A new insight into phase separation in the As–Te glasses from the (p, T) phase diagram of As_2Te_3

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Abstract

An example of general applicability in the systematic construction of the (p, T) phase diagram of a dimorphic substance by using fragmentary data reported in the literature is presented for As_2Te_3. Appropriate equations of state allowed locations of the melting triple point of the high pressure β-form at very low temperature. This case of dimorphism may explain the observation of glass separation in the As–Te system by assuming the existence of another (i.e. metastable) liquidus.

INTRODUCTION

Since its discovery in 1958 [1], the so-called phase separation in glasses has been related to the existence of liquid–liquid miscibility gaps in the corresponding phase diagrams and based upon the theory of spinodal decomposition [2]. The capability to generate phase-separated glasses has been connected either to a metastable extension of the liquid–liquid phase domain at temperatures lower than that of the monotectic invariant or to the appearance of a stable sigmoid liquidus line upon a metastable miscibility gap [3]. On the other hand, Cahn has pointed out another case [4] in which demixing appears, for the whole period during which it occurs, as a precursor reaction which prevents a metastable or unstable liquid from crystallizing into a stable solid.

In a previous investigation of the As–Te phase diagram [5], one of us obtained sub-liquidus separated–glassy phases, but did not observe any significant inflection point along the As-rich liquidus curve. So Cahn's interpretation seemed inapplicable to these experimental results, since it implies the existence of a metastable liquidus which could not be verified.

However, we shall show in this paper that the recently detected metastable β-variety of As_2Te_3 [6] has to melt at a much lower temperature

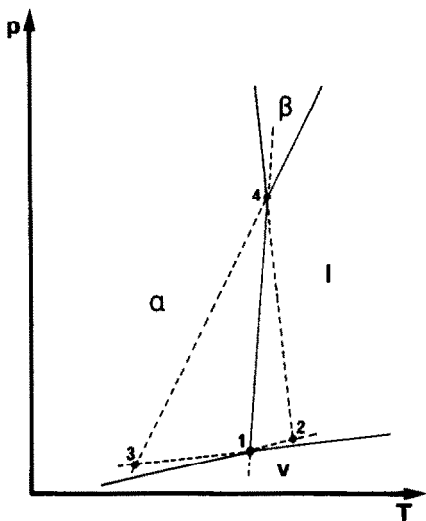Fig. 1. Schematic drawing of the (p, T) diagram of As_2Te_3 two-phase equilibrium curves: (———) stable; (---) metastable. Triple points: α–l–v(1), α–β–v(2), β–l–v(3) and α–β–l(4).

than does the stable α-form, for which melting has been, in turn, considered as a limiting case between congruency and non-congruency [5].

Another melting point at a lower temperature would then imply the existence of a second As-rich liquidus and of a deep metastable eutectic or monotectic depression. In this case, Cahn's arguments can take account of the sub-liquidus phase separation in the As–Te glasses.

The (p, T) phase diagram of As_2Te_3

From the high-pressure experimental work by Kirkinskii and Yakushev [7] it turned out that the fragmentary (p, T) diagram of As_2Te_3 belongs to one of the four theoretical cases identified by Bakhuis Roozeboom [8] concerning dimorphism, as reported in a schematic diagram (Fig. 1), in which the two-phase equilibrium curves have been represented by straight lines, as suggested by Oonk [9].

In a very recent paper [10], we have concluded that the β-form first obtained by Han Wan Shu et al. [6] and the one detected by Kirkinskii and Yakushev [7] are very likely the same, and that both forms are denser than the stable α-variety. Moreover, by a differential scanning calorimetry (DSC) study (T range 298–600 K), we have proved that the aforementioned β-modification does not melt but irreversibly transforms into the stable α-variety at ≈ 513 K, in accordance with what Han Wan Shu et al. observed.

Here, then, we attempt to locate the metastable fusion of β-As$_2$Te$_3$ at low temperature from the study of the (p, T) phase diagram of As$_2$Te$_3$, where, for the sake of simplification, the normal melting of α-As$_2$Te$_3$ has been considered to be congruent.

Another goal is to present in this paper an example of systematic construction of a pressure–temperature (p, T) phase diagram from scarce data in the literature by means of (p, T) equations of state able to describe coherently the equilibria between phases and the triple points. The required features are good interpolating and extrapolating ability and thermodynamic consistency. The chosen equation should preferably incorporate the values of other thermodynamic quantities, for instance, the experimental enthalpy (or entropy) change at a phase transition.

If an exact thermodynamic equation, such as the Clausius–Clapeyron equation, is not suited for application to a given equilibrium curve, an empirical relation may be fitted to the experimental results provided that the criteria discussed above are respected.

Vapour–solid equilibrium

This equilibrium is ruled by the Clausius–Clapeyron equation already proposed by Northrop [11] to fit the set of experimental results for the vapour pressure of α-As$_2$Te$_3$

$$\ln p = -A/T + B \tag{1}$$

where $A = -18\,535.8$ and $B = 16.98$; p is in MPa and T is in K.

Considering that the sublimation enthalpy ΔH_s does not vary with temperature, one obtains $\Delta H_s = 154.1$ kJ mol^{-1}. Because the experimental temperature range is not far from the α–l–v triple point temperature $(T^* = 653$ K$)$ we extrapolated the equilibrium pressure at this temperature $(p = 1.1 \times 10^{-5}$ MPa$)$. (The normal melting point of α-As$_2$Te$_3$ corresponds to this triple point because the dead volume of the evacuated sealed-off containers, in which melting experiments are commonly performed to prevent oxidation and sublimation, may be considered as being occupied by a saturating vapour).

Vapour–liquid equilibrium

Saturated vapour pressure results on arsenic telluride were reported by Ustyugov et al. [12] in the temperature range 1052–1200 K. They interpolated the results by means of the Clausius–Clapeyron equation, in which vaporisation enthalpy ΔH_v was considered as being a constant. They obtained the following results: $\Delta H_v = 116.07$ kJ mol^{-1}; boiling temperature $T_b = 1300.4$ K.

Since in our case the (p, T) equation would have been used for extrapolations involving condensed state at low temperature, we looked for a form able to incorporate the vaporisation enthalpy at the triple point and to fit correctly to the estimated equilibrium pressure at the triple point temperature together with the results given by Ustyugov et al. Vaporisation enthalpy was estimated by the difference between sublimation enthalpy and the value of melting enthalpy nearest to the average of those values resulting from previous experimental work [13–16]. Finally we obtained $\Delta H_v^* = 98.24$ kJ mol^{-1}.

Vaporisation enthalpy was treated as a parabolic function of temperature

$$\Delta H_v = a_0 + a_1 T + a_2 T^2$$

forced to incorporate the value ΔH_v^* at T^*.

Hence, one could write

$$\Delta H_v^* = a_0 + a_1 T^* + a_2 T^{*2}$$

and define the parameter a_2

$$a_2 = (\Delta H_v^* - a_0 - a_1 T^*)/T^{*2}$$

The differential form of the Clausius–Clapeyron equation could then be written as

$$\frac{dp}{p} = \frac{a_0 + a_1 T + \left[(\Delta H_v^* - a_0 - a_1 T^*)/T^{*2}\right] T^2}{RT^2} \, dT$$

where R is the gas constant.

Integration and ordering of the different terms gives

$$\ln p = A_0\left(\frac{1}{T} + \frac{1}{T^{*2}}\right) + A_1\left(\frac{T}{T^*} - \ln T\right) + A_2^* T + B \tag{2}$$

where

$$A_0 = -a_0/R; \quad A_1 = -a_1/R; \quad A_2^* = \Delta H_v^*/RT^{*2}$$

and B is an integration constant. The three parameters A_0, A_1 and B are determined by linear least-squares regression of the experimental results. Table 1 reports the results of the interpolation, the values of the three parameters and some extrapolated pressure values at temperatures lower than T^*. At 1126 K, the mean value of the temperature range investigated by Ustyugov et al., the predicted value for ΔH_v is 115.2 kJ mol^{-1}, very near to that computed by them (116.1 kJ mol^{-1}). The predicted boiling temperature is 1283 K instead of 1300.4 K. However, the proposed equation is not suitable for extrapolation at $T > 1200$ K, as indicated by the too high pressure value predicted at this temperature.

TABLE 1

Calculated pressure values p_{calc} for vapour–liquid equilibrium of α-As_2Te_3 and percentage deviations Δ in the representation of the experimental values p_{exp} from ref. 11 by means of the equation below

T (K)	$p_{exp}(\times 10^5)$ (MPa)	$p_{calc}(\times 10^5)$ (MPa)	Δ
1052	800	828	3.50
1067	947	982	3.70
1080	1133	1137	0.35
1089	1267	1257	−0.79
1099	1427	1405	−1.54
1105	1507	1501	−0.4
1117	1760	1713	−2.67
1122	1907	1809	−5.14
1131	2053	1996	−2.78
1148	2360	2401	1.74
1156	2666	2619	−1.76
1162	2880	2794	−2.99
1176	3253	3248	−0.15
1181	3386	3427	1.21
1200	4026	4200	4.32

Interpolating equation:

$$\ln p = A_0[f_0(T)] + A_1[f_1(T)] + A_2^* T + B$$

where

$$f_0(T) = \frac{1}{T} + \frac{T}{T^{*2}}$$

$$f_1(T) = \frac{T}{T^*} - \ln T$$

$A_0 = -31099.9$; $A_1 = 49.1575$; $A_2^* = 0.02771$; $B = 335.211$; $T^* = 653$ K.

Extrapolated values:

T(K)	p_{calc} (MPa)
600	2.2×10^{-6}
400	1.3×10^{-11}
200	3.5×10^{-33}

By equalising eqns. (1) and (2) the calculated pressure and temperature values for the α–l–v triple point turn out to be 1.1×10^{-5} MPa and 652.8 K, respectively, very close to those used in the regression of the experimental points.

High pressure equilibria involving solid As_2Te_3

The following curves have to be considered: (a) the transition between α- and β-As_2Te_3; (b) the melting curves of the α- and β-forms.

All three were investigated by Kirkinskii and Yakushev [7], who pointed out that above 780 MPa the congruent character of the melting of α-As$_2$Te$_3$ is replaced by incongruent melting with decomposition of the initial compound into elementary arsenic and a liquid. In building up the phase diagram, we did not take account of the liquidus curve which meets the upper extremity of the α–l equilibrium curve at $\approx$ 790 MPa, because this was not significant for the determination of the α–β–l triple point. Moreover, the investigation of the high-pressure liquid phase, whose properties are affected by the presence of elementary arsenic, was outside the aims of this paper.

Data were obtained by accurate readings from the graph given by the authors [7]. However, they did not report any experimental results for the equilibrium between the two solid varieties, but only an interpolating straight line over which can be read data at the same pressure values attributed to the points belonging to the β-As$_2$Te$_3$ melting curve. The (p_0, T_0) coordinates of the α–β–l triple point were estimated to be 819.1 MPa and 729.4 K, respectively.

a. The α-As$_2$Te$_3$ / β-As$_2$Te$_3$ equilibrium

With respect to this equilibrium, according to the authors, we kept a linear form for the (p, T) equation which was forced to incorporate the α–β–l triple point, that is to say

$$p = p_0\left[a\left(\frac{T}{T_0} - 1\right) + 1\right]$$

Parameter a was optimized by least-squares regression of the experimental results in Table 2. The negative slope of the straight line agrees with the densities of β-As$_2$Te$_3$ being higher than those of α-As$_2$Te$_3$ for all their equilibrium points, as could also be argued by the results available at room temperature and pressure [6,17,18,19].

b. The melting curves

Melting data are frequently smoothed by fitting them to the empirical Simon–Glatzel equation of the form

$$p = p_a\left[\left(\frac{T}{T_0}\right)^c - 1\right]$$

where p_a, T_0 and c are parameters to be obtained from the experimental data. Of the three, only T_0 has a physical meaning in that it represents the temperature at zero pressure. The main drawback in using this equation is that it requires a complicated regression procedure, since it cannot be put in a linear form. So, for representing these high-pressure phase equilibria, we decided to use two more simple original equations which also incorporate the (p_0, T_0) point.

TABLE 2

Calculated pressure values p_{calc} for α- and β-As_2Te_3 equilibrium and percentage deviations Δ in the representation of experimental values p_{exp} (graphically reported in ref. 7 by means of the equation below

T (K)	p_{exp} (MPa)	p_{calc} (MPa)	Δ
681.3	1733.6	1743.9	0.59
690.3	1606.6	1570.8	-2.23
700.4	1373.5	1376.7	0.23
701.4	1350.1	1357.4	0.54
706.9	1242.4	1251.7	0.75
711.7	1154.6	1159.4	0.42
713.7	1114.5	1120.9	0.57
715.9	1074.9	1078.6	0.34
717.0	1053.9	1057.5	0.34
721.3	963.7	974.8	1.15
724.7	913.3	909.5	-0.42
728.3	840.7	840.2	-0.06

Interpolating equation:

$$p = p_0\left[a\left(\frac{T}{T_0} - 1\right) + 1\right]$$

$a = -17.121$; $p_0 = 819.1$ MPa; $T_0 = 729.4$ K.

The points of the α-As_2Te_3 melting curve were fitted by means of a linear combination between a term where pressure depends on temperature by a power law and a second one where this dependence is linear. The relationship becomes

$$p = AT^c + BT$$

By forcing the equation to incorporate the triple point (p_0, T_0) one obtains

$$p - p_0 = A(T^c - T_0^c) + B(T - T_0)$$

In terms of reduced variables $p_r = p/p_0$ and $T_r = T/T_0$ we may write

$$p_r = a(T_r^c - 1) + b(T_r - 1) + 1 \tag{3}$$

Equation (3) is linear with respect to parameters a and b provided that c is a frozen parameter, the value of which has to be modified at each iterative step of the regression routine until very accurate interpolation is achieved. In the present case the expression was able also to account for the α-l-v triple point. The slope of the melting line

$$\frac{dp_r}{dT_r} = acT_r^{c-1} + b$$

turns out to be both positive and increasing as temperature increases if a, b and c are positive and c is greater than 2. In the case with b negative,

the (p_r, T_r) function may show a minimum point which is located outside the experimental temperature range toward lower temperatures. If this occurs thermodynamic reliability of eqn. (3) is lacking, as is the ability to make extrapolations in this direction. For this reason we were prevented from applying the equation to the melting curve of β-As$_2$Te$_3$; the points of this curve, however, were almost as satisfactorily smoothed by fitting them to the power law function of temperature derived from eqn. (3) by nullifying parameter b and by putting a equal to unity.

Fits to the α- and β-As$_2$Te$_3$ melting curves are reported in Tables 3 and 4, respectively.

Finally, one may argue that eqn. (3) is the most general one for the three high-pressure phase equilibria under consideration.

The metastable triple points

a. The α–β–v triple point was obtained by equalising the α–β and the α–v equilibrium curve equations extrapolated outside the experimental range of their application. The temperature turned out to be 772 K and the pressure was equal to 9×10^{-4} MPa.

b. Conversely, the extrapolated β–1 and 1–v curves are superimposed at near zero pressure ($p < 10^{-10}$ MPa) at ≈ 70 K. This temperature may be reasonably considered as that of the β–1–v triple point, since all along the upper low temperature range only a mere convergence between the two curves was observed.

Although it depends on the choice of the fitting equations, the present result might reflect the occurrence, in the As-rich part of the As–Te diagram, of a metastable eutectic or monotectic depression deeper than was expected if the Clausius–Clapeyron equation had been incorrectly applied also to the high-pressure equilibrium curves. In this case we would have obtained a β–1–v triple point temperature of 224 K. Incidentally, the above interpretation remains applicable wherever the metastable invariant is localised in the low-temperature range.

CONCLUDING REMARKS

Let us now discuss in more detail the basic argument graphically shown in Fig. 2A or 2B according to a congruent or to a non-congruent melting of the respective As$_2$Te$_3$ varieties.

The common feature in these graphs, as anticipated in the introduction, is the presence of two liquidus curves arising from the arsenic melting temperature, which delimit a region containing the figure point (●); this corresponds to As–Te compositions and to annealing temperatures at which separation of vitreous phases may occur [5].

TABLE 3

Calculated pressure values p_{calc} for the melting equilibrium curve of α-As$_2$Te$_3$ and percentage deviations Δ in the representation of experimental values [7] by means of the equation below

T (K)	p_{exp} (MPa)	p_{calc} (MPa)	Δ
673.8	181.5	180.6	−0.50
676.3	201.4	202.4	0.50
680.9	242.4	242.9	0.21
684.1	270.5	271.4	0.33
688.6	313.8	312.1	−0.54
696.1	384.1	382.2	−0.49
702.3	441.5	443.7	0.50
705.2	476.6	474.0	−0.55
708.1	502.3	505.6	0.66
712.8	552.7	560.4	1.39
714.9	592.5	586.7	−0.98
720.2	661.6	659.6	−0.30
722.2	691.5	690.1	−0.20
723.7	711.9	714.3	0.34
725.0	733.0	736.3	0.45
726.6	764.6	764.9	0.04
727.6	788.1	783.6	−0.57

Interpolating equation:

$$p = p_0 \left\{ a \left[\left(\frac{T}{T_0} \right)^c - 1 \right] + b \left(\frac{T}{T_0} - 1 \right) + 1 \right\}$$

$a = 0.20723$; $b = 7.55322$; $c = 51.4846$; $p_0 = 819.1$ MPa; $T_0 = 729.4$ K.

The α–l–v triple point is predicted to be in the range 652.7–652.8 K

Other extrapolated values:

T (K)	p_{calc} (MPa)
655	18.96
660	61.69
665	104.6
670	147.7

In both figures, the liquidus curves related to β-As$_2$Te$_3$ would be metastable and located at temperatures lower than those at which vitreous materials are obtained by annealing raw glassy products. Consequently, these glassy materials, although initially homogeneous, are unstable and may evolve towards a transitory heterogeneous vitreous state, the occurrence of which is allowed by the existence of a metastable As-sided liquidus. This is analogous to cooling an x-composition mixture from the temperature of the figure point (●).

TABLE 4

Calculated pressure values p_{calc} for the melting equilibrium curve of β-As$_2$Te$_3$ and percentage deviations Δ in the representation of experimental values [7] by means of the equation below derived from that in Table 3 by putting $a = 1$ and $b = 0$

T (K)	p_{exp} (MPa)	p_{calc} (MPa)	Δ
730.9	840.7	841.2	0.06
734.3	913.3	893.2	−2.20
736.4	904.0	926.9	2.53
738.1	963.7	955.0	−0.90
743.0	1053.9	1040.4	−1.28
744.7	1074.9	1071.6	−0.31
747.1	1113.6	1117.2	0.32
748.8	1154.6	1150.5	−0.36
753.6	1242.4	1249.7	0.59
756.0	1350.1	1302.2	−3.55
758.3	1373.5	1354.5	−1.38
768.8	1606.6	1618.4	0.73
773.1	1733.6	1739.5	0.34
785.1	2082.0	2123.3	1.98

Interpolating equation:

$$p = p_0\left(\frac{T}{T_0}\right)^c$$

$p_0 = 819.1$ MPa; $T_0 = 729.4$ K; $c = 12.9439$.

Extrapolated values:

T (K)	p_{calc} (MPa)
200	4.4×10^{-5}
75	1.3×10^{-10}
70	5.5×10^{-11}

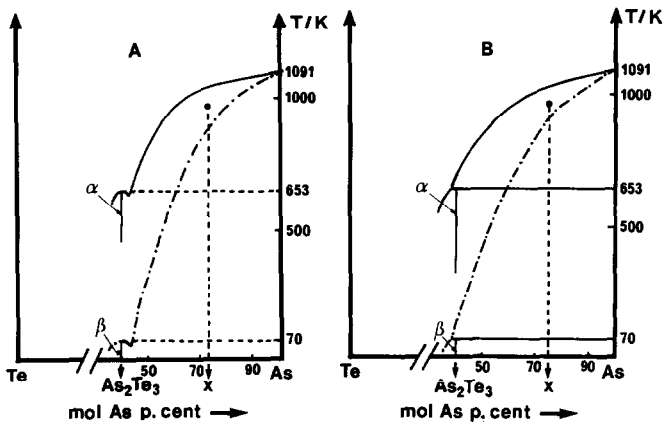
Fig. 2. As-rich part of the As–Te diagram. A: case of congruent melting of α- and β-As$_2$Te$_3$; B: case of non-congruent melting of α- and β-As$_2$Te$_3$.

Finally, this interpretation, which does not require a metastable liquid–liquid miscibility gap to occur, is consistent with volume relaxation or prenucleation phenomena due to the nature of the dimorphism of As_2Te_3.

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