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Polyassociative thermodynamical model of A^2B^6 semiconductor melt and P - T - X equilibria in Cd-Hg-Te system: 1. Phase equilibria in initial two-component systems. Hg-Te system

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Abstract. In the framework of the theory for associated solutions comprising several complexes of various compositions in a liquid phase, analyzed are phase equilibria in Cd-Hg-Te systems. Checking this theory as to the description of phase equilibria in a system as well as a search of model thermodynamic parameters were performed by the way of sequential computer processing the respective experimental results for initial two-component materials. Hg-Te system was chosen as the first model one. It was ascertained that HgTe, HgTe₂ and Te are dominating complexes in the liquid phase of this system. Determined were the complex-creative parameters in the liquid phase. As to P - T - X equilibria in Hg-Te system, we reached a satisfying accordance between calculation and experimental data.

Keywords: polyassociative thermodynamical model, phase equilibrium.

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In the first approximation, the thermodynamical description of the growing process in the case of single crystals and films is based on the data upon their phase equilibria in the system or, in the same sense, upon data of their state diagram. The main works devoted to phase equilibria in A^2B^6 semiconductor systems are the following [1-3].

In these investigations, authors analyzed experimental results concerning this topic, considered some prominent features of phase equilibria. To these, first of all, they related the presence of the sharp singular peak inherent to liquidus lines at the compound melting temperature (it is clearly pronounced in Cd-Te system and rather weakly in Hg-Te one), essential asymmetry of liquidus lines characteristic to an equiatomic composition in state diagram ranges enriched by metal and metalloid components (Fig. 1). It is noteworthy that high volatility of both components is the distinctive feature of A^2B^6 semiconductor state diagrams. The latter essentially complicates a thermodynamical analysis of the system, as it assumes simultaneous consideration of both the state of crystal with its melt equilibrium and the melt with its gas phase composed of two volatile components.

The most complete thermodynamical description of A^2B^6 systems was obtained using the theory of associated solutions [1-3]. The only allowance upon weak dissociation of these compounds during their melting as well as the presence of stable complexes with equiatomic composition in the liquid phase enabled to explain arising the singular maxima in solubility curves and reach quantitative correspondence between calculations dealing with compositions of equilibrium phases in these systems.

When describing phase equilibria in Hg-Te and Cd-Te systems, the main liquid-phase associates in [1-3] were Hg-Te and Cd-Te complexes, respectively. At the same time, associates of this composition, in principle, cannot provide asymmetry of the liquidus curve as to a mean composition of the melt in the diagram state regions enriched by metal and metalloid components of the given compound. This circumstance resulted in necessity for authors of [1-3] to complicate their thermodynamical model of the melt structure using a subregular approximation of the simple solution theory [4] for modelling interaction of free components with the associate. The offered rather complicated thermodynamical construction enabled to achieve highly adequate description of

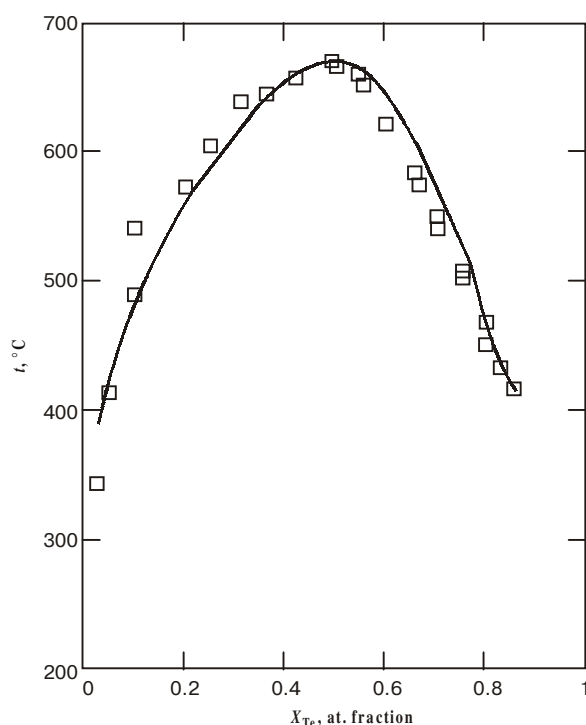


Fig. 1. Liquidus of Hg-Te system. Experimental data from [14,15].

experimental results as to the phase equilibria in Hg-Te and Cd-Te systems. However, the number of fitting parameters for the model, direct determination of which is a difficult task, increased up to 12 for the alone two-component system [1-3]. To compare, it should be noted that for description of phase equilibria using a quasi-regular approximation of the theory for simple solutions in A^3B^5 semiconductor systems, only two fitting parameters are sufficient [11]. As a consequence of the considerable amount of model parameters, there arises cumbersome of its mathematical interpretation, laboriousness in searching model parameters, difficulties in their theoretical treatment. However, the main deficiency of this approach is an essential growth of the fitting parameter number when proceeding to a description of phase equilibria in three- and multi-component systems. Thus, to describe the state diagram for the ternary system Cd-Hg-Te [1-3], it was necessary to use 26 parameters, while for the quaternary systems this number will become very large. Obviously, in the latter case, one can say about transformation of the rigorously determined thermodynamical model for solution into some imitational one, when, through the large number of parameters, the model converts into the pure statistical one having a regression type.

Currently, a solution of this task to describe complex semiconductor systems is related to application of thermodynamical models that are able to account for the presence of several associates with various compositions in interacting phases (the so-called "polyassociative model") [5-7]. Indeed, if temperature dependences of creation con-

stants for liquid-phase associates differ, then, with temperature changing along the liquidus line, their concentrations will change in different ways. It should develop as a result of a concentration dependence for free mixing energy in the model of subregular solution and influence on symmetry of the state diagram as to the melt equiatomic composition. These ideas were realized by us in [5] when analyzing phase equilibria in magnetic semiconductor systems and offered for applying them in A^2B^6 systems [6,7]. As a considerable advantage of this approach, it is worth to recognize that for a thermodynamical description of the melt structure, the ideal approximation of the theory for polyassociative solutions is, as a rule, sufficient [5-7].

In this cycle of investigations using the model of polyassociative solutions with several complexes in the liquid phase, we performed an analysis of P - T - X equilibria for the three-component solid solution $Cd_xHg_{x-1}Te$ and binary systems creating it. To its base, we put the assumptions about the melt thermodynamical structure for the analyzed system, which were mentioned in [5-7]. To solve the set problem, it is necessary to previously carry out the P - T - X analysis of equilibria in initial two-component systems. It will enable both to argue applicability of the mentioned theoretical model conceptions of the melt structure to description of A^2B^6 system state diagram and to determine thermodynamical parameters for complex creation in initial the most simple melts.

As the first model system necessary to make the state diagram for the three-component solid solution $Cd_xHg_{x-1}Te$, in this work we chose Hg-Te system. It is this compound that is provided by reliable experimental data both upon system liquidus and partial pressures of each melt component in enriched and exhausted parts of the state diagram. It enabled to critically estimate both possibilities of the polyassociative solution model and the prospect to apply it when describing equilibria in multi-component A^2B^6 systems over the whole area of the state diagram.

It is noteworthy that rather thoroughly investigated in experiments Cd-Te system is less suitable for solution of this principle task. It is related with the fact that the component vapor pressure over the melt in this system is sharply decreased with decreasing their solubility [3]. The latter fact results in essential difficulties when experimentally determining component pressures during their changes in a wide range of values. Therefore, to prove some quantitative correspondence between estimations and experimental data over the whole field of the compositional diagram is a rather difficult problem in the case. It leads to necessity to begin this thermodynamical analysis from tailoring the state diagram of Hg-Te system.

Accordingly to the theory of associated solutions with several complexes of different compositions in a liquid phase, interrelation between the total contents of a given component and complexes with it as well as Hg_pTe_q composition has the following form [1,5-7]:

$$\begin{aligned}
 X_{\text{Hg}}G - \sum_{p=0} \sum_{q=0} p x_{\text{Hg}_p\text{Te}_q} &= 0; \\
 X_{\text{Te}}G - \sum_{p=0} \sum_{q=0} q x_{\text{Hg}_p\text{Te}_q} &= 0; \\
 G = 1 + \sum_{p=0} \sum_{q=0} (p+q-1) x_{\text{Hg}_p\text{Te}_q}, & \quad (1)
 \end{aligned}$$

where X_{Hg} , X_{Te} are atomic fractions of mercury and tellurium in the melt and $x_{\text{Hg}_p\text{Te}_q}$ is a molar fraction in the liquid phase, respectively. Indexes p and q change from $p = 0, q = 1$ and $p = 1, q = 0$, which corresponds to free tellurium or mercury as well as to the simplest complexes Te_2 ($p = 0, q = 2$) and HgTe ($p = 1, q = 1$), and then these are increased in accord to growing complexity of the associate composition.

Associate concentrations are related to concentrations of creating them free elements due to the law of mass action:

$$\frac{x_{\text{Hg}}^p x_{\text{Te}}^q}{x_{\text{Hg}_p\text{Te}_q}} = K_{pq}(T), \quad (2)$$

where K_{pq} is the constant of Hg_pTe_q complex dissociation.

In the chosen approximation, partial pressures of tellurium and mercury above the melt can be calculated accordingly to the Raoult-Henry law written with concentrations of free mercury and tellurium atoms in the liquid phase:

$$\begin{aligned}
 p_{\text{Hg}} &= x_{\text{Hg}} p_{\text{Hg}}^0(T); \\
 p_{\text{Te}} &= x_{\text{Te}}^2 p_{\text{Te}_2}^0(T), \quad (3)
 \end{aligned}$$

where p_{Hg}^0 and $p_{\text{Te}_2}^0$ are saturation pressures for mercury and diatomic tellurium at the given temperature. It is implied in the above formulae that atoms of Hg and Te included into the liquid-phase associates do not influence on the vapor pressure in the system. Let us note that, in the whole, semiconductor melt is not an ideal solution of initial components, because of the presence of relatively stable complexes. The term of ideal interaction is used only to describe mixing energy between associates. Therefore, the vapor pressure above the melt in this non-ideal structure allows using just the Raoult-Henry law contrary to the more simple analog that corresponds to a classical ideal solution.

Data concerning values of the saturated pressure for mercury and diatomic tellurium at high temperatures were adopted from [2]:

$$\lg p_{\text{Hg}}^0(\text{atm}) = -\frac{3099}{T} + 4.920; \quad p > 0.1 \text{ atm}$$

$$\lg p_{\text{Te}_2}^0(\text{atm}) = -\frac{5960,2}{T} + 4.7191; \quad p > 723 \text{ K}$$

Expressions (2) and (3) are written using concentrations of the respective melt components, which implies that the associate solution is the ideal one. Although, at the given stage of our analysis, this assumption can be considered as untimely, however, the following calculations will show that in the analyzed situation, like to that for magnetic semiconductors [5], the ideal approximation of the theory is quite sufficient to describe phase equilibria in the system.

Up to date, direct experimental data upon complex creation in Hg-Te melt are absent in the literature. Indirect data upon the contents of the analyzed system melt, namely, that there are at least two complexes of HgTe and Hg_2Te_3 compositions, are obtained in [12]. This conclusion was made by the authors stemming from the dependency of the melt molar volume on temperature and its composition. Taking this into account authors of the paper decided to perform a theoretical search of compositions for the most probable associates. Therefore, Eqs (1) are written in their general form via indexes of associate compositions.

For full description of P - T - X equilibrium in the two-component system, expressions (1-3) should be supplemented by the equation for crystal-melt equilibrium. Accordingly to [8], the expression has the following form:

$$\begin{aligned}
 \Delta S^F (T^F - T) + \Delta C_p + RT \ln \frac{x_{\text{Hg}} x_{\text{Te}}}{x_{\text{Hg}}^{St} x_{\text{Te}}^{St}} + \\
 + \int_T^{T^F} dT \int_T^T \frac{\Delta C_p}{T} dT = 0 \quad (4)
 \end{aligned}$$

$$\Delta C_p = C_{\text{Hg}} + C_{\text{Te}} - C_{\text{HgTe}},$$

where T^F , ΔS^F are, respectively, temperature and melting entropy of the compound. The index St stands for the liquid phase of stoichiometric composition, C_i are molar specific heats of initial elements and compounds.

In this expression, to describe the crystal-melt equilibrium, we used preferentially the crystallization quasi-chemical reaction of the following form: $\text{Hg}(1) + \text{Te}(1) = \text{HgTe}(s)$. Let us note that the description of mercury telluride creation from an associated liquid phase is possible through any set of complexes that are present in it [4]. However, obviousness of the expression [4] and our experience in using calculating algorithms [5-7] show that just usage of concentrations characteristic for free atoms in the melt is the best approach. The double integral in Eq. [4] describes the energy contribution into the total balance of energies in the system, which is conditioned by divergency of specific heats for the compound and its initial components in the melt at high temperatures.

As initial parameters, when describing the melting process in these calculations, we took the following values for temperature and melting entropy: $T^F = 943.1 \text{ K}$, $\Delta S^F = 9.25 \text{ e.o.}$ [9]. The difference between compound element specific heats in the liquid phase and that of crystal was estimated using data [10]. In accord to the data,

the difference analyzed had only weak dependence on temperature. Therefore, on calculating the double integral at the term with $\Delta C_p = \text{const}$, the Eq.(3) takes the final form:

$$\Delta S^F(T^F - T) + \Delta C_p \left[(T - T^F) - T \ln \frac{T}{T^F} \right] + RT \ln \frac{x_{\text{Hg}}^{x_{\text{Te}}} x_{\text{Te}}^{x_{\text{Hg}}}}{x_{\text{Hg}}^{S_t} x_{\text{Te}}^{S_t}} = 0. \quad (5)$$

Accordingly to chosen data, the difference of system component specific heats is equal to $\Delta C_p = 0.98 \text{ cal/mol}\cdot\text{K}$.

At the first stage of our calculations, we searched for the most probable compositions of complicated associates that are present in the liquid phase. Our searching technique was based on the found earlier regularity [6,7] that location of system P - T - X lines has only weak dependence on dissociation constants but very strongly depends on complex compositions. Before starting such estimations, it is necessary to stipulate for reliability criteria of choosing a composition of this or another complex. It becomes actual in view of the fact that using the polyassociative model for structure of liquid phase in the analysis *a priori* allows the presence of a temperature dependence for dissociation constants. It seems obvious from the most common physical conceptions that the total concentration of associates in the melt should decrease with increasing temperature.

If the only complex was present in a liquid phase, as it was considered earlier [1-3], then the enthalpy sign when calculating the dissociation constant accordingly to Eq. (2) should be unambiguously negative, which corresponds to growing the constant with increasing temperature. However, at presence of several associates in the melt, the above statement should be reconsidered to some extent and generalized. Indeed, the requirement of decreasing the concentration of each associate in the melt with increasing temperature seems to be extraordinary stringent. At this stage of the analysis, when an independent theoretical approach to the issue upon energies of creating complexes in Hg-Te liquid phase, it is possible to limit ourselves by the requirement of decreasing concentration for multi-atomic complexes when the concentration of simple complexes grows with increasing temperature in the system. This requirement is not discrepant, although it allows different signs of enthalpy contributions into energy of complex creation. At the same time, the requirement of continuous and monotonic changes in the dissociation constant with temperature remains valid. Abovementioned conceptions served as a base for substantiating the possibility of existence of complexes with one or another complicated composition in Hg-Te melt.

Before considering the results of our numerical analysis aimed to phase equilibria, it is necessary to mark the following feature of solutions for Eqs (1-4). It is related to searching associate concentration in a liquid phase with a stoichiometrical composition, that is $x_i^{S_t}$ parameters.

These parameters, in accord to [6], are determined assuming $x_{\text{Te}}^{S_t} = x_{\text{Hg}}^{S_t} = 0.5$ at. fraction at. part in (1) for each set of K_{pq} values. The latter means that any variation of dissociation constants for any complex needs to correct $x_i^{S_t}$ values. This factor makes estimating procedures for searching location of liquidus lines and respective dissociation constants to be rather cumbersome and laborious.

At the same time, analyzed parameters are in tight relations with pressures of component vapors over the melt with stoichiometric compositions at the compound melting temperature. This limitation essentially simplifies the whole searching procedure because of narrowing the range of $x_i^{S_t}$ changes, and eventually these changes still rather weakly depends on K_{pq} set. The later property of the system (1-3) was used in this work.

Quantitative substantiation of the presence of one or another complicated complex in the melt was started in this work from processing data upon phase equilibria in the part of the state diagram that is enriched by metal. Performed calculations showed that it is possible to attain a correspondence between estimations and experimental data in this compositional range, if one allows the presence of the only simplest HgTe complex in the melt. Principle difficulties became to arise when trying to describe P - T - X equilibria in the state diagram part enriched with tellurium. Estimations of phase equilibria taking into account the only HgTe₂ complex, except HgTe, and then HgTe₃ one, did not provide any success. The analysis made taking into account HgTe_{*m*} ($m = 2,3$) associates and totally bound tellurium into Te₂ associate also did not provide obtaining any correspondence to experimental data, even when using essential variation of dissociation constants.

Accumulated experience in performing calculations made with taking into account all mentioned combinations of complexes in the melt enabled us to make the following conclusion as to the most probable associative composition of liquid phase. In accordance to data obtained, the melt can be represented by, at least, the following combination of associates: free atoms of mercury and tellurium as well as Te₂, HgTe and HgTe₂ complexes. It is this set of complexes that could provide the necessary variation range of the system (1-4) solutions due to changes of K_{pq} around experimental data.

As a result of calculations carried out, we ascertained that the complex HgTe was the dominant one in the liquid phase in the state diagram part enriched by metal. The shape of phase equilibrium lines in its metalloid range depended mainly on dissociation constants for complexes HgTe₂ and Te₂. According to these estimations, Te₂ associates play an important role only with decreasing temperature, when analyzed curves are shifted into tellurium part of the diagram. These temperature tendencies in changing parameters of complex creation became a weighty argument in the final choice of associate compositions as they entirely corresponded to the criterion for free energy temperature dependencies of complex creation, which was mentioned above. Found regularities al-

lowed to formulate the algorithm of the final search for numerical values of dissociation constants. Indeed, it is reasonable in this situation, to find in the first approximation the constant $K(\text{HgTe})$ using data for the state diagram part enriched by metal, while $K(\text{HgTe}_2)$ and $K(\text{Te}_2)$ should be determined using data for the range enriched by tellurium. As the influence of Te_2 associates should develop the most essentially at low temperatures, one can state that, for rough estimation of these parameters, the task of searching them can be separated by several practically independent one to another tasks. Using the mentioned property and method of successive approximations, we found the sought-for temperature dependencies of dissociation constants. Calculations showed that the multi-atomic complex HgTe_2 possess a tendency to dissociation in accord with the expression $K(\text{HgTe}_2) = 7.138 \cdot 10^{14} \times$

$$\times \exp \left[\left(-5.339 \cdot 10^4 + \frac{1.912 \cdot 10^7}{T} \right) / T \right], \text{ while data for } K(\text{HgTe}) \text{ corresponded well to the simple exponential one}$$

$K(\text{HgTe}) = 6.22 \cdot 10^{-3} \exp \frac{3032}{T}$, but the dissociation constant for two-atomic tellurium appeared to be independent of temperature $K(\text{Te}_2) = 5$. Concentration values for mercury and tellurium that provide the stoichiometric composition of the melt and correspond to experimental data as to the component vapor pressure at the melting temperature ($p_{\text{Hg}} = 12.5 \text{ atm}$, $p_{\text{Te}_2} = 1.6 \cdot 10^{-3} \text{ atm}$ [9,14]) were equal to $x_{\text{Hg}}^{\text{St}} = 0.2903 \text{ mol. fraction}$, $x_{\text{Te}}^{\text{St}} = 0.2305 \text{ mol. fraction}$.

In Figs 1–3 shown are results of calculations for liquidus lines as well as tellurium and mercury partial pressures along the line of three-phase equilibrium in the system. We are free to assert that the found set of thermodynamical functions and the model of polyassociative solutions itself, as a whole, provide good correspondence between the theory and experiment. To the least extent, the abovementioned statement concerns data upon the mercury pressure in the Te-rich part of the state diagram (Fig. 2). But even this diversity does not exceed 10...15 K as to the equilibrium temperature, which is, in the same way, suitable for thermodynamical calculations.

It is also worth to note that some difficulties in the theoretical description of the mercury equilibrium pressure above the melt were mentioned in [1-3]. In these works, to reach a satisfactory correspondence to experiment in view of the analyzed parameter, authors could manage only when assuming an essential deviation of the gas phase state from the ideal one, when they applied conceptions of this component volatility. Here we should notice that parameters of the chemical reaction providing mercury telluride creation from a gas phase determined in [1-3] directly, through the experimental data upon the equilibrium component pressure above the melt. As a consequence, a mistake in the description of the gas phase state cannot be related to inaccuracy in values of system thermodynamical functions, and, obviously, reflects another

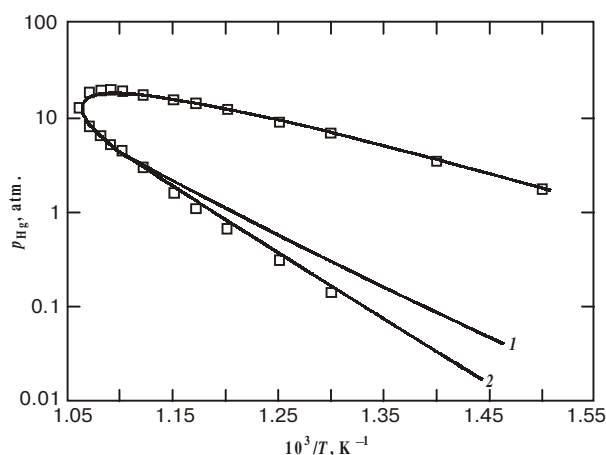


Fig. 2. Dependence of mercury partial pressure on temperature along the three-phase equilibrium line in Hg-Te system. Squares represent experimental from [14], solid lines – calculations for: 1 – $\Delta S^F = 9.25 \text{ e.u.}$; 2 – $\Delta S^F = 14 \text{ e.u.}$

not considered in the model regularities of the system behavior. Fig. 4 shows calculated dependencies of complex concentrations in the melt along Hg-Te system liquidus line. In the framework of the chosen approximation, main tendencies of changes of concentrations inherent to the liquid-phase complexes selected to this analysis seem to be rather natural. As it was expected, the most complicated picture of associate interaction can be observed in Te-rich part of the state diagram. It is the place where Te_2 and HgTe_2 complexes begin to arise in considerable concentrations. In this case, the share of diatomic tellurium complexes begins to influence the liquidus line shape at $x_{\text{Te}} > 0.5 \text{ at. fraction}$ with a monotonic growth of its content in the liquid phase, while the same concentration dependence for HgTe_2 complex has an extremum feature (Fig. 4). Let us note that even at presence of Te_2 and HgTe_2 associates in considerable amounts the most wide-spread complex in the melt is

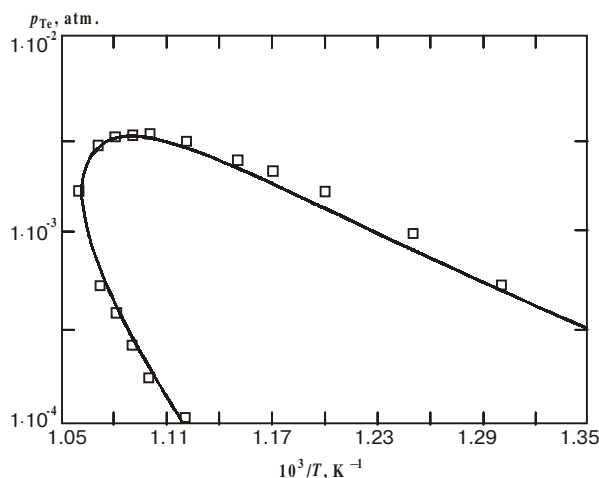


Fig. 3. Dependence of diatomic tellurium partial pressure on temperature along the three-phase equilibrium line in Hg-Te system. Experimental data from [14].

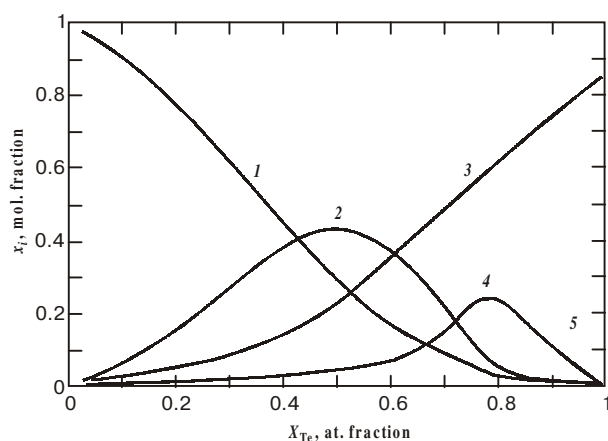


Fig. 4. Dependence of the complex content in liquid phase on the total tellurium concentration in the melt along the three-phase equilibrium line in Hg-Te system: 1 – Hg; 2 – HgTe; 3 – Te; 4 – HgTe₂; 5 – Te₂.

HgTe one, and it is the complex that determines the main parameters of three-phase equilibrium lines in the system. At the same time, it also follows from Fig. 4 that this diatomic complex HgTe cannot provide asymmetry of liquidus lines in metal- and metalloid-enriched parts of the state diagram. This statement results from the symmetry of the calculated dependence for HgTe complex concentration on the tellurium share in Fig. 4 relatively to the melt equiatomic composition. Therefore, to reach the accordance with experimental data, it is necessary to make an assumption about the presence of compound associates in the liquid phase.

In this work, we tried to increase accuracy in description of P - T - X equilibria, especially, relatively to the mercury vapor pressure. It turned out, however, that even essential variation of dissociation constants could not provide any considerable change in P - T dependence behavior in this case. This fact testifies to an essential stability of the model to a choice of its parameters, which is a positive fact. At the same time, for further increase of description reliability, one obviously needs an effective revision of the melt associate composition or application of another ways. Having the aim to increase description adequacy, in the work, we carried out an analysis of the influence of deviation between specific heats of melt and crystal (a factor with ΔC_p) on the change of location of calculated equilibrium lines in the system. Our estimations showed that neglecting the double integral in (4) very weakly influences the calculated lines of P - T - X equilibria. The error in calculations of the liquidus temperature, when using specific heat data from [10], was no more than 1...3 K in dependency on the range of the state diagram. These quantitative corrections are clearly insufficient to avoid the abovementioned inaccuracy in the mercury pressure description.

The only parameter, value of which is not very exactly known, is melting entropy of HgTe compound. This parameter is determined in [9] by statistical process-

ing the experimental data upon phase equilibria in the system. Our experience in processing the data of such experiments with the aim to determine thermodynamical functions of the system [13], even using methods of mathematical statistics, is indicative of low accuracy of results obtained. Therefore, we performed a complex of calculations with various ΔS^F values. It is worth to note here that the change of this model parameter had an essential effect on the calculated mercury vapor pressure in the system. This result is not unexpected. Indeed, when testing the model for simple solutions and describing phase equilibria in Ga-P systems, in [11], to correct calculated data as to the phosphorus pressure along liquidus, authors performed correction of the data upon compound melting entropy. Using the same way and increasing the melting entropy of HgTe up to 14 e.u., we managed with achieving the high degree of adequacy in description of all data set concerning equilibria in the system. Results of these calculations coincide well with the data of Fig. 3 as to the system liquidus and diatomic tellurium vapor pressure as well as correspond to experimental results of Fig. 2 as to the mercury pressure above the melt enriched with tellurium. New corrected values and the look of temperature dependencies of dissociation constants were as follows:

$$K(\text{HgTe}) = 0,1555$$

$$K(\text{HgTe}_2) = 9,4 \cdot 10^{17} \exp \left[\left(6,347 \cdot 10^4 + \frac{2,221 \cdot 10^7}{T} \right) / T \right]$$

$$K(\text{Te}_2) = 5$$

At this stage of theoretical re-estimation of data upon thermodynamical functions of A^2B^6 systems, it is still difficult and premature to prefer melting entropy values found in the work as compared with experimental data [9]. Obviously, only the further analysis of phase equilibria in the framework of polyassociative solution model in such allied systems as Cd-Te and Zn-Te will enable to give an unambiguous answer for the value of this parameter. At the same time, the good correspondence between calculations and experimental data with essential decreasing the parameters of the thermodynamical model when analyzing phase equilibria, can be considered as well argued.

Thus, in the first part of the work, we proved quantitatively applicability of the polyassociative solution model to description of the melt thermodynamical state and to analysis of phase equilibria in Hg-Te system. The following part of the work will be devoted to modelling phase equilibria in Cd-Te system that also comes into Cd-Hg-Te system as the main component, which is under investigation.

References

1. Tse Tung, Ching-Hua Su, Pok-Kai Liao, R.F. Brebrick // *J. Vac. Sci. Technol.* **21**, p.117-124 (1982).
2. R.F. Brebrick // *J. Crystal Growth* **86**, p. 39-48 (1988).

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3. A.S. Jordan // *Metal. Transactions* **1**, p. 239-249 (1970).
4. V.M. Glazov, L.M. Pavlova, *Chemical thermodynamics and phase equilibria* (in Russian). "Metallurgiya", Moscow, 1980.
5. S.A. Lynin, P.P. Moskvina, E.V. Pshenichnov, I.V. Saenko // *Zhurnal Fizicheskoi Khimii* **66**, p. 2310-2315 (1992).
6. V.V. Kuznetsov, K.E. Mironov, P.P. Moskvina. In: *Proceedings of the 4th All-Union Conference "Thermodynamics and Materials Science of Semiconductors"* (in Russian), vol. 2, p. 395. Published by the Moscow Institute for Electron Technique, Moscow, 1989.
7. G.I. Zhovnir L.V. Rashkovetsky, S.V. Kavertsev, P.P. Moskvina. In: *Proc. of the 5th Inter. Conf. „Materials Science & Material Properties for Infrared Optoelectronics"*, p.119, Kyiv, 2000.
8. X. Keycy, M. Panish, *Lasers on heterostructures*, vol. 2, Materials and their operating performances. "Mir", Moscow, 1981.
9. Ching-Hua Su, Pok-Kai Liao, Tse Tung, R.F. Brebrick // *High Temperature Science* **14**, p.181-195 (1981).
10. Handbook for chemists, vol. 1. Ed. by B.P. Nikolsky, O.N. Grigoriev, M.G. Pezin et al. "Khimiya", Moscow, 1962 (in Russian).
11. M.B. Panish // *J. Cryst. Growth* **27**, p.6-20 (1974).
12. V.M. Glazov, L.M. Pavlova // *Zhurnal Fizicheskoi Khimii* **72**, p. 218-224 (1998) (in Russian).
13. V.V. Kuznetsov, P.P. Moskvina, V.S. Sorokin. In: *Proceedings of the 3rd All-Union Conference "Thermodynamics and Materials Science of Semiconductors"* (in Russian), vol. 2, p. 27. Published by the Moscow Institute for Electron Technique, Moscow, 1986.
14. R.F. Brebrick, A.J. Strauss // *J. Phys. Chem. Solids* **26**, p. 989-1002 (1965).
15. J.C. Harman // *J. Electron. Mater.* **9**, p. 945 (1980).