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Thermodynamics of molten K–Te alloys

O Akinlade†

International Centre for Theoretical Physics, Trieste, Italy

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Abstract. The quasi-chemical model is used to explain the free energy of mixing, heat of mixing, excess entropy of mixing and chemical short-range order parameter for potassium–tellurium as functions of concentration. The study reveals that the constituent metals of these alloys undergo major structural changes in atomic and electronic character on alloying. The concentration-dependent behaviour of thermodynamic properties on mixing occurs because of preferential ordering of unlike atoms as nearest neighbours which could simultaneously be understood within the complex formation model. Analysis of the results further suggest that heterocoordination with the formation of K_2Te_3 is likely to exist in the melt. It is concluded that a reasonable degree of chemical order may exist in the whole concentration range, being greatest at about 50 at.% K.

1. Introduction

In spite of the fact that its observed phase diagram is as simple as those observed in other binary alloys [1, 2], the molten potassium–tellurium system shows much anomalous behaviour which makes it interesting from a theoretical viewpoint. As is well known, liquid K is a simple metal. Liquid Te on the other hand has been the subject of intense study [3, 4] because of the anomalous temperature dependence of its electronic and thermodynamic properties. Essentially it is recognized that most of its properties in the molten state are half-way between those of a semimetal and a semiconductor [4]; thus its essential features have been explained on the basis [1, 5, 6] that Te gradually changes from a metallic to a non-metallic state with a decrease in temperature.

Tellurium, as a solid at room temperature, has [1] a conductivity similar to those of semiconductors, while in the molten state the average conductivity is $2500 \Omega^{-1} \text{ cm}^{-1}$, which is typical of a metal. The structure of liquid Te [7, 8] may be seen as consisting of hexagonal rings joined by covalent bonds in the presence of a metallic electron gas. With increasing temperature, the fraction of hexagonal rings in the structure increases, thus leading to a more metallic behaviour.

With the points mentioned above and the fact that there is a large electronegativity difference between potassium and tellurium the observed properties of the molten K–Te system are not unexpected. Purely on the basis of the electronegativity difference, one expects a strong tendency for compound formation as exhibited by K–Pb and Rb–Pb alloys. For these compound-forming alloys, an *ab initio* study of the thermodynamic properties cannot be undertaken at present for reasons which have been highlighted previously [9]. What is most appropriate is to use an empirical approach. The quasi-chemical theory [14],

† Permanent address: Department of Physics, University of Agriculture, Abeokuta, Nigeria.

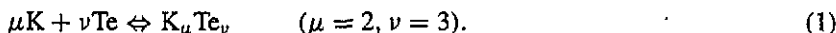
which has been used extensively [9–13] to explain the asymmetry in the thermodynamics of such compound-forming alloys, has been applied here.

Our interest in K–Te stems from the analysis of its experimental thermodynamic data [1]. The result shows that the alloy in the molten state has an excess stability of 520 kJ at its equiatomic composition, the highest known value at such a composition; the entropy of mixing at 55 at.% K is less than $-15 \text{ J mol}^{-1} \text{ K}^{-1}$. This is the lowest known entropy of mixing for any alloy system [1]. This, coupled with the recent availability of experimental data [1] on its thermodynamic properties, makes a theoretical investigation worthwhile.

The layout of our paper is thus as follows. In the next section, we highlight the formalism within the quasi-lattice model needed for our calculations. In section 3 we discuss the calculated results on the free energy of mixing, activity, long-wavelength limit of concentration fluctuations, short-range order parameter, heat of mixing and entropy of mixing compared with experiment where available. Section 4 summarizes our major conclusions.

2. Formalism

In applying the quasi-chemical model, we start by assuming that our binary alloy consists of a pseudo-ternary mixture of K atoms, Te atoms and $K_\mu\text{Te}_\nu$ complexes. $K_2\text{Te}_3$ appears to be [1] a well defined solid; it is likely that such associates in some form also exist in the liquid phase. Accordingly, we presume that the number ν of K atoms and the number μ of Te atoms are energetically favoured to form chemical complexes:



Thus, if there are in the solution n_1 g mol of K atoms, n_2 g mol of Te and n_3 g mol of $K_2\text{Te}_3$, we have from conservation of atoms

$$n_1 = c - 2n_3 \quad n_2 = (1 - c) - 3n_3. \quad (2)$$

The total number $n = n_1 + n_2 + n_3 = 1 - 4n_3$, c being the concentration of Te. In general, the total number of particles in the binary solution, i.e. atoms and molecules, is given by nN , where N is the total number of atoms. In the present work we take $N = 1$; this results in $n = 1$ mol. Most of the expressions given here are the particular case ($\mu = 2$; $\nu = 3$) of more general cases given in [14].

The free energy of mixing of the binary alloy can be expressed as

$$G_M = -n_3g + RT(n_1 \ln n_1 + n_2 \ln n_2 + n_3 \ln 5n_3) + \sum_{i < j} n_i n_j V_{ij}. \quad (3)$$

Here g is the formation energy of the complex and thus the term $-n_3g$ represents the lowering of the free energy of mixing due to the formation of complexes in the alloy. The V_{ij} ($i, j = 1, 2, 3$) are the interaction energies and by definition independent of concentration, although they may depend on temperature and pressure. The equilibrium values of n_3 can be obtained via the condition

$$(\partial G_M / \partial n_3)_{T, P, C} = 0. \quad (4)$$

Using equations (3) and (4), one can show that the equilibrium values of the n -values can be obtained from

$$n_1^2 n_2^3 = 5n_3 \exp(-4) \exp(Y - g/RT) \quad (5)$$

where

$$Y = [(n_1 - 2n_3)V_{13} + (n_2 - 3n_3)V_{23} - (2n_2 + 3n_1)V_{12}]/RT. \quad (6)$$

The expression for the free energy of mixing (equation (3)) can be used to provide an expression for the activity a_K of the K atom as follows:

$$RT \ln a_K = (\partial G_M / \partial N_K)_{T,P,N_{Te}} = G_M + (1-c)(\partial G_M / \partial c)_{T,P,N}. \quad (7)$$

With a_K given by equation (3), one obtains

$$\ln a_K = 1 - n + \ln n + \ln n_1 + \frac{n_3 V_{13}}{RT} + \frac{n_2 V_{12}}{RT} - \sum_{i < j} \sum \frac{n_i n_j V_{ij}}{RT}. \quad (8)$$

The concentration fluctuations $S_{cc}(0)$ in the long-wavelength limit is in general given by

$$S_{cc}(0) = RT / (\partial^2 G_M / \partial c^2)_{T,P}. \quad (9)$$

For compound-forming alloys (such as those that we are considering here) and recognizing that the coordination number Z for the alloy is not known, the expression for $S_{cc}(0)$ can be written in a more general form [10] appropriate for strongly interacting systems:

$$S_{cc}(0) = \frac{\zeta_{cc}}{1 + \Lambda \zeta_{cc}}. \quad (10)$$

In equation (10),

$$\zeta_{cc} = \left(\sum_{i=1}^3 \frac{(n'_i)^2}{n_i} - \frac{\frac{1}{2} Z \delta^2 (n'_3)^2}{\phi} \right)^{-1} \quad (11)$$

and

$$\Lambda = \frac{2}{\phi RT} \sum_{i < j} \sum V_{ij} \left(n'_i n'_j + \frac{\delta n'_3 (n'_i n_j + n_i n'_j)}{\phi} + \frac{\delta^2 (n'_3)^2 n_i n_j}{\phi^2} \right). \quad (12)$$

In equations (11) and (12)

$$\delta = 8/Z \quad \phi = 1 - \delta n_3. \quad (13)$$

The prime on the n denotes its first derivative with respect to c .

Less general expressions can be found in [14]; we note, however, that the difference incorporated here is only in the dependence of $S_{cc}(0)$ on the coordination number Z ; for $Z \rightarrow \infty$, equations (11) and (12) reduce to those in [14]. One notes from the above that all the parameters needed to determine $S_{cc}(0)$ must have been computed previously.

To measure the degree of order in such molten alloys within the present framework, one can compute the Warren–Cowley [15, 16] short-range order parameter α_1 . Experimentally, α_1 can be determined from measured structure factors; however, it is usually very difficult [17, 18] to do this from a practical point of view. Theoretically α_1 can be evaluated from knowledge of $S_{cc}(0)$ using

$$\alpha_1 = \frac{S - 1}{[S(Z - 1) + 1]} \quad (14)$$

Here

$$S = S_{cc}(0)/S_{cc}^{id}(0). \quad (15)$$

Other thermodynamic quantities which might be of interest and can be calculated are the heat H_M of mixing and the excess entropy S_M^E of mixing. H_M is given by

$$H_M = G_M - T(\partial G_M/\partial T)_P. \quad (16)$$

From equations (3) and (16), we obtain

$$H_M = -n_3 \left(g - T \frac{\partial g}{\partial T} \right) + \sum_{i < j} \sum n_i n_j \left(V_{ij} - T \frac{\partial V_{ij}}{\partial T} \right) \quad (17)$$

and hence the entropy of mixing

$$S_M = (H_M - G_M)/T. \quad (18)$$

The excess entropy S_M^E of mixing can be calculated using the expression

$$S_M^E = S_M + R[c \ln c + (1 - c) \ln(1 - c)]. \quad (19)$$

3. Results and discussion

The essential equations have been given in the preceding section; here we give details of our results and a brief discussion. For brevity, this section is subdivided. In order to proceed, the quasi-chemical theory requires that we first determine the energy parameters g and V_{ij} for the alloy. At this juncture, we note that molten K–Te has certain peculiarities when compared with most other alloys, notably as follows. Firstly the experimental value of $\ln \gamma_K$ (where γ_K is the activity coefficient of K; $a_K = c\gamma_K$) is as low as [1] -29.544 at $c_K = 0.001$; this is the least value for any alloy in the current literature. Experimentally $G_M^{\min}/RT \simeq -13.4$, compared with about -3.8 in Tl–Te alloys [14] and about -2.4 for K–Pb [9]; both alloys are considered to be strongly interacting.

The calculation thus proceeds as follows: an approximate value of g is calculated at the chemical concentration $c = \mu/(\mu + \nu)$ using $G_M \simeq -n_3 g$; the energy parameters V_{12} , V_{13} and V_{23} are then fitted and fine tuned in order to reproduce the experimentally measured concentration dependence of the free energy of mixing. The energy parameters g and V_{ij} evaluated for K–Te are thus

$$g/RT = 47.8 \quad V_{12}/RT = -25.2 \quad V_{13}/RT = -166 \quad V_{23}/RT = -13.4. \quad (20)$$

Table 1. Activity $\ln a_K$ of K-Te molten alloys at 773 K.

| c | $\ln a_K$ | |
|------|------------|--------------|
| | Calculated | Observed [1] |
| 0.06 | -31.467 | -32.528 |
| 0.12 | -29.821 | -31.124 |
| 0.18 | -28.582 | -29.842 |
| 0.24 | -27.523 | -29.196 |
| 0.30 | -26.550 | -27.898 |
| 0.36 | -25.605 | -26.540 |
| 0.42 | -24.616 | -24.863 |
| 0.48 | -23.386 | -22.824 |
| 0.52 | -21.162 | -21.267 |
| 0.60 | -14.412 | — |
| 0.66 | -10.252 | — |
| 0.72 | -6.820 | — |
| 0.78 | -4.100 | — |
| 0.84 | -2.079 | — |
| 0.90 | -0.752 | — |
| 0.96 | -0.109 | — |

The values are obviously high compared with those existing in the literature using the quasi-chemical theory [9–13]; however, they look feasible in the light of the two previous remarks made on observed thermodynamic results. Figures 2 and 3 show that our energy parameters reproduce remarkably well the concentration dependence of the free energy of mixing; the results for the activity in table 1, although not as good as those for G_M/RT (figure 2), are also reasonable. We note that experimental results are only available for the concentration range $0 \leq c_K \leq 0.52$; beyond this limit, one can only make predictions.

From a comparison with the results in [14], it is obvious that the value of g/RT which has physical significance is very high and indicates that K-Te for most concentrations is a strongly interacting system. The calculated G_M/RT curve is asymmetric with a minimum at $c_K \simeq 0.58$; a similar behaviour has been found for all other thermodynamic quantities. This is an interesting feature normally observed in other strongly interacting systems [19]. We explain this feature as being a result of two factors: the size effect (the ratio of the atomic volume of K to Te) and the large difference between the electronegativity of the components of the alloy, namely $E_{Te} = 3.59$ while $E_K = 0.82$.

The phase diagram for the K-Te molten alloy as obtained from EMF measurements [1] is presented in figure 1. It follows that, if the energy parameters are evaluated and suitable values are chosen for μ and ν (2 and 3) corresponding to the well defined K_2Te_3 phase in figure 1. With these values of μ and ν equations (2), (5) and (6) can be solved numerically to obtain the values of n_3 , the number of chemical complexes, and thus the values of n_1 and n_2 . The results are plotted in figure 3; we observe that n_3 peaks at the equiatomic composition.

3.1. Concentration fluctuations and the short-range order parameter

Next we look at the concentration-concentration fluctuations in the long-wavelength limit; this is a parameter which has been used extensively [2, 9–12] to study the nature of atomic ordering in molten alloys. The basic idea is that $S_{cc}^{id}(0) = c(1-c)$ is significant in explaining theoretically the degree of interaction in binary mixtures. The fundamental rule is that $S_{cc}(0) \ll S_{cc}^{id}(0)$ is an indication of heterocoordination (preference of unlike atoms to

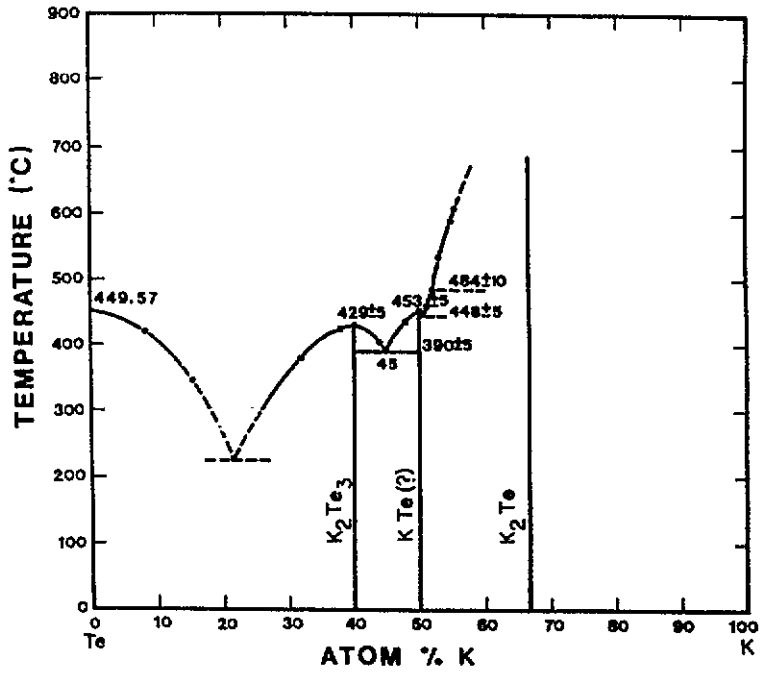


Figure 1. Phase diagram of K-Te alloys [1].

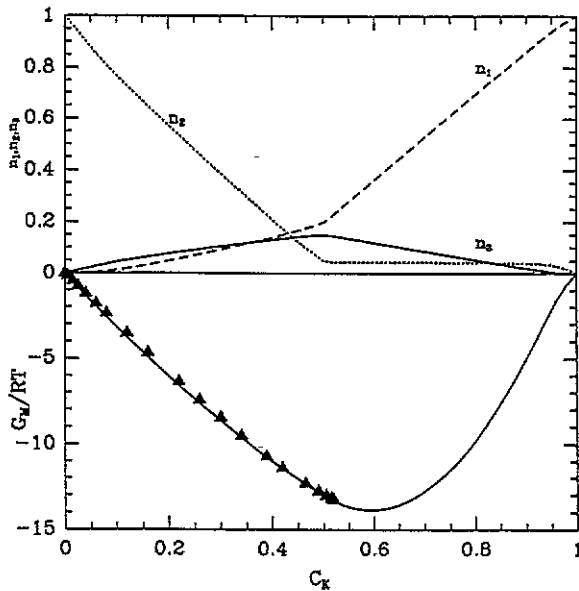


Figure 2. Concentration dependences of n_1 , n_2 and n_3 for K-Te molten alloys, together with the free energy of mixing (—, calculated values; \blacktriangle , experimental values at 773 K).

pair as nearest neighbours) while $S_{cc}(0) > S_{cc}^{id}(0)$ implies a tendency for self-coordination

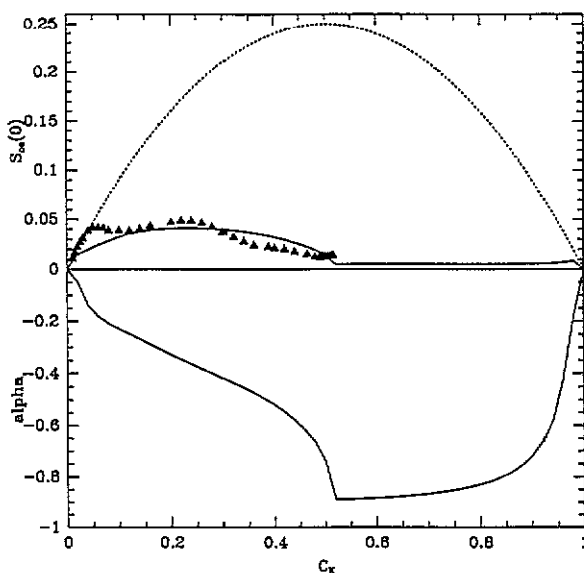


Figure 3. $S_{cc}(0)$ versus concentration for K-Te (....., ideal values; —, calculated values; ▲, experimental values at 773 K) and the calculated Warren-Cowley short-range order parameters alpha.

(preference of like atoms to pair as nearest neighbours) or a tendency for phase separation. In most alloys, it is observed that $S_{cc}(0)$ [10] deviates considerably from the ideal behaviour. It tends to zero for strongly interacting systems while it has intermediate values for weak systems. The position of the $S_{cc}(0)$ versus c curve thus yields information on the nature of the complex formed while its depth signifies strength.

From an experimental point of view, $S_{cc}(0)$ can be determined in two ways. Firstly, it can be found from the thermodynamic relations [20]

$$S_{cc}(0) = RT/(\partial^2 G_M/\partial c^2) = c_K(1 - c_K)/\{c_K[\partial(\ln \gamma_K)/\partial c_K] + 1\} \quad (21)$$

where γ_K represents the activity coefficient of K in the molten alloy. The calculation is usually done (see [9] and references therein) with a least-squares fit to experimental values of $\ln \gamma_K$. A second method, however, exists and is more preferable in the sense that it does not involve the two possible sources of error that could occur in performing a least-squares curve fitting and the attendant differentiation. What one does simply is to express $S_{cc}(0)$ in terms of derived activity coefficients calculated using experimental EMF data and demonstrated graphically in [1] using the definition of the excess stability given by Darken [21]. One can thus express $S_{cc}(0)$ in the form

$$S_{cc}(0) = \frac{RT[c(1 - c)]}{c(1 - c)ES + RT} \quad (22)$$

Thus, once ES is known as in our case, $S_{cc}(0)$ can be calculated. A plot of $S_{cc}(0)$ versus concentration is shown in figure 3 compared with the experimental results from equation (22); the calculated values are obtained from equation (10) with $Z = 12$. It is

obvious from the graph that K-Te is a strongly compound-forming alloy; the calculated $S_{cc}(0)$ does not, however, give too much information when compared with experiment.

Figure 3 indicates a flat region over the concentration range $0.25 < c_K \leq 0.52$ and does not indicate the possible existence of a 1-1 complex KTe as speculated from the phase diagram given in figure 1 [1]. Better insight into the nature of the concentration dependence of compound formation could be obtained by calculating a complementary property α_1 , the Warren-Cowley short-range parameter. For nearest-neighbour sites, it can be defined as

$$\alpha_1 = 1 - P_{AB}/(1 - c) \quad (23)$$

where P_{AB} is the conditional probability of finding a B atom next to a given A atom. From a probabilistic approach, one can easily show that the limiting values of α_1 lie in the range

$$\begin{aligned} \frac{-c}{1-c} \leq \alpha_1 \leq 1 & \quad c \leq \frac{1}{2} \\ \frac{-(1-c)}{c} \leq \alpha_1 \leq 1 & \quad c \geq \frac{1}{2}. \end{aligned} \quad (24)$$

At $c = \frac{1}{2}$, one has $-1 \leq \alpha_1 \leq 1$. The minimum possible value $\alpha_1(\min) = -1$ suggests complete ordering of pairs of nearest neighbours in the A-B configuration while $\alpha_1(\max) = 1$ implies total segregation leading to phase separation. $\alpha_1 = 0$ corresponds to a random distribution. α_1 is computed using equation (14) with $Z = 12$ and the previously calculated $S_{cc}(0)$; the curve is shown in figure 3. It is observed that the α_1 versus c curve is asymmetric and has a minimum value of $\alpha_1 = -0.90$ at $c_K \approx 0.52$; this is comparable with what one expects for a system with complete heterocoordination. Furthermore, one can infer that the Te-rich end of the phase diagram is more ordered than the K-rich end.

We observe that varying the value of Z (the coordination number) only results in changing the depth of the α_1 versus c curve; the general features remain unchanged. To our knowledge, the values obtained for α_1 at equiatomic composition is the least for all the alloys for which the quasi-chemical model has been applied. This indicates that K-Te is a highly ordered system and this deduction is confirmed by derived values of ES [1], which indicates maximum ordering at 12 and 50 at.% K.

3.2. Heat of formation and entropy of mixing

The theoretical expressions given in section 2 have been applied to calculate H_M/RT and the excess entropy of mixing as functions of concentration. It is well known in the theory of binary regular solutions (in the zeroth approximation [22]), or of conformal solutions [23] that the concentration dependence of these quantities can in general be simultaneously fitted with the experimental data only if the interaction parameters are assumed to be temperature dependent. To this end, we have used equation (17) to determine the variation in energy parameters from the experimental values of H_M which can be deduced from [1] and equations (18) and (19) since the excess entropy of mixing are tabulated. The results are

$$\begin{aligned} \partial g/\partial T = -13.22R & \quad \partial V_{12}/\partial T = -2.75R & \quad \partial V_{13}/\partial T = 6.55R \\ \partial V_{23}/\partial T = -4.85R. & & \end{aligned} \quad (25)$$

The computed results for H_M/RT and S_M^E/R are shown in figure 4. It should be noted that our parameters describe to a good extent the concentration dependence of H_M/RT although there are slight discrepancies at $c_K > 0.5$ and this is enhanced in the plot of the excess entropy. Figure 4 indicates that theoretically the entropy is asymmetrical around the equiatomic composition. Generally, however, the values obtained for both thermodynamic quantities agree reasonably well with the experiment.

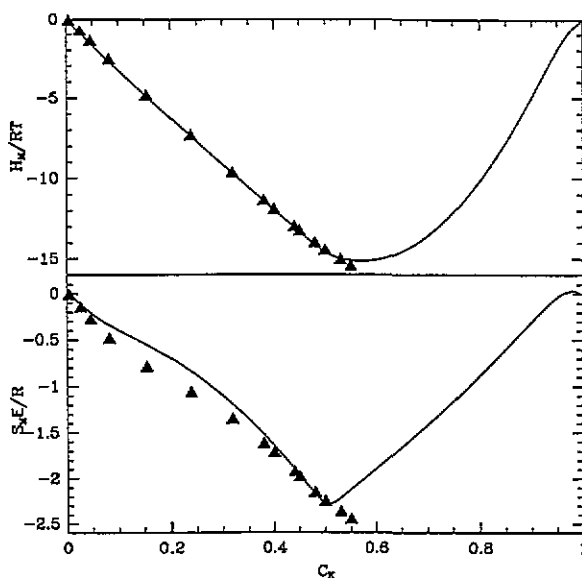


Figure 4. Computed and observed values of the heat of formation and excess entropy of mixing of K-Te molten alloys: —, calculated; \blacktriangle , experiment.

4. Concluding remarks

In the present paper, we have used first-order quasi-chemical theory to provide and in some cases to predict the concentration dependence of various thermodynamic functions such as free energy of mixing, heat of mixing and entropy of mixing of K-Te alloys. The following deductions have been made from our calculations.

The thermodynamic functions computed for K-Te molten alloys show an asymmetric behaviour around the equiatomic composition. By assuming the formation of a K_2Te_3 complex, we reproduce the experimental behaviour of the free energy of mixing; the values obtained for our interaction parameters are relatively high and we explain this on the basis of the fact that K-Te molten alloys have very small values for their observed G_M^{\min}/RT .

Underlying all these calculations is an observation that the energy parameters of K-Te are strongly temperature dependent. Our calculations of $S_{cc}(0)$ and the short-range order parameter indicate that the molten K-Te alloy is highly ordered near its equiatomic composition and this indicates evidence for the possible existence of a KTe solid alloy as speculated in the experimental phase diagram (figure 1). The calculated order parameters show that the Te-rich end of the molten alloy is more ordered than the K-rich end.

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