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Origin of the looped two-melt phase in the liquid S–Te system

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Abstract. Recently established new thermodynamic relations among experimentally available data are used to evaluate the contribution of the structural change in the liquid S–Te system to the Darken stability. The analysis of the Darken stability shows that the unusual looped two-melt phase separation that takes place in a small composition interval well above the liquidus line is a consequence of the change in the local order of the liquid. Delicate balance between the entropy term and the contribution from the structural change realizes this unique two-melt phase separation. This local order change that is expected in a small composition range has actually been observed by neutron diffraction measurements.

1. Introduction

Liquid chalcogenide elements (S, Se and Te) and their mixtures show variety of physico-chemical properties (Gerlach and Gross 1979). Liquid S melts at $T_m = 117^\circ\text{C}$ and undergoes a polymerization transition at 159°C in which a change from ring to long chain molecules takes place. By adding Se, the onset temperature of the polymerization transition shifts to the lower temperatures at the rate of $-5.5\text{ K at.}\%^{-1}$ (Tsuchiya *et al* 1999). Se ($T_m = 220^\circ\text{C}$) keeps its chain structure (divalency) up to above 1000°C and transforms to a denser structure around 1500°C under moderate pressure (Fisher *et al* 1980). Te melts into a liquid with a coordination number slightly larger than 2 that keeps increasing with increasing temperature. In the supercooled state, the coordination number approaches $z = 2$ (Menelle *et al* 1989). The gradual transition from a state with two neighbours to a state with a larger number of first neighbours (referred to as ‘structural change’ in the following) is accompanied by a broad extremum around 356°C in the three thermodynamic response functions (the constant pressure specific heat, thermal expansion coefficient and isothermal compressibility) as a function of temperature (Tsuchiya 1991a) and is the origin of the nonmetal–metal transition (Bichara *et al* 1996). It has been shown that the addition of S or Se stabilizes the low temperature form (divalency) of Te (Thurn and Ruska 1976). Consequently the transition region around the extrema in the thermodynamic response function shifts to the higher temperatures (Tsuchiya 1991b, 1994).

Although the overall dependence on composition and temperature of physico-chemical properties is much the same, the stability of mixture is quite different in S–Te and Se–Te systems. The phase diagram of the S–Te system is shown in figure 1 (Tsuchiya 1992). The liquid S–Te system has an unusual two-melt region bound by a closed loop in the

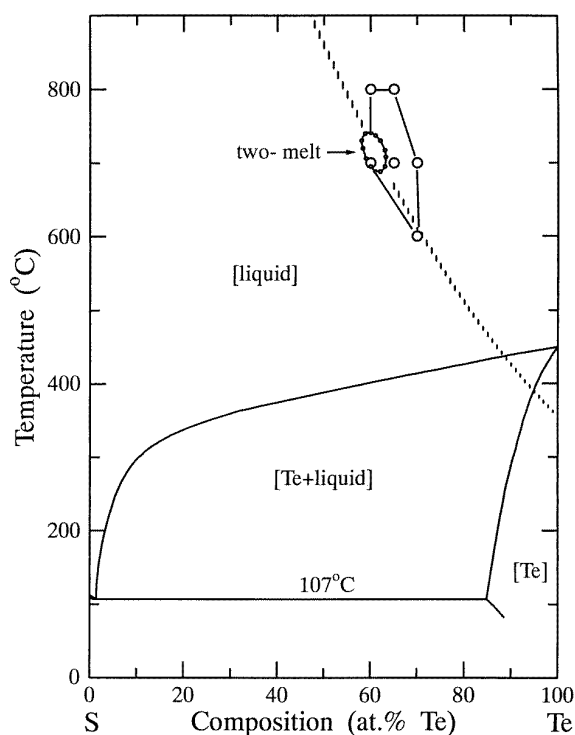


Figure 1. Looped two-melt phase (Tsuchiya 1992) in the phase diagram of the S–Te system (Hansen and Anderko 1958). The hatched line shows the T^* – x curve or the location of a ridge connecting extrema in the thermodynamic response functions (Tsuchiya 1994). Open circles indicate x – T points at which the Darken stability evaluated using equation (17) becomes negative due to structural changes, see the text. The distorted pentagon is a guide for the eye.

composition–temperature (x – T) plane. In other words, a S–Te alloy in a small composition range around 60 at.% Te melts to a homogeneous liquid, then separates into two melts at temperatures some 300 °C above the equilibrium liquidus temperature. It again becomes homogeneous at still higher temperatures. The two-melt region is located in an extremely narrow range centred at about 60.8 at.% Te and 715 °C, which is on the ridge connecting extrema in the thermodynamic response functions in the x – T plane. For the Se–Te system, no apparent experiments indicating the macroscopic instability of mixture have been reported. Only high resolution neutron diffraction experiments on $\text{Se}_{25}\text{Te}_{75}$ at two temperatures suggested that segregation tendency on an atomic scale developed at the higher temperature (Misawa and Suzuki 1982).

To explain the thermodynamic properties of the liquid Se–Te system, Tsuchiya and Seymour (1982) developed an inhomogeneous structural model. By assuming the thermal equilibrium of two forms of microscopic domains of a Se–Te alloy, all the available thermodynamic data could be explained consistently (Tsuchiya 1986a). Amzil *et al* (1996) recast the same ideas in the framework of a modified regular solution model. In the meantime, it has been shown with the inhomogeneous structure model that the structural change in the melt could be the driving force for the segregation tendency in the S–Te and Se–Te systems (Tsuchiya 1992, Tsuchiya *et al* 1996). With a set of plausible parameters, the model could reproduce the looped two-melt phase in the S–Te system (Tsuchiya 1992).

Quite recently one of the present authors (YT) has derived new thermodynamic relations (Tsuchiya 1999) that enable us to connect the three thermodynamic response functions to the Darken stability (Darken 1967). The relations have proved that the excess part of the Darken stability (δD) caused by structural changes is definitely negative, and thus the structural change in a binary mixture stimulates tendency towards phase separation. They also show that the quantity δD can be evaluated from experimental data. The aim of this paper is to present an application of these new thermodynamic relations to the S–Te system: the contribution of the structural change to the Darken stability can be evaluated from the data of molar volume, isothermal compressibility and specific heat as a function of temperature and composition. We then show that this unusual phase separation can be explained by using the available thermodynamic data and that it results from the structural change in the melt. Discussion is made in relation to recent neutron diffraction experiments performed independently by two groups, one at Tsukuba (Kakinuma *et al* 1999) and the other at Saclay (Coulet *et al* 1999).

2. Thermodynamic relations

A detailed derivation of the new thermodynamic relations has been reported elsewhere (Tsuchiya 1999). We briefly present it here. Assuming that structural change in a S–Te mixture can be described by a single parameter $C(T, P, x)$, where T is temperature, P pressure and x the fraction of Te, the Gibbs free energy (G) can be written as (Davies and Jones 1953, Tsuchiya 1991a)

$$G = G(T, P, x, C(T, P, x)). \quad (1)$$

We suppose that C changes continuously from $C = 0$ at low temperatures to $C = 1$ at high temperatures. Thermal equilibrium requires

$$(\partial G / \partial C)_{T, P, x} = 0. \quad (2)$$

This condition specifies C as a function of T , P and x . The total differential (dG) of the Gibbs free energy is given by

$$\begin{aligned} dG &= (\partial G / \partial T)_{P, x, C} dT + (\partial G / \partial P)_{T, x, C} dP + (\partial G / \partial x)_{T, P, C} dx \\ &= -S dT + V dP + \Delta\mu dx \end{aligned} \quad (3)$$

where S , V and $\Delta\mu$ denote the entropy, volume and difference in the chemical potentials for S and Te, respectively.

Further assuming that G is differentiable up to the second order with respect to any of the state variables and C , we have six terms for the second derivative of G . Three diagonal terms like $\partial^2 G / \partial T^2$, $\partial^2 G / \partial P^2$ and $\partial^2 G / \partial x^2$ give the constant specific heat, C_P , isothermal compressibility, κ_T , and Darken stability, D , respectively. The other three cross terms like $\partial^2 G / \partial T \partial P$, $\partial^2 G / \partial P \partial x$ and $\partial^2 G / \partial x \partial T$ give the thermal expansion coefficient, α_P , the difference in the partial volume, ΔV , and the difference in partial entropy, ΔS , for S and Te, respectively.

Any of thermodynamic response functions takes a form like $\phi_0 + \delta\phi$ if the structure changes steeply by changing temperature, pressure and/or composition. ϕ_0 represents a thermodynamic response function expected if there were no structural changes and $\delta\phi$ the contribution caused by the change in the order parameter C with respect to T , P or x . We consider the specific heat, C_P , as an example. Starting from the identity

$$T^{-1} C_P = (\partial S / \partial T)_{P, x} = (\partial S / \partial T)_{P, x, C} + (\partial S / \partial C)_{T, P, x} (\partial C / \partial T)_{P, x, C} \quad (4)$$

and making use of the relations $(\partial C/\partial T)_{P,x,A}(\partial T/\partial A)_{P,x,C}(\partial A/\partial C)_{T,P,x} = -1$ and $(\partial T/\partial A)_{P,x,C} = (\partial S/\partial C)_{T,P,x}^{-1}$, we have

$$C_P = C_{P0} + \delta C_P \equiv T(\partial S/\partial T)_{P,x,C} - T(\partial S/\partial C)_{T,P,x}^2(\partial C/\partial A)_{T,P,x}. \quad (5)$$

Here A is the affinity defined by $A = -(\partial G/\partial C)_{T,P,x}$. In a system in thermal equilibrium $A = 0$. Indeed if a second order phase transition occurs $(\partial A/\partial C)_{T,P,x}$ approaches zero and $(\partial C/\partial A)_{T,P,x}$ diverges as a transition point is approached (Prigogine and Defay 1954). Therefore, in the case of a second order phase transition, for example, δC_P gives rise to a divergence of the specific heat at a transition (or lambda) point, whereas in the present case a 'structural change' (that does not correspond to any singularity in any derivative of the Gibbs energy) $(\partial C/\partial A)_{T,P,x}$ remains finite although a significant enhancement is to be expected in the transitional region.

Proceeding in the same way, the following two groups of $\delta\phi$ may be obtained.

(i)

$$\delta C_P = -T(\partial S/\partial C)_{T,P,x}^2(\partial C/\partial A)_{T,P,x} \quad (6)$$

$$\delta\kappa_T = -V^{-1}(\partial V/\partial C)_{T,P,x}^2(\partial C/\partial A)_{T,P,x} \quad (7)$$

$$\delta D = (\partial\Delta\mu/\partial C)_{T,P,x}^2(\partial C/\partial A)_{T,P,x} \quad (8)$$

(ii)

$$\delta\alpha_P = V^{-1}(\partial V/\partial C)_{T,P,x}(\partial S/\partial C)_{T,P,x}(\partial C/\partial A)_{T,P,x} \quad (9)$$

$$\delta\Delta S = -(\partial S/\partial C)_{T,P,x}(\partial\Delta\mu/\partial C)_{T,P,x}(\partial C/\partial A)_{T,P,x} \quad (10)$$

$$\delta\Delta V = -(\partial\Delta\mu/\partial C)_{T,P,x}(\partial V/\partial C)_{T,P,x}(\partial C/\partial A)_{T,P,x}. \quad (11)$$

The excess quantity in the first group has a definite sign, which arises from the thermodynamic stability condition, $(\partial C/\partial A)_{T,P,x} = -(\partial^2 G/\partial C^2)_{T,P,x} < 0$, as shown above. δC_P and $\delta\kappa_T$ are always positive while δD is always negative in a system in thermal equilibrium. In contrast the excess quantity in the second group is of undetermined sign depending on the sign of $(\partial V/\partial C)_{T,P,x}$, $(\partial S/\partial C)_{T,P,x}$ or $(\partial\Delta\mu/\partial C)_{T,P,x}$.

It is seen that the dependences on T , P and x of these excess thermodynamic response functions are not all independent but related to each other through $(\partial C/\partial A)_{T,P,x}$. Straightforward calculations show that the $\delta\phi$ satisfy the following relations (Tsuchiya 1999).

(iii) Relations among δC_P , $\delta\kappa_T$ and $\delta\alpha_P$.

$$\delta C_P = TV\delta\alpha_P(\partial P/\partial T)_{x,C} \quad (12)$$

$$\delta\kappa_T = \delta\alpha_P(\partial T/\partial P)_{x,C} \quad (13)$$

$$\delta C_P\delta\kappa_T = TV(\delta\alpha_P)^2 \quad (14)$$

where $(\partial P/\partial T)_{x,C}$ is the constant C slope in the T - P plane.

(iv) Relations among $\delta\kappa_T$, δD and $\delta\Delta V$.

$$\delta\kappa_T = V^{-1}(\delta\Delta V)(\partial x/\partial P)_{T,C} \quad (15)$$

$$\delta D = -(\delta\Delta V)(\partial P/\partial x)_{T,C} \quad (16)$$

$$\delta\kappa_T\delta D = -V^{-1}(\delta\Delta V)^2 \quad (17)$$

where $(\partial x/\partial P)_C$ is the constant C slope in the P - x plane.

(v) Relations among δC_P , δD and $\delta \Delta S$.

$$\delta D = (\delta \Delta S)(\partial T / \partial x)_{P,C} \quad (18)$$

$$\delta C_P = -T(\delta \Delta S)(\partial x / \partial T)_{P,C} \quad (19)$$

$$\delta C_P \delta D = -T(\delta \Delta S)^2 \quad (20)$$

where $(\partial T / \partial x)_{P,C}$ is the constant C slope in the x – T plane.

The relations (iii) are analogous to Pippard relations for the second kind of phase transition (Pippard 1964). The new relations (iv) and (v) connect the contribution of Darken stability caused by structural changes to the other thermodynamic response functions. The Darken stability function is related to the concentration–concentration fluctuations $S_{cc}(0)$ by $D = RT S_{cc}(0)^{-1}$ (Darken 1967, Bhatia and Thornton 1970). Then the negative sign of δD implies that the structural changes in a binary mixture inevitably enhance the instability with respect to the concentration fluctuations. The total D or $S_{cc}(0)$ has been evaluated for a number of systems with various thermodynamic measurements. δD has been unable to be partitioned from the total D so far, however.

3. Application to the looped two-melt phase in the S–Te system

Since the test of relations analogous to Pippard relations in (iii) for the structural changes in the liquid S–Te system has been reported elsewhere (Tsuchiya 1994), we evaluate δD through the new relations in (iv) and (v) (equations (17) and (20), respectively) to resolve a two-melt phase separation with a looped boundary.

We start with the analysis using the relations in (iv). Figure 2 shows the isotherms of the molar volume (V) every 100 °C from 400 to 800 °C (Tsuchiya 1992). At 400 °C V as a function of composition changes almost linearly up to 80 at.% Te and then decreases to the value in Te. With increasing temperature, the composition range where volume contracts moves to the S rich side and the volume contraction becomes larger. The number of data is too small to numerically calculate the difference in the partial volumes, $\Delta V = dV/dx$, because a small scatter in the data causes a large scatter in the derivative. Further we could not find a single polynomial equation of composition fitting to the data with reasonably small residue. Then the non-linear equation (1) of Tsuchiya and Seymour (1982) was used to obtain a curve to fit the molar volume as a function of composition. Using the fitted curves through the data in figure 2, the difference in the partial volume, $\Delta V = dV/dx$, was calculated and is plotted in figure 3. A pronounced negative peak appears in the composition range where the volume contracts, which corresponds to $\delta \Delta V$. The base line for $\delta \Delta V$, $(\partial V / \partial x)_{T,P,C}$, would be given by a smooth interpolation curve between the asymptotic values of ΔV at pure S and Te since it is constant as observed on the S rich side at low temperatures and on the Te rich side at high temperatures where there are no structural changes ($C = 0$ or 1). In the present analysis, $(\partial V / \partial x)_{T,P,C}$ obtained by the aforesaid non-linear fitting was used to a first approximation. It is represented by broken curves in figure 3. The error introduced in this approximation would be at most 5% of $\delta \Delta V$ and does not change the final conclusion.

In figure 4, the isotherms of the isothermal compressibility, κ_T , are plotted (Tsuchiya 1994). A few points at high temperatures at the S rich composition have been estimated by extrapolating the sound velocity, molar volume and specific heat as a function of temperature. The line connecting the data has been drawn by making use of a commercially available spline fitting program. At low temperatures κ_T has a pronounced peak around the same composition where $\delta \Delta V$ has a negative peak. This peak indicates that the excess compressibility, $\delta \kappa_T$, is

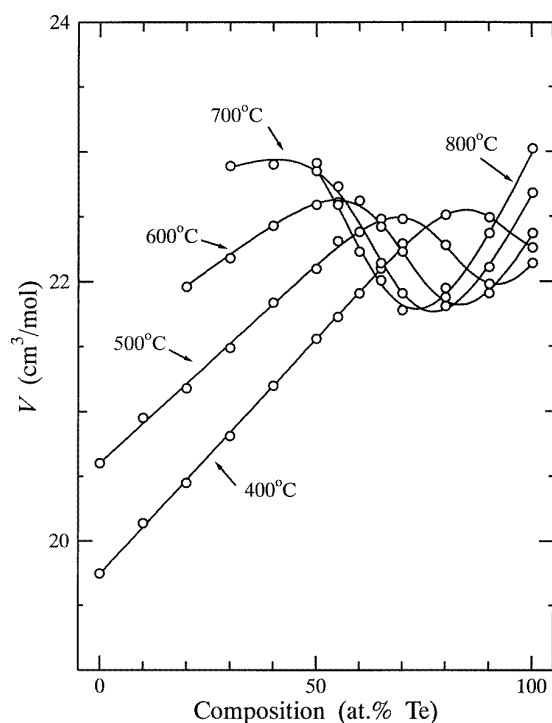


Figure 2. Isotherms of the molar volume of the S-Te system (Tsuchiya 1992). The lines through the data have been determined by non-linear fitting with equation (1) in Tsuchiya and Seymour (1982).

positive in agreement with the thermodynamic relations presented above. The baseline for the evaluation of $\delta\kappa_T$ has been drawn by using a model with binary hard spheres (Shimoji 1977). The hard spheres for S and Te have been chosen so as to reproduce the data on the S side at low temperatures and those on the Te side at high temperatures because effects due to structural changes under consideration are supposed to be small. $\delta\Delta V$ and $\delta\kappa_T$ evaluated at 500 and 700 °C have been plotted in figure 5. At 700 °C, the phase separation actually occurs in the small composition interval around 60 at.% Te. $\delta\Delta V$ and $\delta\kappa_T$ around the extremum are interpolations, therefore. A small shift between the positions of the extrema of $\delta\Delta V$ and $\delta\kappa_T$ at each temperature can be observed. We suppose that it results from the uncertainty in drawing the baselines. Putting those data into equation (17), δD can be calculated. The results at 500 °C are compared in figure 7 with the results from relation (20) and all results are plotted in figure 8 to explain the origin of the two-melt phase with looped boundary.

Evaluation of δD through equation (20) was possible only at 500 °C because the data for C_P on the S side were available only at low temperatures and their extrapolation to higher temperatures causes large error in determining the mixing entropy. It should be mentioned that the extrapolation of C_P does not introduce serious error in evaluating κ_T because C_P contributes to the dilatation term in the isothermal compressibility which is only about 10% or less of the total compressibility. Figure 6 shows the isotherm of the constant pressure specific heat (Kakinuma and Ohno 1987), mixing entropy and difference in the partial mixing entropy, $\Delta S_{mix} = dS_{mix}/dx$, at 500 °C. The mixing entropy S_{mix} has been evaluated using the data

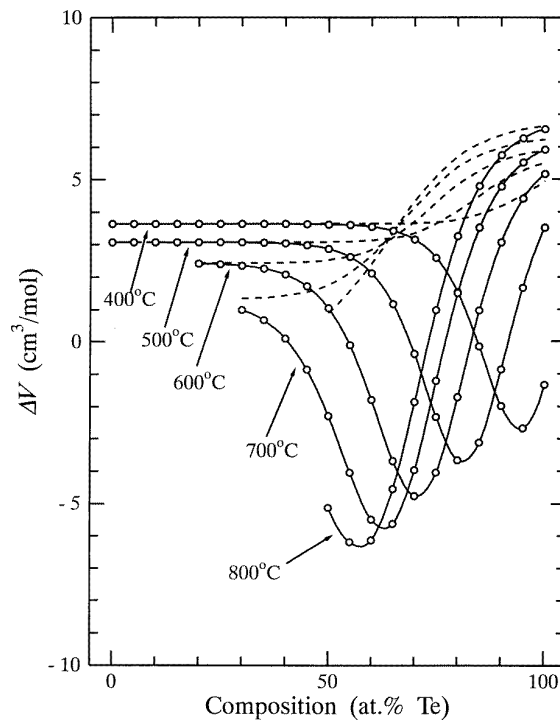


Figure 3. Difference in the partial volumes, $\Delta V = dV/dx$, for S and Te in the S–Te system. Broken lines are baselines for evaluation of $\delta\Delta V$, see the text.

at 468 °C (Maekawa *et al* 1973) and C_P as a function of temperature (Kakinuma and Ohno 1987, Tsuchiya 1991a) using the thermodynamic relations. The peak in C_P is caused by δC_P . A simple average of C_P for the S rich alloys has been chosen as C_{P0} or the specific heat expected for alloys with no structural change to a first approximation, because structural changes under consideration do not occur on the S side at this temperature. ΔS_{mix} has a peak around the composition where C_P shows a peak. As shown in a previous paper (Tsuchiya 1986b), the mixing entropy of the S–Te alloy is the sum of an ideal mixing entropy term and of a term including the effect of structural change in the Te rich alloys. By definition of the mixing entropy it also involves the term originating from the contribution from the structural transition in pure Te (change in the reference state), and it is proportional to the Te composition. The latter term give rise to a constant term in $\Delta S_{mix} = dS_{mix}/dx$. Assuming an ideal mixture of S and Te, therefore, the base line for $\delta\Delta S$ is given by $-\ln[x/(1-x)] + \text{const}$, where const represents the aforesaid contribution due to the change in the reference state in Te. It can be determined by fitting the curve to the experimental data along the S side. The calculated value of const was about $-0.51(R)$. This is not in contradiction with the value expected from the entropy difference in the structural change in liquid Te (Tsuchiya 1991a). Figure 7 compares δD values at 500 °C calculated using equations (17) and (20).

A maximum or minimum in the thermodynamic response functions (C_P , κ_T and α_P) as a function of temperature occurs around the temperature where the structural transition to the high temperature form has proceeded about half way and the order parameter, C , is about $\frac{1}{2}$. The positions of extrema, T^* , increase with S composition as shown by a hatched curve in figure 1, whose derivative with respect to the composition may be related to δD . Eliminating

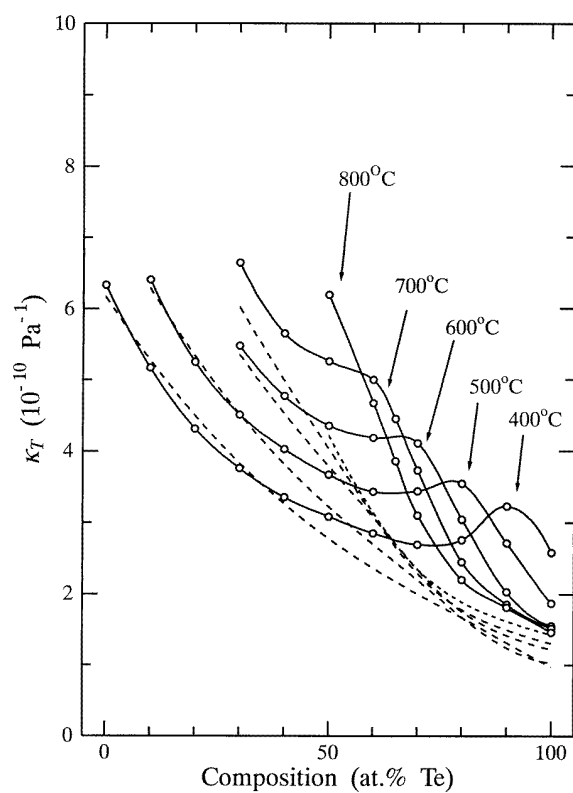


Figure 4. Isotherms of the isothermal compressibility, κ_T , in the S-Te system. Broken lines are baselines for evaluation of $\delta\kappa_T$, explained in the text.

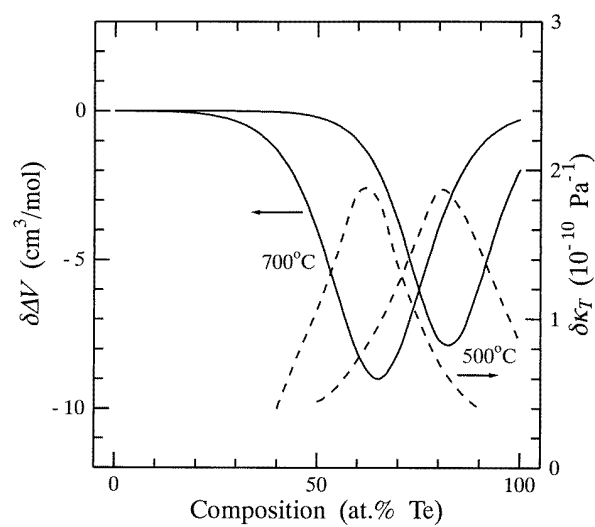


Figure 5. $\delta\Delta V$ (solid curves) and $\delta\kappa_T$ (broken curves), the contributions of structural changes to the difference in the partial volumes and isothermal compressibility, respectively, at 500 and 700°C.

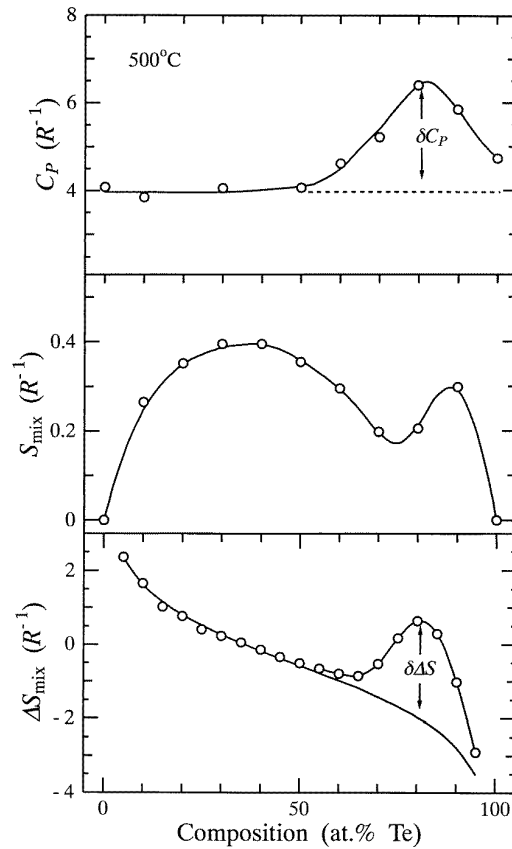


Figure 6. Constant pressure specific heat, C_p (Kakinuma and Ohno 1987), mixing entropy, S_{mix} , and difference in the partial mixing entropy, ΔS_{mix} , for the liquid S–Te system at 500 °C, where R is the universal gas constant. δC_p and $\delta\Delta S$ represent the contribution brought about by the structural change.

$\delta\Delta S$ from equations (18) and (19), we obtain

$$\delta D = -T^{-1}\delta C_p(\partial T/\partial x)_{P,C}^2. \quad (21)$$

Since the slope of T^* , dT^*/dx , is approximately equal to the value of $(\partial T/\partial x)_{P,C}$ at $P \sim 0$ and $C \sim \frac{1}{2}$, we can estimate δD along the hatched curve using the δC_p value at its maximum. It is noted that $\delta\Delta S$ is not needed in this analysis. Figure 9(a) shows the peak values of C_p for the respective S–Te alloys as a function of composition (Kakinuma and Ohno 1987) where C_{p0} is the same quantity as in figure 6. The results are shown in figure 9(b) in which all T^* data were fitted to a quadratic function of composition.

Keeping in view the experimental uncertainties as well as the uncertainty in the assignments of the baselines, the values obtained for the δD through relations (17), (20) and (21) are in reasonable agreement as compared in figures 7 and 9. The sign of δD is negative as predicted by the new relations and takes a pronounced minimum in the transitional region. The phase separation tendency, therefore, develops in the liquid S–Te system in an x – T region where the thermodynamic response functions (C_p , κ_T and/or α_p) show an extremum. These observations can be made even considering the error bars in δD .

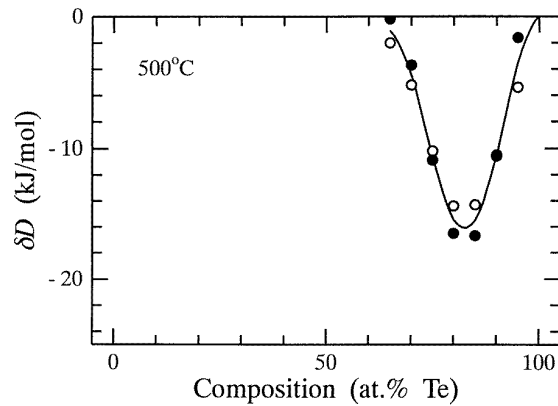


Figure 7. Excess Darken stability δD brought about by the structural changes in the S–Te system at 500 °C. Solid circles and open circles have been estimated, respectively, from equations (17) and (20).

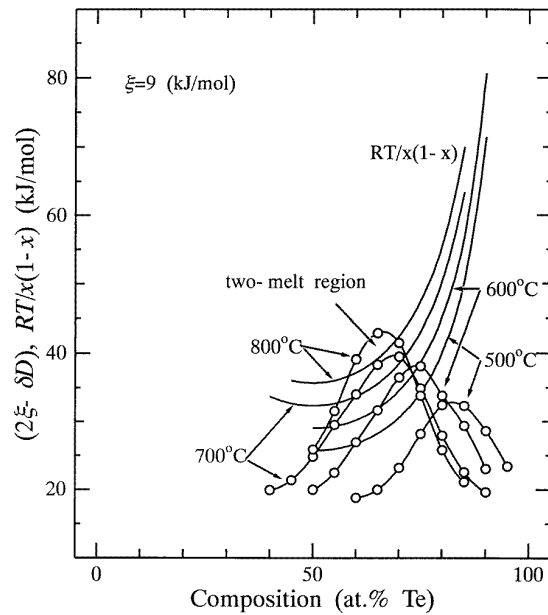


Figure 8. Comparison of $(2\xi - \delta D)$ and the entropy term, $RT/x(1-x)$, where ξ is 9 kJ mol^{-1} (Tsuchiya 1986b). The x – T points, where $RT/x(1-x) - (2\xi - \delta D) < 0$, evaluated every 100 °C and 5 at.% are plotted in figure 1, at which a homogeneous S–Te mixture becomes unstable.

4. Discussion

The concentration–concentration fluctuation $S_{cc}(0)$ at the zero limit wavelength for the present Gibbs free energy is given by (cf equation (9)),

$$S_{cc}(0)^{-1} = (RT)^{-1}(D_0 + \delta D) = (RT)^{-1}\{(\partial^2 G/\partial x^2)_{T,P,C} + (\partial \Delta\mu/\partial C)_{T,P,x}^2 (\partial C/\partial A)_{T,P,x}\}.$$

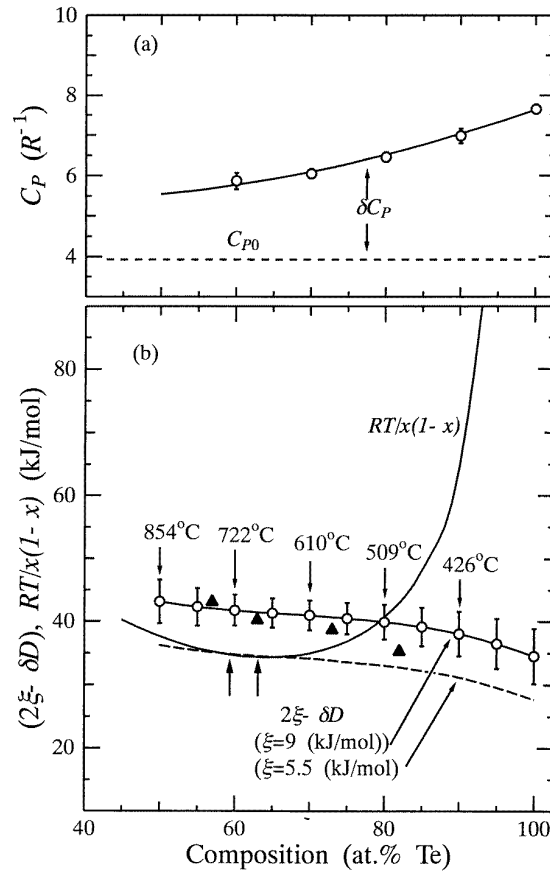


Figure 9. (a) Specific heat, C_p , of S-Te alloys at the peak as a function of composition (Kakinuma and Ohno 1987). The curve through the data is a quadratic fitting. δC_p is given by the difference, $C_p - C_{p0}$. (b) Comparison of $(2\xi - \delta D)$ and the entropy term, $RT/x(1-x)$, along the T^*-x curve in figure 1. Error bars correspond to the uncertainty in dT^*/dx and δC_p . Solid triangles are the peak values of $(2\xi - \delta D)$ from equation (17) plotted in figure 8. The broken curve is $(2\xi - \delta D)$ for $\xi = 5.5 \text{ kJ mol}^{-1}$. Two arrows on the entropy curve indicate the observed boundary of the two-melt phase along the T^*-x curve.

The first term on the right hand side represents expected Darken stability if there were no structural change. It was examined previously (Tsuchiya 1986b) using the thermodynamic quantities of mixing from Maekawa *et al* (1973). To a first approximation, it takes the form

$$D_0 = RT/x(1-x) - 2\xi \quad (22)$$

where a regular solution of S and Te has been assumed. ξ is the interchange parameter and was evaluated to be 9 kJ mol^{-1} at 468°C (Tsuchiya 1986b). $RT/x(1-x)$ and $(2\xi - \delta D)$ calculated at 500, 600, 700 and 800°C through equation (17) have been plotted as a function of composition in figure 8. As the fraction of S increases, the composition around which the structural change occurs (characterized by a peak in $-\delta D$) shifts to the mid-range composition. Consequently, the difference between D_0 and $-\delta D$ becomes smaller as the temperature rises because the shift of the peak in $-\delta D$ to the mid-range of composition is more effective in reducing the total D while the entropy term, $RT/x(1-x)$, increases the stability. As a consequence an $x-T$ range appears at high temperatures in which $D_0 + \delta D$ becomes negative,

which is shown in figure 8. In this range the S–Te mixture becomes unstable with respect to the concentration fluctuations. Figure 9(b) shows same quantities along the T^*-x curve in figure 1 calculated from the relation (21) together with the peak values of $(2\xi - \delta D)$ from equation (17). Starting from Te side, $-\delta D$, hence $(2\xi - \delta D)$ gradually increases while the entropy term decreases rapidly to take a broad minimum around 64 at.% Te. Below 78 at.% of Te, the total D becomes negative and appears to become positive again beyond about 40 at.%. The phase separation is predicted between these compositions.

Figure 1 compares the $x-T$ region where the new thermodynamic relation (17) predicts the instability and the two-melt region found by a γ -ray attenuation method. In view of the uncertainty in the present numerical analysis overlap of both regions is qualitatively satisfactory. Quantitatively, however, the present analysis obviously overestimates the instability. Furthermore the centre of the unstable region appears to be shifted to the Te side as compared with the observed two-melt region. Since the excess quantities evaluated from different thermodynamic response functions result in almost the same magnitude of the δD , the discrepancy could be ascribed to the different values of ξ . The previous value of $\xi = 9 \text{ kJ mol}^{-1}$ has been determined to fit the heat of mixing in the low temperature form of S–Te alloy in which the coordination number z is about 2. As shown in the following paragraph, on the other hand, the coordination number increases to more than $z = 2$ in the transition region, which suggests a different value of ξ in this region. If the value of ξ is arbitrarily reduced to 5.5 kJ mol^{-1} , the unstable $x-T$ region can reproduce quantitatively the looped two-melt phase as shown in figure 9. This would imply that the interchange parameter is dependent on z and becomes smaller with increasing z . Correspondingly it would also decrease as the composition goes through a peak in $-\delta D$ from the S to Te side at a fixed temperature in a way similar to how the coordination number increases (figure 10). The effect of this is to shift the centre of the unstable region estimated from equation (17) to the Se side, the right direction to obtain better agreement. We therefore conclude that the peculiar two-melt phase separation with a looped boundary is caused by the local structural change.

To clarify the structural change in the liquid S–Te system at an atomic scale two independent neutron diffraction experiments, one at Tsukuba (Kakinuma *et al* 1999) and the other at Saclay (Coulet *et al* 1999) have been performed. The total coordination number as a function of composition at three temperatures obtained at Saclay is reproduced in figure 10. The coordination number has been evaluated with a model assuming that the first peak in the radial distribution function, $g(r)$, consists of three or four Gaussian functions, the parameters of which were fitted to the high q part of $S(q)$. On the Te side, the total coordination number is larger than 2. By adding S, it decreases to about 2. The rate of decrease is particularly large in the composition range where thermodynamic response function takes an extremum. With increasing temperature the decrease becomes more prominent and occurs in the more S rich side in agreement with the thermodynamic observations. Meanwhile the high resolution experiments at Tsukuba could resolve the three atom pairs and their inter-atomic distances have been determined as a function of composition (Kakinuma *et al* 1999). The results indicate that the partial coordination number between S–Te in the two-melt region drastically decreases from the one expected from a random mixture.

In Figure 10, the composition dependence of the total coordination number is also compared with the previous calculations of the fraction of S–Te in a high temperature form using an inhomogeneous structure model (Tsuchiya 1992). Although a systematic shift between calculated and experimental values is observed, the calculations can reproduce the general experimental trend. The concentration and temperature evolution of the coordination numbers determined by neutron scattering is certainly meaningful, but their absolute value might be subject to a systematic error. Anyway, the neutron diffraction experiments provide the evidence

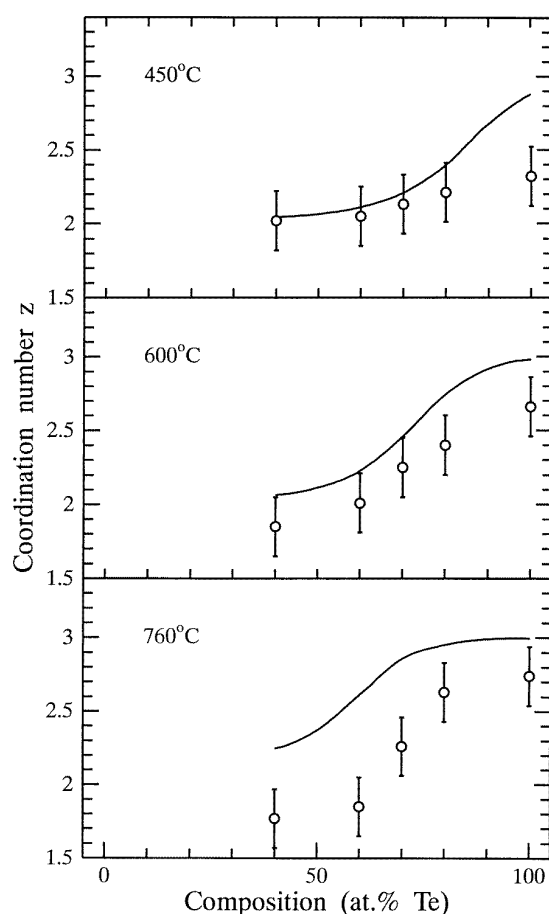


Figure 10. Comparison of the total coordination number, z (Coulet *et al* 1999) with the fraction of an S–Te alloy in a high temperature form (Tsuchiya 1992). The latter is normalized to 3 and 2, in a high temperature and a low temperature form, respectively.

that changes in local order similar to those observed in Te and also in Se–Te alloys take place in the S–Te system in the x – T region suggested by thermodynamic investigations.

As mentioned in the introduction the overall behaviour of physico-chemical properties is much the same for both S–Te and Se–Te systems. So, why does this unique two-melt phase appear only in the S–Te system? The calculations presented here show that this phase separation results from the delicate balance between two terms: a regular solution term that stands for the thermodynamic properties of the melt without structural change, and a term resulting from the structural change in the melt. The magnitude of each contribution has to be considered. The interchange parameter favours phase separation and is larger (9 or ~ 5.5 kJ mol $^{-1}$) in the S–Te system, whereas it weakly favours order (-1.9 kJ mol $^{-1}$) in the Se–Te alloy (Tsuchiya 1986b). These values agree with the phase equilibria in the solid state: Se–Te alloys form a continuous solid solution at any composition while S and Te atoms do not mix up (Hansen and Anderko 1958). In the case of S–Te alloys the repulsive interaction between the S and Te pair works cooperatively with the structural change to favour an instability with respect to the concentration fluctuations.

5. Conclusions

The new thermodynamic relations have been applied to evaluate the contribution from structural changes to the stability function in the S–Te system. The excess contribution to the Darken stability caused by the structural change has been partitioned and is negative as predicted. It has been shown that with changing temperature and composition the excess contribution becomes large enough to cause the instability of liquid S–Te alloy in a small x – T region. These thermodynamic arguments indicate that thermally driven local order changes can induce divergent concentration fluctuations and is the origin of the unique closed loop miscibility gap localized in a very narrow region in the liquid S–Te system.

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References

- Amzil A, Gilbert M, Bichara C and Mathieu J-C 1996 *J. Phys.: Condens. Matter* **8** 5281
Bhatia A B and Thornton D E 1970 *Phys. Rev. B* **2** 2004
Bichara C, Raty J-Y and Gaspard J-P 1996 *Phys. Rev. B* **53** 206
Coulet M-V, Bellissent R, Bionducci M and Bichara C 1999 *Europhys. Lett.* **45** 175
Darken L S 1967 *Trans. AIME* **329** 80
Davies R O and Jones G O 1953 *Adv. Phys.* **2** 370
Fisher R, Schmutzler R W and Hensel F 1980 *J. Non-Cryst. Solids* **35, 36** 1295
Gerlach E and Gross P (eds) 1979 *The Physics of Selenium and Tellurium* (Berlin: Springer)
Hansen M and Anderko K 1958 *Constitution of Binary Alloys* 2nd edn (New York: McGraw-Hill)
Kakinuma F, Fukunaga T and Suzuki K 1999 *J. Phys. Soc. Japan* **68** 1912
Kakinuma F and Ohno T 1987 *J. Phys. Soc. Japan* **56** 619
Maekawa T, Yokokawa T and Niwa K 1973 *Bull. Chem. Soc. Japan* **46** 761
Menelle A, Bellissent R and Flank A-M 1989 *Physica B* **156/157** 174
Misawa M and Suzuki K 1982 *J. Physique Coll. C* **8** 203
Pippard A B 1964 *Elements of Classical Thermodynamics* (Cambridge: Cambridge University Press)
Prigogine I and Defay R 1954 *Thermodynamique Chimique* trans. D Everett (London: Longmans Green) p 291
Shimoji M 1977 *Liquid Metals* (London: Academic)
Thurn H and Ruska J 1976 *J. Non-Cryst. Solids* **22** 331
Tsuchiya Y 1986a *J. Phys. C: Solid State Phys.* **19** 1389
—1986b *J. Phys. C: Solid State Phys.* **19** 2865
—1991a *J. Phys.: Condens. Matter* **3** 3163
—1991b *J. Phys. Soc. Japan* **60** 960
—1992 *J. Phys.: Condens. Matter* **4** 4335
—1994 *J. Phys.: Condens. Matter* **6** 2451
—1999 *J. Phys.: Condens. Matter* **11** 593
Tsuchiya Y, Kakinuma F and Bergman C 1996 *J. Non-Cryst. Solids* **143/146** 143
Tsuchiya Y, Sato R and Kakinuma F 1999 *J. Non-Cryst. Solids* at press
Tsuchiya Y and Seymour E F W 1982 *J. Phys. C: Solid State Phys.* **15** L689