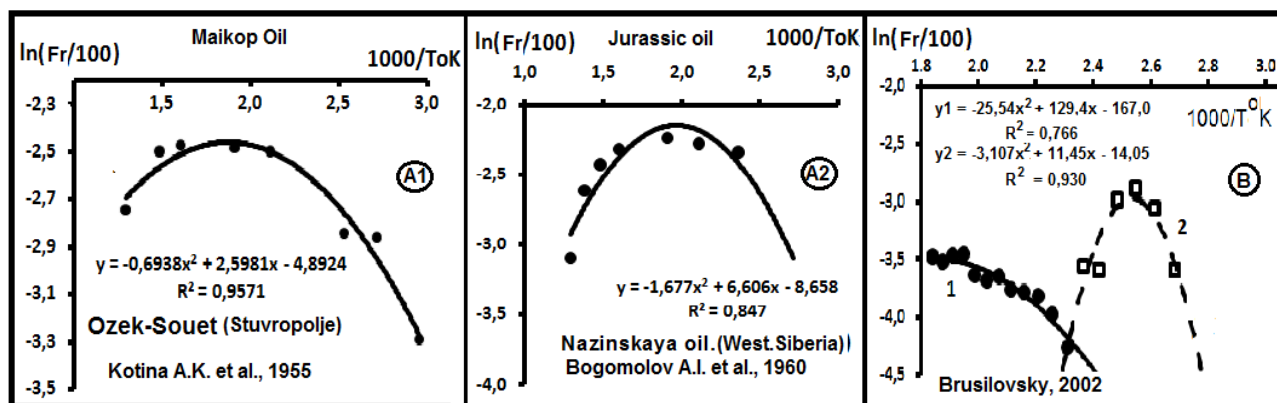


Fig.1. Dynamics of production of sublimates at the A1 and A2 fields of oil.B.- Dynamics of production of sublimates from degassed oil

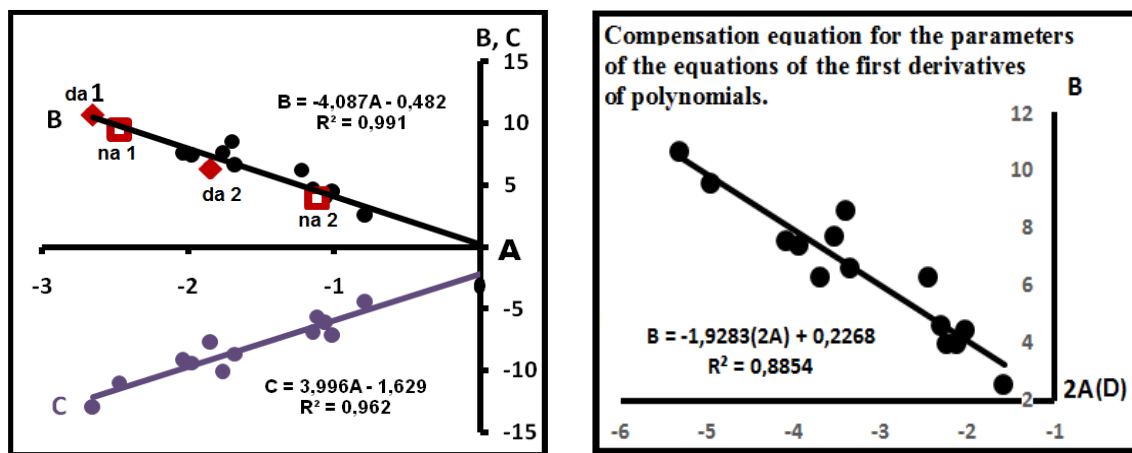


Fig. 2. Compensation equations for the parameters of polynomial (parabolic) second-order equations.

Fig.3. Compensation equation for parameters equations of the first derivatives of polynomials of the second degree

Table 1. Parameters of polynomial equations describing sublimates from oils.

No pp	Deposits	Time	The equation parameters $y = Ax^2 + Bx + C$				Region
			A	B	C	A²	
1	Upsa.	N	-1.767	7.667	-10.13	-1.232	Georgia.
2	Chaladidi.	K	-0.788	2.517	-4.469	-0.976	Georgia.
3	Ozek-Souet, well 69. Yes.	K	-2.655	10.65	-12.98	-1.165	Stavropol
4	Ozek-Souet, well 69. na	K	-2.476	9.501	-10.97	-0.735	Stavropol
5	Ozek-Souet, well.42. Yes.	J	-1.12	3.946	-5.644	-0.849	Stavropol
6	Ozek-Souet, well 42. na	J	-1.846	6.282	-7.748	-0.733	Stavropol
7	Nazinskaya oil.	J	-1.677	6.606	-8.658	-1.026	W. Siberia.
8	Nazinskaya oil.	J	-2.041	7.551	-9.19	-0.820	W. Siberia.
9	Zolny Ovrage, well 3.	C	-1.974	7.389	-9.373	-0.992	Volga-Ural.
10	Krasnoyarsk, well 42	C	-1.061	3.964	-6.137	-1.087	Volga-Ural.
11	Krasnoyarsk, well 41	C	-1.704	8.556	-13.78	-2.612	Volga-Ural.
12	Krasnokamsk, table.159.	C	-1.148	4.6	-6.951	-1.176	Volga-Ural.
13	Zolny Ovrage, well 87	D	-1.012	4.451	-7.191	-1.37	Volga-Ural.
14	Brusilovsky,2002		-1.226	6.251	-9.856	-1.803	

Properties of polynomial (parabolic) equations. The data obtained testify to the wide distribution in the geological environment of polynomial equations of the form $y = Ax^2 + Bx + C$.

Their properties have not been studied enough. In a real situation, the set of parameters of linear equations are generalized using compensation equations. Therefore, the parameters of polynomial equations were also subjected to compensation analysis (Makarov, 2006). The results are shown in Fig. 2, which shows that these conditions are satisfied, the corresponding equations have the form (2) and (3) and are presented in Fig. 2

$$B = mA + M, \quad (2)$$

$$C = kA + K \quad (3)$$

These data suggest that, whatever the oil, between the parameters of a parabolic equations there is a stable linear relationship. In the diagram in Fig.3. points and pa are also made for two samples. For convenience of analysis, they are marked with numbers 1 and 2 (da-1, da-2 and na-1, na-2), and the points are highlighted in color. As the comparison shows, these points, moving along compensation, never go beyond its limits. At singular points, which

we call the intersection points of curves, parabolic equations can be transformed into quadratic equations. Indeed, at these points $y_1 = y_2$; then two parabolas are combined into a parabola $(A_2 - A_1)x^2 + (B_2 - B_1)x + (C_2 - C_1) = 0$ or

$$x^2 + \frac{B_2 - B_1}{A_2 - A_1}x + \frac{C_2 - C_1}{A_2 - A_1} = x^2 + \frac{\Delta B}{\Delta A}x + \frac{\Delta C}{\Delta A} = 0$$

A comparison of the coefficients in this equation with the compensation parameters in Fig. 2 shows that, statistically, the first ones are the angular coefficients of the corresponding compensations (Fig. 2), therefore we can write:

$$x^2 + mx + k = 0. \quad (4)$$

Finally, Table 1 shows that the parameters A, B and C are related by the relation $2A \approx B + C$ (see column A'). To reveal the meaning of compensations, we find the first derivative with respect to x of the equation $Y = Ax^2 + Bx + C$, which has the form $1/(Fr/100) = 100/Fr = 2Ax + B$. In fig. 3 shows the compensation diagram for the parameters of the derivatives. A comparison shows an analogy between them. Derivatives are described by straight line equations, and these straight lines intersect at a point with the parameters $D_0 = (2A_0) =$

1.928 and $B_0 = 0.227$. According to (Brusilovsky, 2002), with an increase in T of sublimation, an increase in the molecular weight and a standard density of sublimation of oil occurs (see table 2). Thus, a comparison of all these data shows that they have such a property as compensation. Compensation ($A - B$) has a more or less clear meaning, and it is associated with compensations of the first derivatives to these polynomials. It has a close meaning ($B - C$). It is connected with the first derivative with respect to x already of a polynomial of the third degree $Y = Ax^3 + Bx^2 + Cx + D$.

Interpretation of the polynomial (parabolic) equation. The conducted studies reveal several regularities: a) despite the fact that the contents of fractions in oils are different, all points are located regularly; b) the distribution of points is well

described by a parabolic equation that has a generalized form:

$$\ln (Fr/100) \approx - [A (1/T - 1/T_0)^2] + V. \quad (5)$$

The interpretation of this equation is possible in two directions:

1). According to the existing points of view, “parabolic-type equations describe the processes ... of diffusion (the movement of medium particles, leading to the transfer of matter and leveling of concentrations) and are determined by the condition $B^2 - 4AC = 0$ (Chuprov, Kaneva, 2012). Since in this case the effect of only one parameter (temperature) is considered, the diffusion equation takes the form (Chuprov, Kaneva, 2012).

$\frac{d\Phi_p}{dT} = D \frac{d^2\Phi_p}{dT^2}$, here D is the coefficient of proportionality. This approach is not informative, further it is not considered.

Table 2. The behavior of the components in the separated oil

Deposites	Times	T_0C	ΔH kcal,	Fr _o , %	Region
Upsa.	<i>N</i>	194.3	2.641	13	Georgia.
Chaladidi.	<i>K</i>	420.3	1.764	9	Georgia.
Ozek-Souet, well 69. Yes.	<i>K</i>	539.4	3.237	10	Stavropol
Ozek-Souet, well 69. na	<i>K</i>	547.1	3.126	16	Stavropol
Ozek-Souet, well.42. Yes.	<i>J</i>	525.5	2.7	9	Stavropol
Ozek-Souet, well.42. na	<i>J</i>	327.8	2.103	11	Stavropol
Nazinskaya oil.	<i>J</i>	384.5	2.573	24	Western Siberia.
Nazinskaya oil.	<i>J</i>	499.3	2.839	11	Zap Siberia.
Zolny ovrag, well 3.	<i>C</i>	477.7	2.792	9	Volga-Ural.
Krasnoyarsk, well 42	<i>C</i>	137.7	2.016	9	Volga-Ural.
Krasnoyarsk, well 41	<i>C</i>	261.8	2.129	10	Volga-Ural.
Krasnokamsk, table.159.	<i>C</i>	246.95	2.594	5	Volga-Ural.
Zolny Ovrag, well 87	<i>D</i>	100.5	1.999	10	Volga-Ural.
Brusilovsky [2002]	-	119(122)*	2.2	15	-

2). Thermodynamic approach. Considering the physical nature of these equations, we note first of all that “fraction” means the relative amount of released substance, i.e. if the absolute amount of the released substance is n , and the total amount of the overhang is N , then the fraction $Fr = n \cdot 100/N$. In a rough approximation, it can be assumed that the value of the n/N components is conventionally equal to the ratios of their mole fractions. They reflect the state of the thermodynamic equilibrium distribution of sublimates between residual oil and air.

In physical chemistry, the type of distribution of impurities between the melt and the crystalline phase is known. One of them is represented by the equation (Makarov, 2006) $\ln(N_i/N_c) = (-\Delta H_{p_i}/R) (1/T - 1/T_0)$, where N_i and N_c are the molar fractions of the impurity in the molten and crystalline phases, ΔH_{ml} and T_{ml} are respectively the heat and melting point of

the solvent, T is the current temperature. This equation does not quite correspond to equation (5). The main difference is the presence of T^2 in (5). The closest thing to this situation is that of the fractionation of isotopes of light elements, derived from statistical thermodynamics. Note that the comparison is due to the analogy in the distribution of impurities between the melt and the crystal on the one hand and, as in our case, the distribution of impurities (sublimation) between the liquid substance (oil) and gas (air). This analogy allowed the use of thermodynamic studies in the liquid-crystal system. Taking into account these data, as well as adherence to the principles of dimension, expression (5) can be represented as an equation

$$\ln (Fr_i/100) - \ln (Fr_o/100) \approx - [(\Delta H_i/R)^2 (1/T - 1/T_0)^2] \quad (6),$$

where ΔH_i is the possible true enthalpy (dissolution) of the sublimation of the oil substance, i.e. the heat of

dissolution of the impurity released in the form of sublimation, Fr_0 - the amount of the fraction released at T_0 . It is accepted that $B = \ln (Fr_0 / 100)$. It is shown that a change in the parameter T_0 is more or less clearly manifested, the value of which decreases with age. The same trend is observed in the change of the ΔH_0 parameter. In both cases, the highest values of the parameters are characteristic of the oils among the

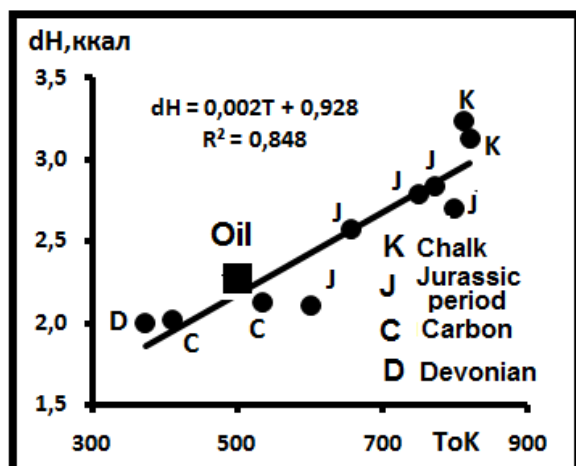


Fig.4. The diagram of the joint behavior of $T^{\circ}K$ and ΔH_0 .

Cretaceous sediments. In tab. 2 shows the results of determining the thermodynamic parameters of sublimates. According to them, the maximum temperature of dissolution reaches $\sim 550^{\circ}C$. Figure 4 shows the character joint behavior of $T^{\circ}C$ and ΔH_0 . For comparison, the data on technical oil CO - 100 are also placed here. The age of the rocks containing oil is indicated in the graph in Latin letters. According to these data, there is a positive relationship between these parameters during the entire time the oil is located. This indicates an approximate constancy in time of the $\Delta H/T$ ratio. In turn, this relation has the entropy dimension, which allows us to propose the equality $\Delta S_{ml} \approx 2 \text{ cal}/(M \cdot K) = 8.334J/(M \cdot K)$ and mark its approximate constancy in time in the studied parameter space.

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Shornikov S.I.¹, Shornikova M.S.² Thermodynamic properties of the CaO–FeO melts

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Abstract. Within the framework of the developed semi-empirical model, the calculations were made of thermodynamic properties of the CaO–FeO melts in the temperature region 1300–2200 K. The calculated values of the oxide activities and the mixing energies of melts are compared with available experimental information.

Keywords: thermodynamic properties of oxide melts, the CaO–FeO system

Physical and chemical properties of compounds of the CaO–FeO system and their melts, which are part of multicomponent oxide systems, are of considerable interest for geochemistry and engineering. Oelsen and Maetz (1941) was the first who constructed a phase diagram of this system contains only one compound – calcio-wustite $Ca_2Fe_2O_5$, which decomposed at 1423 K. It was later confirmed by Schurmann and Kraume (1976). However, Allen and Snow (1955) reported a lower decomposition temperature of $Ca_2Fe_2O_5$, equal to 1381 ± 3 K, and found a compound $CaFe_2O_3$, dissociating at 1406 ± 3 K. Note that Fischer and Fleischer (1961), like other researchers, found no compounds in the CaO–FeO system. When sintering the sludge at the temperature region 1173–1523 K in the composition of the synthesized material (Srikanth et al. 2005), as well as in the waste of electrolysis production (Bazhin et al., 2017), it was found the compound $CaFeO_2$, the structure of which was studied in detail in (Tassel et al., 2009; Matsumoto et al., 2010; Gupta et al., 2016). Shugurov et al. (2005) have conducted quantum-mechanical calculations for the complex gaseous oxide ($CaFeO_2$), the calculated value of the enthalpy of formation ($\Delta_f H_{298}$) was equal

to -213.7 kJ/mol. The phase diagram of the CaO–FeO system, shown in Fig. 1, is a compilation of the results obtained by Abbattista et al. (1975) and Schurmann and Kraume (1976), and assumptions about the presence of CaFeO_2 in the CaO–FeO system.

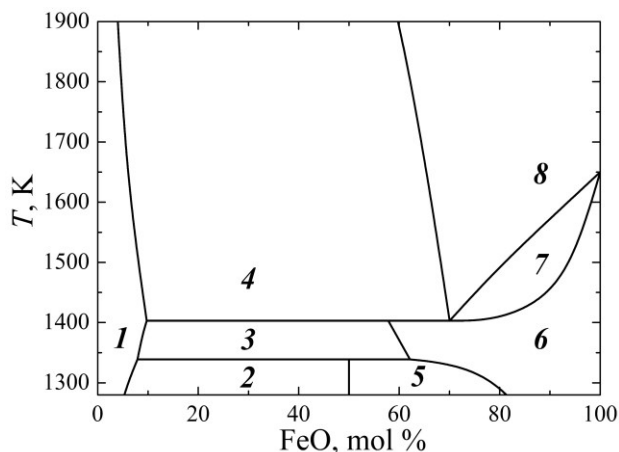


Fig. 1. The phase diagram of the CaO–FeO system: **1** – CaO (solid solution); **2** – CaO + CaFeO_2 ; **3** – CaO (solid solution) + CaFeO_2 ; **4** – CaO (solid solution) + liquid; **5** – CaFeO_2 + FeO (solid solution); **6** – FeO (solid solution); **7** – FeO (solid solution) + liquid; **8** – liquid.

The values of iron oxide activity (a_{FeO}) in the CaO–FeO system were determined experimentally at temperatures of 1473–1873 K in (Fujita et al., 1968; Ban-Ya et al., 1980; Iwase et al. 1984). The values of a_{CaO} in the CaO–FeO system were calculated from the values of a_{FeO} , that it caused their deviations.

The results of theoretical work carried out in the frame of various models (Hillert et al., 1990; Selleby and Sundman, 1996; Selleby, 1997; Hidayat et al., 2016) were concerned to the calculations of the phase diagram of the Ca–Fe–O system mainly. As for the results of the calculations of the iron and calcium oxide activities in the CaO–FeO system (Wu et al., 1993; Bygden et al., 1994; Bjorkvall et al., 2001; Tao, 2006; Yang et al. 2012), then there are significant differences between them and deviations from the experimental values, which may be due to the rather complex structure of the system (Fig. 1).

In the present study we calculated the thermodynamic properties of the CaO–FeO melts in

the temperature range 1300–2200 K within the framework of the theory of ideal associated solutions in order to clarify the parameters of the semi-empirical model used to calculate the activities in the melts of the CaO – MgO – FeO – Al_2O_3 – TiO_2 – SiO_2 multicomponent oxide system in a wide range of compositions and temperatures. The model parameters, as before (Shornikov, 2016), were calculated from experimental and theoretical data (Glushko et al., 1978–1982; Bale et al., 2016).

The initial thermodynamic data considered 5 condensed phases (3 solid and 2 liquid) and 11 gas species, these components are listed in the Table 1. The same table gives the calculated values of the Gibbs formation energies from elements (ΔG°_f) for the compounds and the vapor species over the CaO–FeO system. They were used for the calculation of the equilibrium conditions in the system at a given composition and temperature. The required equation solution for the total Gibbs energy for the system studied was found by the Gibbs energy minimization method.

As can be seen from Fig. 2, the calculated values of iron oxide activities in the CaO–FeO melts satisfactorily correspond to the experimental results obtained by Ban-Ya et al. (1980) in the study of equilibria of hydrogen–water gas mixtures with slag at 1673 K and Fujita et al. (1968) in the study of the distribution of oxygen between molten iron and slag at 1833 K. The results of calculations of FeO activities in the CaO–FeO melts are consistent with the information previously obtained by Bjorkvall et al. (2001) in the framework of the semiempirical model based on the Temkin's theory of ionic melts. Note that the value of a_{CaO} calculated by Bjorkvall et al. (2001) slightly lower than those obtained in the present study, that contradicts to the data on the position of the "CaO (solid solution) + liquid" field in the phase diagram of the CaO–FeO system (Fig. 1). Values of FeO and CaO activities in the CaO–FeO melts calculated by Wu et al. (1993) in the framework of the quasichemical model to a lesser degree correspond to experimental data compared with those obtained by Bjorkvall et al. (2001) and in the present study.

Table 1. The Gibbs energy of formation from elements of condensed phases and vapor species over the CaO–FeO system at 1873 K, calculated in present study.

Condensed phases				Gas phase	
Solid phases	ΔG°_{1873} , kJ/mol	Liquid phases	ΔG°_{1873} , kJ/mol	Vapor species	ΔG°_{1873} , kJ/mol
CaO	–435.296	CaO	–422.317	Ca	–9.985
CaFeO ₂	–599.816			Ca ₂	90.363
FeO	–153.762	FeO	–157.951	CaO	–68.953
				Fe	145.501
				Fe ₂	399.724
				FeO	76.891
				FeO ₂	34.624
				O	130.138
				O ₂	0.000
				O ₃	266.369
				O ₄	181.230

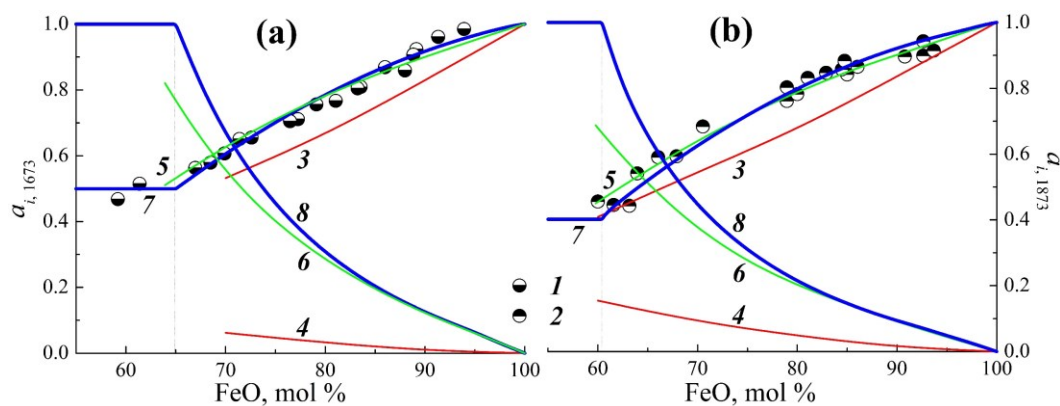


Fig. 2. Activities of FeO (1–3, 5, 7) and CaO (4, 6, 8) in the CaO–FeO melts at 1673 (a) and 1873 K (b) determined in experiments: 1 – Ban-Ya et al. (1980) and 2 – Fujita et al. (1968), and calculated: 3 and 4 – Wu et al. (1993), 5 and 6 – Bjorkvall et al. (2001), 7 and 8 – in the present study. The vertical dashed line marks the boundary of the "CaO (solid solution) + liquid" region and the melt.

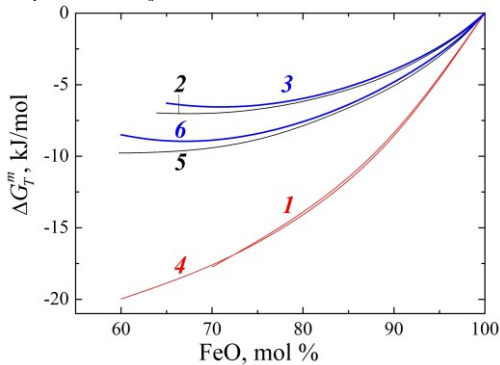


Fig. 3. The calculated mixing energy in the CaO–FeO melts at 1673 (1–3) and 1873 K (4–6): 1 and 4 – Wu et al. (1993), 2 and 5 – Bjorkvall et al. (2001), 3 and 6 – in the present study.

Fig.3 represents the values of the mixing energies (ΔG^m) in the CaO–FeO melts at 1673 and 1873 K. It is possible to notice, that the ΔG^m values obtained in the present work and Bjorkvall et al. (2001) are close. The minimum of the ΔG^m values is in the region of the eutectic composition of solid solutions of CaO and FeO (fields 4 and 7 in Fig. 1) and is in the range from –6.5 to –9.0 kJ/mol in the considered temperature range. The ΔG^m values determined by Wu et al. (1993) almost in 2 times differ from these data.

The present study was supported by RAS Presidium's Program #7 (*Experimental and theoretical studies of Solar system objects and star planetary systems. Transients in astrophysics*) and the Russian Foundation for Basic Research (grant #19-05-00801A).

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Shornikov S. I. Thermodynamic properties of the MgO–TiO₂ melts

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Abstract. Within the framework of the developed semi-empirical model, the calculations were made of thermodynamic properties of the MgO–TiO₂ melts in the temperature region 1800–2500 K. The calculated values of the oxide activities and the mixing energies of melts are compared with available experimental information.

Keywords: thermodynamic properties of oxide melts, the MgO–TiO₂ system

The physico-chemical properties of the MgO–TiO₂ system are of interest for petrology and industrial technologies (titanium metallurgy, production of radioceramics). The qandilite Mg₂TiO₄, geikielite MgTiO₃, and carroite MgTi₂O₅ (Coughanour and DeProse, 1953) are identified on the phase diagram of the MgO–TiO₂ system (Fig. 1). Their positions were refined subsequently (Massazza and Sirchia, 1958; Shindo, 1980). The standard enthalpies and entropies of formation of magnesium titanates were determined by calorimetric methods (Shomate, 1946; Todd, 1952; Kelley et al., 1954; Wechsler and Navrotsky, 1984; Robie et al., 1989).

High-temperature heat capacities of magnesium titanates were determined in the temperature range 300–1820 K (Naylor and Cook, 1946; Orr and Coughlin, 1952; Robie et al., 1989; Ilatovskaia et al., 2018). However, these data did not correspond to the calculated values of the energies of formation of magnesium titanates, based on the studies of heterogeneous equilibria in oxide systems at 1573 and 1673 K by Muan et al. (Brezny and Muan, 1971; Evans and Muan, 1971). Bale et al. (2016) estimated the melting enthalpy of MgTi_2O_5 at 1930 K, equal to 54.343 kJ/mol. Lopatin and Semenov (2001) observed the (Mg), (TiO) and (TiO_2) vapor species in the gas phase over the magnesium titanates by the Knudsen effusion mass spectrometric method in the temperature range 2100–2400 K; the (MgO) and (MgTiO_3) vapor species were estimated to be not more than 0.1 % of the (Mg) amount. The estimate of the enthalpy of the (MgTiO_3) formation was $\Delta_f H_{298} \approx -856$ kJ/mol. The results of experimental studies of magnesium titanates are given in Table 1.

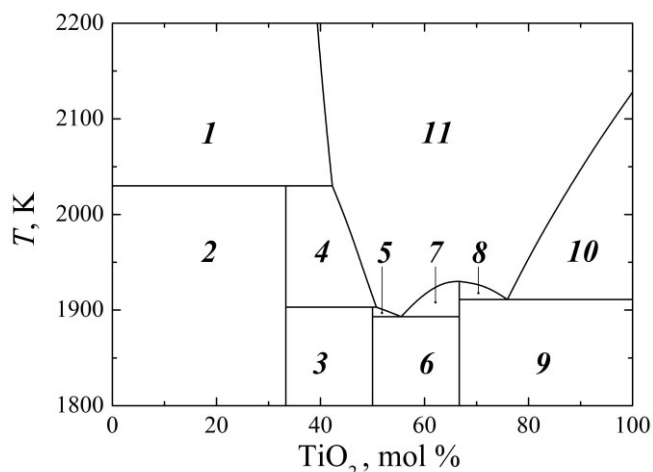


Fig. 1. The phase diagram of the MgO-TiO_2 system: *I* – MgO + liquid; *2* – MgO + Mg_2TiO_4 ; *3* – Mg_2TiO_4 + MgTiO_3 ; *4* – Mg_2TiO_4 + liquid; *5* – MgTiO_3 + liquid; *6* – MgTiO_3 + MgTi_2O_5 ; *7* and *8* – MgTi_2O_5 + liquid; *9* – MgTi_2O_5 + TiO_2 ; *10* – TiO_2 + liquid; *II* – liquid.

Table 1. The enthalpy, the entropy and the Gibbs energy of formation of magnesium titanates from the simple oxides (per 1 mol of compound).

Compound	T , K	$\Delta_f H_T$, kJ/mol	$\Delta_f S_T$, J/(mol×K)	$\Delta_f G_T$, kJ/mol	Reference
Mg_2TiO_4	298		-0.26 ± 0.21		Todd, 1952
–“–	298	-5.69 ± 0.33			Kelley et al., 1954
–“–	973	-1.40 ± 0.73			Wechsler and Navrotsky, 1984
–“–	1573			-7.11 ± 0.70	Brezny and Muan, 1971
–“–	1673			-8.09 ± 1.26	Evans and Muan, 1971
–“–	1700–2030	-0.68 ± 0.09	5.34 ± 0.05		Bale et al., 2016
MgTiO_3	298		-2.30 ± 0.21		Shomate, 1946
–“–	298	-13.26 ± 0.46			Kelley et al., 1954
–“–	298		-1.39 ± 0.15		Robie et al., 1989
–“–	973	-10.55 ± 0.65			Wechsler and Navrotsky, 1984
–“–	1573			-10.04 ± 2.09	Brezny and Muan, 1971
–“–	1673			-10.67 ± 1.05	Evans and Muan, 1971
–“–	1700–1903	-10.26 ± 0.06	0.91 ± 0.03		Bale et al., 2016
MgTi_2O_5	298		-0.23 ± 0.28		Todd, 1952
–“–	298	-6.22 ± 0.60			Kelley et al., 1954
–“–	973	-4.67 ± 0.57			Wechsler and Navrotsky, 1984
–“–	1573			-9.48 ± 1.39	Brezny and Muan, 1971
–“–	1673			-10.18 ± 1.12	Evans and Muan, 1971
–“–	1700–1930	-3.27 ± 0.05	4.24 ± 0.03		Bale et al., 2016

Table 2. The standard Gibbs energies of condensed phases and vapor species over the MgO–TiO₂ system at 2173 K calculated in present study.

Condensed phases				Gas phase	
Solid phases	ΔG°_{2173} , kJ/mol	Liquid phases	ΔG°_{2173} , kJ/mol	Vapor species	ΔG°_{2173} , kJ/mol
MgO	–355.987	MgO	–329.234	Mg	–72.400
Mg ₂ TiO ₄	–1300.488			Mg ₂	20.659
MgTiO ₃	–932.105			MgO	–120.207
MgTi ₂ O ₅	–1496.736	MgTi ₂ O ₅	–1511.848	Ti	170.472
TiO ₂	–551.661	TiO ₂	–551.278	TiO	–136.688
				TiO ₂	–334.779
				Ti ₂ O ₃	–641.289
				Ti ₂ O ₄	–794.803
				O	110.091
				O ₂	0.000
				O ₃	283.608
				O ₄	209.765

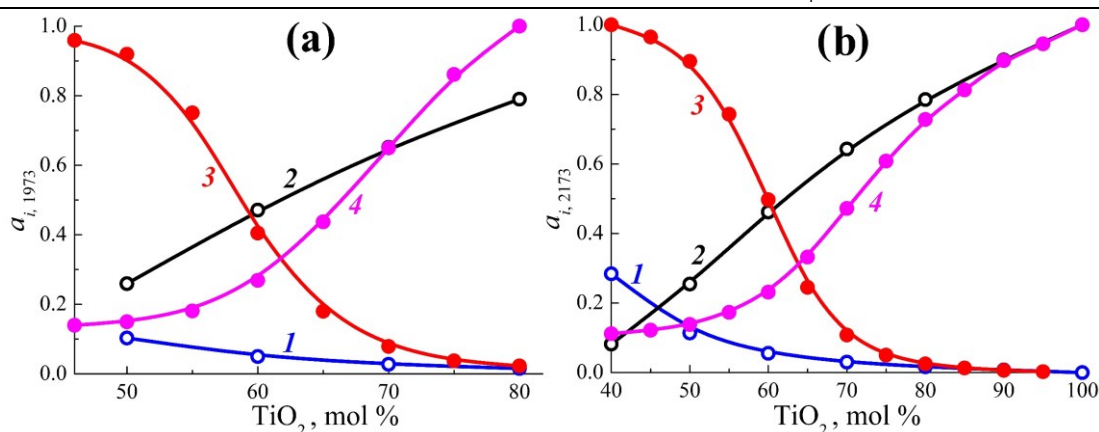


Fig. 2. The activities of MgO (1, 3) and TiO₂ (2, 4) in the MgO–TiO₂ melts at 1973 (a) and 2173 K (b) calculated: 1 and 2 – Eriksson and Pelton (1993), 3 and 4 – in the present study.

The results of numerous theoretical studies carried out within the framework of various models concerned to the calculations of the phase diagram of the MgO–TiO₂ system (Ilatovskaia and Fabrichnaya, 2019). The activity values of magnesium and titanium oxides in the MgO–TiO₂ melts in the temperature range 1973–2373 K were calculated using of quasi-chemical model in the only study (Eriksson and Pelton, 1993), which has not compared still both with experimental data and with the results of other theoretical calculations.

In the present study we calculated the oxide activities (a_i) and the mixing energies (ΔG^m) in the MgO–TiO₂ melts in the temperature range 1800–2500 K on the base of the theory of ideal associated solutions in order to clarify the parameters of the semi-empirical model used to calculate the activities in the melts of the CaO–MgO–FeO–Al₂O₃–TiO₂–SiO₂ multicomponent oxide system in a wide range of compositions and temperatures. The model parameters, as before (Shornikov, 2016), were calculated from experimental and theoretical data (Glushko et al., 1978–1982; Bale et al., 2016).

The initial thermodynamic data included 5 condensed phases (3 solid and 2 liquid) and 11 gas species, these components are listed in the Table 1. The same table gives the calculated values of the Gibbs formation energies from elements (ΔG°_f) for the compounds and the vapor species over the MgO–TiO₂ system. They were used for the calculation of the equilibrium conditions in the system at a given composition and temperature. The required equation solution for the total Gibbs energy for the system studied was found by the Gibbs energy minimization method.

The comparison of the calculated values of oxides activity in the MgO–TiO₂ melts with those presented by Eriksson and Pelton (1993) shows their significant difference. The a_i values calculated by Eriksson and Pelton (1993) are not consistent with the data (Brezny and Muan, 1971; Evans and Muan, 1971) at 1973 K in the region close to the "Mg₂TiO₄ + liquid" field (Fig. 2a) and the calculated values are far from 1 at 2173 K in a region close to the "MgO + liquid" field (Fig. 2b). The difference in the ΔG^m values is more than 10 kJ/mol at concentrations close

to MgTiO_3 (Fig. 3), where we observed the ΔG^m minimum calculated by Eriksson and Pelton (1993).

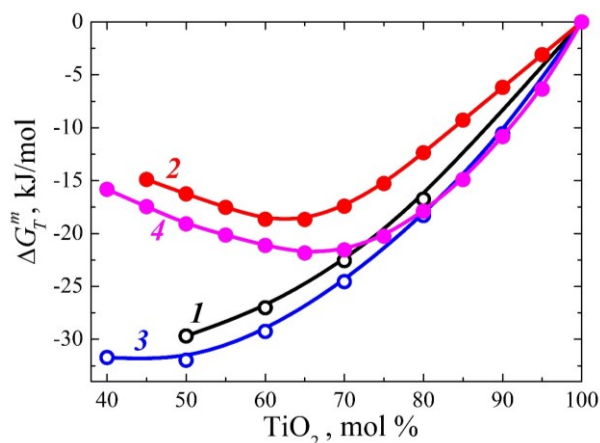


Fig. 3. The mixing energies in the MgO-TiO_2 melts at 1773 (1, 2) and 2173 K (3, 4), calculated: 1 and 3 – Eriksson and Pelton (1993), 2 and 4 – in the present study.

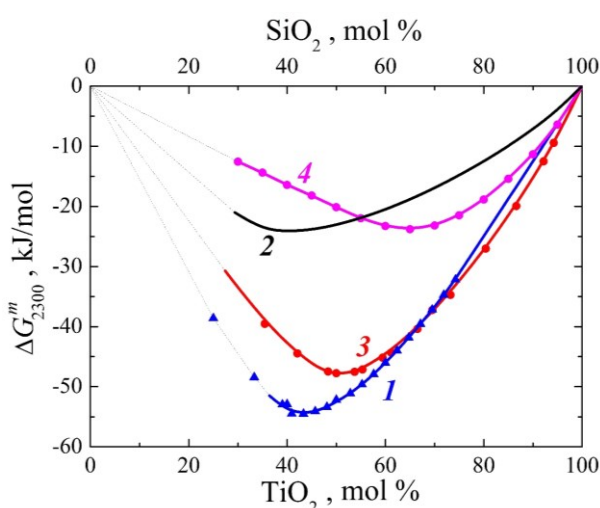


Fig. 4. The mixing energies in the CaO-SiO_2 (1), MgO-SiO_2 (2), CaO-TiO_2 (3) and MgO-TiO_2 (4) melts at 2300 K determined in (Shornikov and Archakov, 2000; Shornikov, 2006; Shornikov, 2019) and in the present study, respectively. Dotted lines correspond to heterogeneous areas.

As we can see from Fig. 4, the ΔG^m minimum value in the MgO-TiO_2 melts is in the region of MgTi_2O_5 congruent melting compound and corresponds in magnitude to similar silicate and titanate melts of the CaO-SiO_2 , MgO-SiO_2 and CaO-TiO_2 systems studied earlier (Shornikov and Archakov, 2000; Shornikov, 2006; Shornikov, 2019).

The present study was supported by RAS Presidium's Program #7 (*Experimental and theoretical studies of Solar system objects and star planetary systems. Transients in astrophysics*) and the Russian Foundation for Basic Research (grant #19-05-00801A).

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Stolyarova T.A.¹, Brichkina E.A.¹, Osadchii E.G.¹, Baranov A.V.^{1,2} Calorimetric determination of the standard enthalpy of mohite (Cu₂SnS₃) formation. UDC 544.332

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Abstract. Value of the standard reaction enthalpy of mohite (Cu₂SnS₃) formation from sulfides have been obtained experimentally according to the reaction $2\text{CuS} + \text{SnS} \rightarrow \text{Cu}_2\text{SnS}_3$: $\Delta_r H_{298.15}^\circ(\text{Cu}_2\text{SnS}_3) = -(50.83 \pm 0.47) \text{ kJ} \cdot \text{mol}^{-1}$. The measurements were carried out with 10 run series in vacuum-block calorimeter. Using literature data for the binary sulfides the value of standard enthalpy of mohite formation from the elements were calculated $\Delta_r H_{298.15}^\circ(\text{Cu}_2\text{SnS}_3) = -(263.61 \pm 2.28) \text{ kJ} \cdot \text{mol}^{-1}$.

Keywords: standard enthalpy, mohite, Cu₂SnS₃, calorimetry

Mohite is a rare mineral that occurs in hydrothermal veins, but the Cu₂SnS₃ compound can be used as a precursor for the synthesis of materials with photovoltaic properties. Also, the compound may appear as a result of dissociation of stannine or kesterite materials.

A calorimetric determination of the Cu₂SnS₃ standard enthalpy formation from sulfides CuS and SnS was carried out by comparing the amount of heat transferred to the sample system as an electrical energy for carrying out the reaction and the amount of heat obtained during the system cooling, which includes the heat released during the reaction. According to preliminary tests, the synthesis of Cu₂SnS₃ from the sulphides in evacuated quartz glass ampoules takes place at a temperature of ~ 850 °C for 6–7 minutes, in consistent with the reaction (R1): $2\text{CuS} + \text{SnS} \rightarrow \text{Cu}_2\text{SnS}_3$ (R1)

The sulfide (CuS and SnS) synthesis was carried out from the elements of high and especially high purity: high purity copper, powder (99.999%), high purity tin, bar (99.999%); crystalline sulfur (99.99%, Alfa Aesar). The CuS synthesis operations: synthesis 400 °C – regrinding – annealing 300 °C (with separated Cu) – regrinding – annealing 300 °C (with separated Cu). The SnS synthesis operations: synthesis 350 °C – synthesis 650 °C – regrinding – annealing 350 °C (with separated Sn) – regrinding – annealing 350 °C (with separated Sn). The sulfide compositions were confirmed with X-ray phase analysis (Bruker D2 PHASER diffractometer, CoK_{α1} radiation, $\lambda = 1.78897 \text{ \AA}$) The total weight of the mixture in each of the samples is about 1.8 g.

Calorimetric studies were carried out in a high-temperature vacuum-block calorimeter, manufactured and improved in the Laboratory of Electrochemistry, Thermodynamics and Physics of Minerals IEM RAS (laboratory number VBC-3) and described previously in the works (Vasilyev, Soboleva, 1962; Fleisher, Stolyarova, 1978). The process of calorimeter operation control, visualization and data processing were carried out using especially developed control unit, interface and computer program (Zhdanov et al., 2005).

A quartz glass ampoule with a targeted mixture of the sulfides was pumped out to a residual pressure of 10⁻² Pa, sealed in a flame of an oxygen torch, and placed in a resistance furnace inside a massive copper block. The block was filled with argon under a pressure of 10⁶ Pa (to improve the heat exchange between the heater and the copper block). The vacuum block (isothermal shell, where the massive copper block was placed in) was pumped out to a residual pressure of 10³ Pa, that was kept constant during the whole experiment. The temperature of the isothermal shell (298.15 ± 0.02) K was maintained with a 300-liter thermostat with a propeller stirrer. The set thermostat temperature was maintained using a special thermal controller.

Electric power was measured with an accuracy of 0.02%. The temperature rise during the experiment was measured with a resistance thermometer consisting of nine tiny platinum temperature sensors equally spaced along the massive block; the total resistance was 988 Ohms at 298.15 K. The calorimeter with an ampoule (where the investigated reaction had already occurred) in a resistance furnace was calibrated using electrical power in conditions identical to the conditions of the experiment (heating time, the amount of electrical power and the value of the start temperature).

The heating time of all experiments was fixed automatically. The total time of the experiment duration (50 min) was also fixed. The accuracy of thermal value is 0.05%. Reheating did not cause an

additional thermal effect. This fact confirms the complete passage of the reaction during the first heating. X-ray phase analysis of the calorimetric experiments products has confirmed the presence of the only substance Cu_2SnS_3 in them.

There are only theoretically calculated (DFT - using density functional theory and DFT-D2 - based on the Van der Waals forces of molecular (atomic) interaction) data on the mohite formation enthalpy in the literature (Shigemi, Wada, 2018):

$$\Delta H_f^{\text{DFT}} = -241.4 \text{ kJ} \cdot \text{mol}^{-1},$$

$$\Delta H_f^{\text{DFT-D2}} = -338.8 \text{ kJ} \cdot \text{mol}^{-1}.$$

In this work, a series of 10 experiments was carried out in a shigh-temperature vacuum-block calorimeter. The measurement results are shown in **Table 1**.

The value of mohite formation enthalpy, according to the reaction of formation from sulfides (R1):

$$\Delta_f H_{298.15 \text{ K}}^0(\text{R1}) = -(50.83 \pm 0.47) \text{ kJ} \cdot \text{mol}^{-1}.$$

Using literature data of enthalpy formation from elements for sulfides CuS and SnS:

$$\Delta_f H_{298.15 \text{ K}}^0(\text{CuS, cr}) = -(53.14 \pm 2.28) \text{ kJ} \cdot \text{mol}^{-1} \text{ (Cemic, Kleppa, 1988),}$$

$$\Delta_f H_{298.15 \text{ K}}^0(\text{SnS, cr}) = -(106.5 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1} \text{ (Robie, Hemingway, 1995),}$$

the value of mohite formation enthalpy from elements:

$$\begin{aligned} \Delta_f H_{298.15 \text{ K}}^0(\text{Cu}_2\text{SnS}_3, \text{cr}) &= \\ &= \Delta_f H_{298.15 \text{ K}}^0(\text{R1}) + 2\Delta_f H_{298.15 \text{ K}}^0(\text{CuS, cr}) + \Delta_f H_{298.15 \text{ K}}^0(\text{SnS, cr}) \\ \Delta_f H_{298.15 \text{ K}}^0(\text{Cu}_2\text{SnS}_3, \text{cr}) &= -(263.61 \pm 2.28) \text{ kJ} \cdot \text{mol}^{-1}. \end{aligned}$$

Table 1. The enthalpy of mohite formation from sulfides (M.M.= 342.0 g/mol).

Number of experiment	Sample weight (g)	$\Delta R + \sigma$ (Ohm)	The amount of heat, released during the experiment (J)			$-\Delta_f H_{298.15}^0$ kJ/mol
			total	on the heater	in the reaction	
1	1.7977	28.3292	82154.7	81888.5	266.2	50.64
2	1.7975	28.3229	82136.4	81863.0	273.4	52.02
3	1.7994	28.3651	82258.8	81997.2	261.6	49.72
4	1.8031	28.436	82464.4	82192.2	272.2	51.63
5	1.7993	28.4376	82469.0	82202.6	266.4	50.64
6	1.8009	28.3179	82121.9	81851.0	270.9	51.45
7	1.8011	28.3329	82165.4	81904.6	260.8	49.52
8	1.8041	28.3289	82153.8	81880.9	272.9	51.73
9	1.8005	28.2948	82176.8	81905.6	271.2	51.51
10	1.8008	28.2916	82167.3	81906.9	260.4	49.45
The average:						50.83 $\pm$ 0.47

Note: $\Delta R + \sigma$ – the thermometer resistance value with the correction for thermal exchange, 1-8– samples– calorimeter thermal value $W = (2900.0 \pm 1.0) \text{ J} \cdot \text{Ohm}^{-1}$, 9-10 $W = (2904.3 \pm 1.0) \text{ J} \cdot \text{Ohm}^{-1}$.

The authors are grateful to the engineers M.V. Fokeev and N.N. Zhdanov for conducting calorimetric experiments and Dokina T.N. for X-ray measurements.

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