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Modeling of the Thermodynamic Properties of Lead–Tellurium Liquid Alloys

A. G. Morachevskii

Peter the Great State Polytechnic University, Politekhnikeskaya ul. 29, St. Petersburg, 195251 Russia
e-mail: morachevski@mail.ru

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Abstract—Application of the Redlich–Kister polynomial with varied number of parameters for describing the concentration dependence of thermodynamic systems of liquid metallic systems with a strong interaction between their components is considered for the example of the lead–tellurium system. Particular attention is given to the range of dilute solutions of tellurium in liquid lead.

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Tellurium belongs to characteristic impurities in liquid lead produced from ore raw materials. The purification to remove tellurium is performed by the intermetallide technology via interaction with sodium [1, 2]. A considerable interest is manifested in studying the structural specific structural features of Pb–Te melts due to the semiconductor properties of lead telluride and to the ionic nature of liquid alloys in this system [3, 4]. Liquid lead–tellurium alloys belong to systems with strongly pronounced interaction between the components.

The main goal of the present study was to analytically represent the concentration dependence of the thermodynamic functions of the Pb–Te system, with particular attention paid to the range of dilute solutions of tellurium in liquid lead. The phase diagram of the Pb–Te system is characterized by the formation of a congruently melting PbTe compound (mp 1197 K); there is a eutectic on the tellurium side ($T = 684$ K, $x_{\text{Te}} = 0.891$), and the eutectic is nearly degenerated on the lead side (Fig. 1) [4–6].

The most complete data on the thermodynamic properties of liquid Pb–Te alloys have been obtained by the EMF method, with lead being the potential-forming component [7, 8]. Because the EMF method is the main technique for studying the thermodynamic properties of liquid Pb–Te alloys, it is impossible to experimentally determine the activity of lead with sufficient accuracy in

alloys with very low tellurium content, and the subsequent calculation of the activity coefficient of tellurium with the Gibbs–Duhem equation fails to provide reliable results.

It has been shown previously [9–11] that the Redlich–Kister polynomial with varied number of

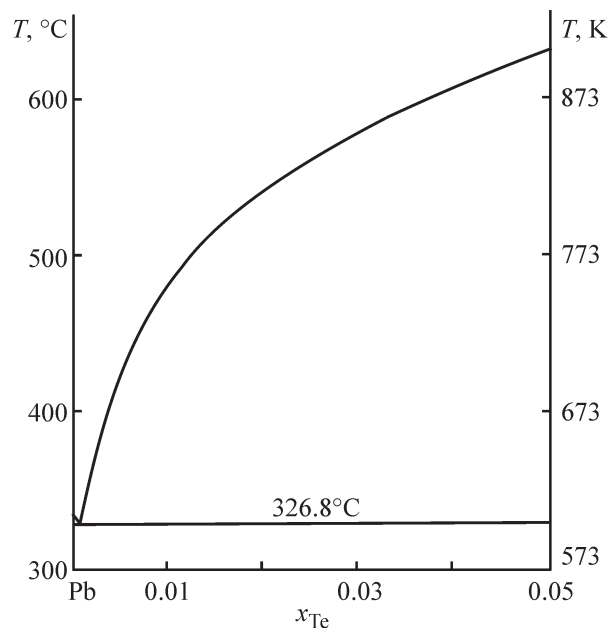


Fig. 1. Lead-rich part of the phase diagram of the lead–tellurium system.

Table 1. Coefficients of Eqs. (1)–(3) and correlation coefficients R^2

Coefficient	Equation		
	(1)	(2)	(3)
b	-6.22189	-6.21618	-6.32184
c	-0.97799	-1.12412	-1.34266
d	3.28053	3.26451	5.61138
e	–	0.41995	0.96701
f	–	–	-4.45224
R^2	0.99867	0.99873	0.99980

coefficients is among the most universal algebraic expressions for describing the concentration dependence of thermodynamic functions in systems with any type of interaction between the components. The concentration dependence of the dimensionless Q function is mostly described at a fixed temperature by polynomials with three, four, or five coefficients:

$$Q = \Delta G^{\text{ex}}/RT = x(1-x)[b + c(2x-1) + d(2x-1)^2], \quad (1)$$

$$Q = x(1-x)[b + c(2x-1) + d(2x-1)^2 + e(2x-1)^3], \quad (2)$$

$$Q = x(1-x)[b + c(2x-1) + d(2x-1)^2 + e(2x-1)^3 + f(2x-1)^4], \quad (3)$$

where ΔG^{ex} is the integral molar excess Gibbs energy

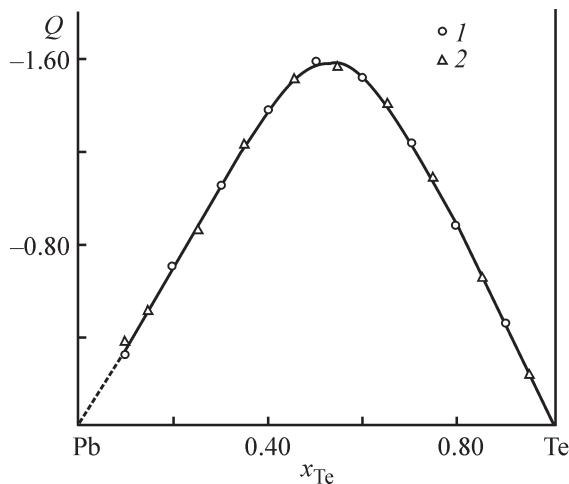


Fig. 2. Dependence of the dimensionless Q function on composition of the lead–tellurium system at 1200 K. (1) Calculated from the experimental data [7] and (2) described with the use of polynomial (3).

for a Pb–Te liquid alloy, and x is the molar fraction of tellurium in the melt (x_{Te}).

The results obtained in calculating the coefficients of Eqs. (1)–(3) at 1200 K on the basis of the experimental data from [7] are listed in Table 1.

The processing was made with values of the Q function at $0.1 \leq x \leq 0.95$ (15 compositions). It can be seen from the correlation coefficients that all the three equations satisfactorily describe the experimental data. As an example, Fig. 2 compares the values calculated for the Q function from the experimental data [7] with those corresponding to polynomial (3).

According to [7], the activity coefficients of lead, γ_{Pb} , in the lead-rich part of the Pb–Te system are 1.004 ($x_{\text{Pb}} = 0.90$), 1.008 ($x_{\text{Pb}} = 0.85$), 1.005 ($x_{\text{Pb}} = 0.80$). This is indicative of very small positive deviations from the Raoult law. Close values of γ_{Pb} were reported in [8] for 1123 K: 1.017 ($x_{\text{Pb}} = 0.90$) and 1.027 ($x_{\text{Pb}} = 0.80$). According to the Gibbs–Duhem equation written as

$$x_{\text{Pb}}(\partial \ln \gamma_{\text{Pb}} / \partial x_{\text{Te}}) + x_{\text{Te}}(\partial \ln \gamma_{\text{Te}} / \partial x_{\text{Te}}) = 0, \quad (4)$$

it would be expected for tellurium dissolved in liquid lead that deviations from the Henry law are at a minimum.

The experimental dependence of $\ln \gamma_{\text{Pb}}$ on the alloy composition [7] and the similar dependence for $\ln \gamma_{\text{Te}}$,

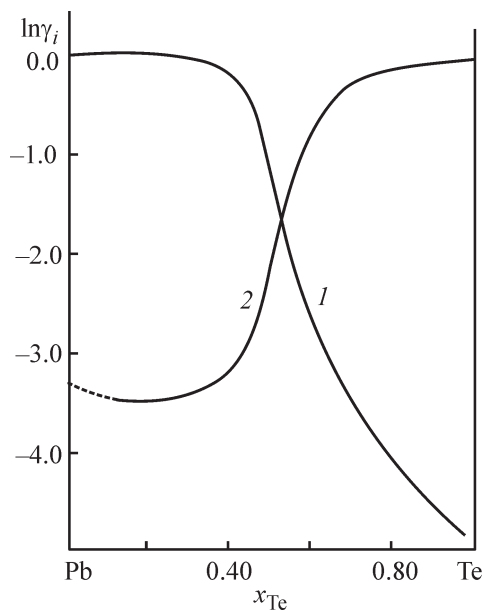


Fig. 3. Isotherms of the logarithm of the activity coefficient of (1) lead and (2) tellurium at 1200 K.

calculated from these data by the Gibbs–Duhem equation, are presented in Fig. 3. The data do not cover the composition range adjacent to lead ($x_{\text{Te}} \leq 0.10$). It is known that the analytical representation of the concentration dependence of the Q function with polynomial or other algebraic expressions makes it possible to estimate the activity coefficients of the components at the infinite dilution ($\ln \gamma_i^\infty$) and to extrapolate the experimental data to the range of dilute solutions [12]. However, the specificity of systems with strong interaction between their components and, ultimately, the rather extended composition ranges with the minimum deviations from the limiting laws manifests itself for the Pb–Te system. In this case, the dependence of the Q function on the alloy composition is noticeably affected in the range of dilute compositions adjacent to lead by the number of parameters in the polynomial being used. This is well seen from the values of the Q function in Table 1 and from Fig. 4 illustrating the tabulated data. The influence exerted by the number of coefficients in Eqs. (1)–(3) on Q is manifested in the tellurium-lean range of compositions ($x_{\text{Te}} \leq 0.15$), this difference being negligible for tellurium richer alloys.

Previously, a dependence of this kind of the Q function on the number of coefficients in the Redlich–Kister polynomial in the range of dilute solutions has been observed in the lead–selenium system that is close in the nature of deviations from the ideal behavior [13]. Even being not too significant, the discrepancies in the values of the Q function strongly affect the estimated limiting activity coefficient γ_{Te} of tellurium dissolved in liquid lead. By definition,

$$Q = x_{\text{Pb}} \ln \gamma_{\text{Pb}} + x_{\text{Te}} \ln \gamma_{\text{Te}}. \quad (5)$$

According to the general thermodynamic relations [10]:

$$\ln \gamma_{\text{Te}} = Q + (1 - x_{\text{Te}}) \left(\frac{\partial Q}{\partial x_{\text{Te}}} \right)_T. \quad (6)$$

Substitution of the expressions for Q from Eqs. (1)–(3) and, accordingly, the quantities $(\partial Q / \partial x_{\text{Te}})_T$ makes it possible to obtain for the limiting values of the activity coefficients of tellurium ($\gamma_{\text{Te}}^\infty$, $x_{\text{Te}} \rightarrow 0$) the following dependences:

$$\ln \gamma_{\text{Te}}^\infty = b - c + d, \quad (7)$$

$$\ln \gamma_{\text{Te}}^\infty = b - c + d - e, \quad (8)$$

$$\ln \gamma_{\text{Te}}^\infty = b - c + d - e + f. \quad (9)$$

This gives, on the basis of the data in Table 1, the following values of $\ln \gamma_{\text{Te}}^\infty$: -1.96337 , -2.24751 , -4.78705 . Accordingly, the values of $\gamma_{\text{Te}}^\infty$ are found to be 0.1404, 0.1057, and 0.0083.

Let us consider how the function $Q/x_{\text{Pb}}x_{\text{Te}}$ depends on the alloy composition on the basis of the available experimental data [7]. It follows from Eq. (5) that

$$Q/x_{\text{Pb}}x_{\text{Te}} = \ln \gamma_{\text{Pb}}/x_{\text{Te}} + \ln \gamma_{\text{Te}}/x_{\text{Pb}}. \quad (10)$$

At $x_{\text{Te}} \rightarrow 0$ ($x_{\text{Pb}} \rightarrow 1$), $\gamma_{\text{Te}} \rightarrow \gamma_{\text{Te}}^\infty$, and $\gamma_{\text{Pb}} \rightarrow 1$, Eq. (1) takes the form

$$(Q/x_{\text{Pb}}x_{\text{Te}})_{x_{\text{Te}} \rightarrow 0} = \lim_{x_{\text{Te}} \rightarrow 0} (\ln \gamma_{\text{Pb}}/x_{\text{Te}}) + \ln \gamma_{\text{Te}}^\infty. \quad (11)$$

Evaluation of indeterminate forms with consideration for Eq. (4) suggests that, at $x_{\text{Te}} = 0$ ($x_{\text{Pb}} = 1$), the first term in the right-hand part of Eq. (11) is zero [10]. Then, this equation takes the form

$$(Q/x_{\text{Pb}}x_{\text{Te}})_{x_{\text{Te}} \rightarrow 0} = \ln \gamma_{\text{Te}}^\infty.$$

It can be seen in Fig. 5 that a rather arbitrary extrapolation of the function $Q/x_{\text{Pb}}x_{\text{Te}}$, calculated from the available experimental data [7], yields $\ln \gamma_{\text{Te}}^\infty =$

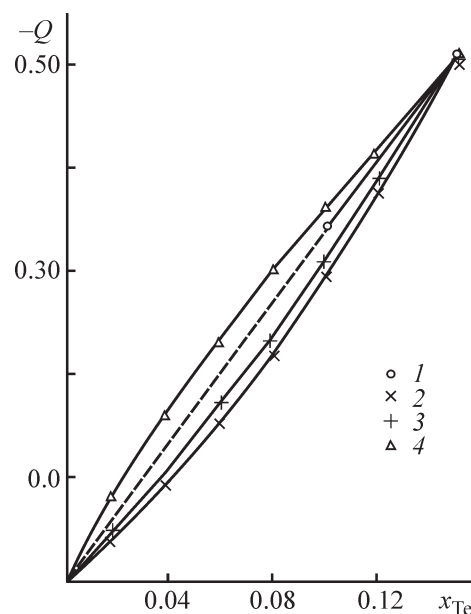


Fig. 4. Dependence of the Q function on composition of dilute solutions of tellurium in liquid lead. (1) Calculated from the experimental data [7] and described with the use of (2) polynomial (1), (3) polynomial (2), and (4) polynomial (3).

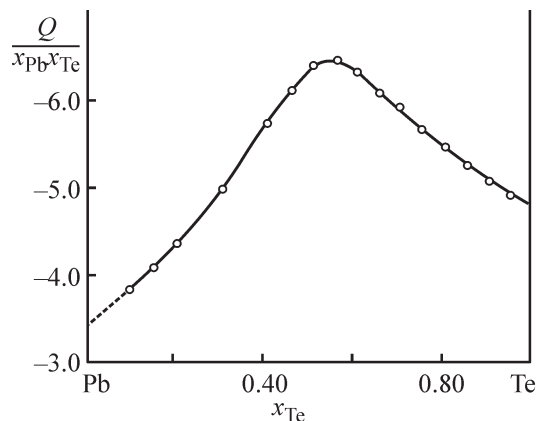


Fig. 5. Dependence of $Q/x_{\text{Pb}}x_{\text{Te}}$ on composition of the Pb–Te alloy, calculated from the data of [7].

–3.45 and $\gamma_{\text{Te}}^{\circ} = 0.0317$. It can be seen in Fig. 4 that all the discrepancies between the values of the $Q/x_{\text{Pb}}x_{\text{Te}}$ function calculated from the experimental data and by polynomials (1)–(3) are localized within the range of compositions adjacent to pure lead: $0 \leq x_{\text{Te}} \leq 0.10$. These discrepancies lead to so different values of $\ln \gamma_{\text{Te}}^{\circ}$.

As already noted, a large degree of order is observed for the Pb–Te system in the liquid state, which enables its thermodynamic description in terms of the model of an ideal associated solution [9, 10, 14]. The presence in the system of only a single symmetrically built intermetallic compound (AP type) makes it possible to restrict the consideration to only a single PbTe associate. The analytical representation of the Q function and, accordingly, of other thermodynamic functions strongly simplifies calculations [9, 10]. The following standard

Table 2. Values of the Q function in Pb–Te liquid alloys at 1200 K in the range of low tellurium contents

x_{Te}	Equation (1)	Equation (2)	Equation (3)	Input data
0.02	–0.0443	–0.0490	–0.0822	–
0.04	–0.0977	–0.1054	–0.1643	–
0.06	–0.1591	–0.1684	–0.2326	–
0.08	–0.2271	–0.2368	–0.3098	–
0.10	–0.3006	–0.3098	–0.3578	–0.3445
0.12	–0.3784	–0.3886	–0.4193	–
0.15	–0.5011	–0.5067	–0.5068	–0.5194

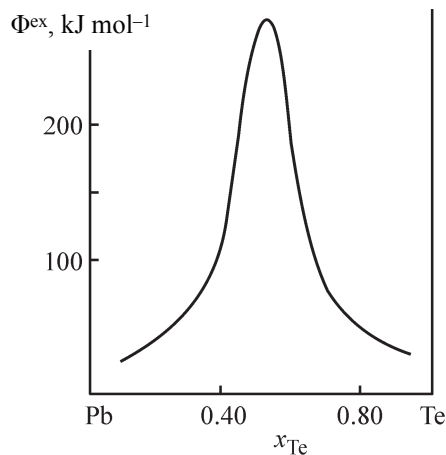


Fig. 6. Dependence of the excess stability Φ^{ex} on composition of the Pb–Te alloy, calculated by polynomial (3).

characteristics were obtained for the PbTe associate at a temperature of 1200 K: $\Delta G^{\circ} = -42.7 \text{ kJ mol}^{-1}$ and $\Delta H^{\circ} = -56.3 \text{ kJ mol}^{-1}$. According to [15], another method of calculation from the results of other experimental studies at 1100 K yielded for PbTe associates somewhat different characteristics: $\Delta G^{\circ} = -47.9 \text{ kJ mol}^{-1}$ and $\Delta H^{\circ} = -56.1 \text{ kJ mol}^{-1}$.

The analytical representation of the Q function and, accordingly, of the integral molar excess Gibbs energy substantially improves the calculation accuracy of the Darken excess stability function [10]:

$$\Phi^{\text{ex}} = (\partial^2 \Delta G^{\text{ex}} / \partial x_{\text{Te}}^2)_T.$$

The results of this calculation are presented in Fig. 6.

CONCLUSIONS

(1) It was shown that Redlich–Kister polynomials with varied number of coefficients (3, 4, 5) can be used to describe for liquid alloys of the lead–tellurium system (1200 K) the concentration dependence of the Q function ($\Delta G^{\text{ex}}/RT$) with large correlation coefficient $R^2 \geq 0.9985$. Raising the number of coefficients (from 3 to 5) makes the correlation coefficient only slightly larger.

(2) The lead–tellurium system with a single symmetrically built compound PbTe belongs to systems with a pronounced structural order in the liquid state and has rather large composition ranges in which the limiting solutions are obeyed for dilute solutions with an acceptable accuracy. It was shown that it is not a good idea to calculate the limiting activity coefficients of the

components in systems of this kind by using the values of the parameters of the polynomial equations.

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