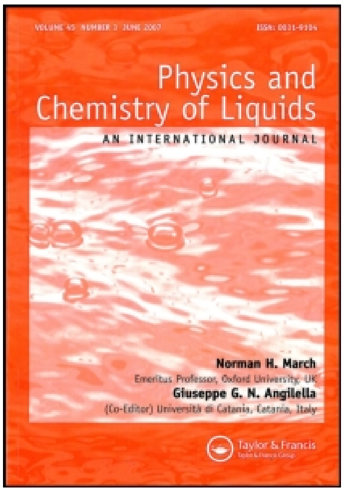

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Determination of the Free Enthalpy of Formation of the Au-Te Melts by Knudsen-Cell Effusion Combined with a Mass-Spectrometer

A. Yassin[a][b]; R. Chastel[a]; R. Castanet[a]
[a] Centre de Thermodynamique et de Microcalorimétrie du CNRS, Marseille, France [b] Department of physics, University of Baghdad, Baghdad, Iraq

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DETERMINATION OF THE FREE ENTHALPY OF FORMATION OF THE Au-Te MELTS BY KNUDSEN-CELL EFFUSION COMBINED WITH A MASS-SPECTROMETER

A. YASSIN*, R. CHASTEL and R. CASTANET

*Centre de Thermodynamique et de Microcalorimétrie du CNRS
26 rue du 141eme R.I.A. F-13003, Marseille, France*

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The vapor pressure of Te over the Au-Te melts was measured in the $0.48 \leqslant x_{Te} \leqslant 0.67$ range with the help of a Knudsen cell apparatus combined with a varian-Mat mass-spectrometer.

The activity of Te and the partial Gibbs energy of Te in the melt, $a_{\mathrm{Te}}$and $g_{\mathrm{Te}}^{xs,f}$, were deduced respectively. The integral Gibbs energy of formation of the melt, $g^{xs,f}$ was calculated from Gibbs-Duhem integration. $g^{xs,f}$ at 753K shows a minimum of -1.94 kJ.mol^{-1} at $x_{\mathrm{Te}} = 0.55$.

From the Gibbs energy of formation of the melt and the thermodynamic properties of pure Te the phase boundary corresponding to the liquid + pure Te was calculated in good agreement with the experimental phase diagram. From the enthalpy of formation of the $AuTe_2$ compound combined with Gibbs energy of the melt we also calculated the entropy of formation of the compound at its melting point and we could calculate the liquidus line of the $AuTe_2$ + liquid domain. The agreement with the experimental phase diagram is good too.

Keywords: Mass spectrometry; gibbs energy; phase diagram; knudsen cell; activity; Au–Te system

1. INTRODUCTION

The phase diagram of the Au–Te system [1] from the data of [2–4] exhibits only one intermediate compound with low melting temperature

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*Department of physics, University of Baghdad, Al-Jadriyah, Baghdad-Iraq.

(737 K), two eutectic points ($x_{\mathrm{Te}} = 0.53$ at 720 K and $x_{\mathrm{Te}} = 0.88$ at 689 K) where x_{Te} is the mole fraction of Te (Fig. 1). The enthalpy of formation of the melt is now well-known since Yassin *et al.* [5] have determined definitely its composition and temperature dependences. Their results are in good agreement with that of Ishida [6] and Castanet *et al.* [7] at low temperature ($\Delta h^f_{\min} = -1.10$ kJ.mol^{-1} at $x_{\mathrm{Te}} = 0.63$ for $737 < T < 819$ K). Δh^f is slightly negative on the Te-rich side and becomes positive on the other side. It increases with temperature between $819 < T < 872$ K and does not depend on temperature again for $T > 872$ K.

However the Gibbs energy of formation of the liquid phase is still unknown since the activity of tellurium, a_{Te}, is numerically available only for one composition ($x_{\mathrm{Te}} = 0.667$ over the temperature range

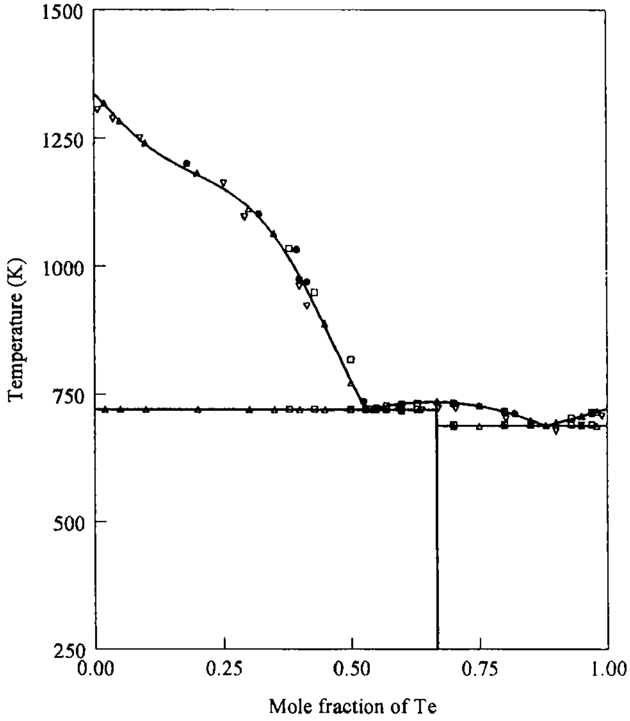

FIGURE 1 Phase diagram of the Au–Te system according to [1].
● : from ref. [2] □: from ref. [10] Δ : from ref. [3] ∇ : from ref. [4]

774–844 K) from [8]. Predel *et al.* [9] measured a_{Te} at 1281K but their results were published without any numerical data, and the temperature was not constant according to private communication [2].

That is why the aim of this work was to measure the activity of Te in the Au–Te melts in order to obtain its free enthalpy of formation. The data obtained from Knudsen effusion will be used to make again the critical assessment of the thermodynamic properties of the system. Such an assessment was already performed by Feutelais *et al.* [10] before our last calorimetric investigations [5] which lead to a very different thermodynamic behavior of the liquid phase.

2. EXPERIMENTAL

a. Alloy Preparation

The alloys were synthesized by weighing pure components (purchased from Kock-Light, purity 5*N*) in suitable proportions according to the phase diagram. The mechanical mixtures were sealed in quartz ampoules under vacuum (~1.3 Pascal) before melting. Each ampoule was annealed for about ten hours at a temperature above the melting point of the alloy. After several cycles of melting and crystallization, the temperature was lowered to about 10 K below the melting point and the sample was annealed for the time necessary to reach the equilibrium state, then slowly cooled to room temperature. All the alloys were verified by differential calorimetric analysis (DCA) technique where the fusion temperature was checked and compared with the phase diagram. As an example, Figure 2 shows the thermogram obtained for $x_{Te} = 0.6$. The points *E* and *L* correspond to the temperatures of the rich-Au eutectic and to the liquidus respectively in agreement with the phase diagram.

b. Apparatus and Method

The DCA were performed with the help of a high temperature Tian-Calvet calorimeter with a heating rate ~ $15 \mathrm{K.h}^{-1}$.

The apparatus used for the vapor pressure measurements is a single focusing Varian Mat mass spectrometer of the CH5 type combined with one effusion cell. The Knudsen cell was in vitreous carbon (CV2500 Le

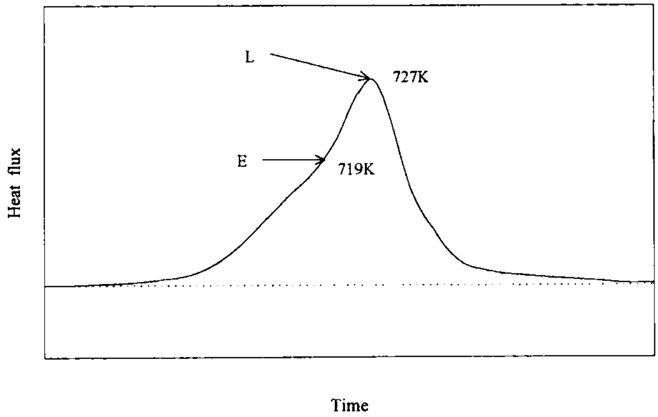

FIGURE 2 Thermogram obtained by differential calorimetric analysis on a sample of $x_{Te} = 0.6$ with a heating rate of 15 K.h^{-1}. *E*: Eutectic level (719 K). L: Liquidus (727 K).

Carbonne-Lorraine, France). It was placed in a dense graphite container (5890 PT, Le Carbonne-Lorraine, France) in order to avoid any temperature gradient. The electron energy used to ionize the effusing species was 14eV to minimise the fragmentation process. The weight loss during the experiment was obtained by weighing the cell and its contents at room temperature before and after each experiment.

The vapor effusing from the Knudsen cell was analyzed with the help of the mass spectrometer previously described [11]. The partial vapor pressure of the specie *i*, P_i, can be obtained from the following relation:

$$P_i = I_i^+ . T / S_i \qquad (1)$$

Where T is the absolute temperature, I_i^+ and S_i are respectively the intensity of the ionic current and a proportionality factor (including several terms) corresponding to the specie *i* [12].

Since the application domain of the mass spectrometer corresponds to very low pressures ($P < 0.1$ Pascal), the partial vapor pressure P_i can be assimilated to the fugacities and the activity of the specie *i*, a_i, can be written:

$$a_i(x_i,T) = \frac{P_i}{P_i^0} = \frac{I_i^+}{I_i^{0+}} \tag{2}$$

where I_i^+ and I_i^{0+} are the intensities corresponding to the specie i in equilibrium with the mixture and pure i respectively. This relation can be applied only when S_i takes the same value for the two determinations which is only realized with multicell mass spectrometers. Then, we had to measure I_i^+ and I_i^{0+} from two separate experiments and to compare the results. Each alloy investigated had a composition corresponding to the two-phase domain AuTe$_2$-Au rich eutectic ($0.53 \leqslant x_{\mathrm{Te}} \leqslant 0.667$) at low temperature. Then, we crossed over for each of them the eutectic level at 720 K. Since at this temperature the tellurium pressure is the same for every composition we could normalize the values of $\ln I_{\mathrm{Te}2}^+ . T$ and avoid the errors due to eventual variations of S_i. Moreover, because of the strong increase of the pressure of tellurium above its melting point, the conditions of Knudsen effusion and those of the detection of the ionic current by the spectrometer were not satisfied. Then, in order to avoid also the determination of S_i, we measured three times the vapor pressure of pure tellurium at its melting point (723 K). We could compare in this way the values of $\ln I_{\mathrm{Te}2}^+ . T$ at 753 K to a mean value of $\ln I_{\mathrm{Te}2}^{0+} . T$ also at 753 K determined by extrapolation from the experimental measurements at 723 K and the slope derived from the enthalpy of vaporization of Te$_2$ taken from the literature [13].

In the temperature range investigated, the tellurium vapor is mainly constituted by the Te$_2$ specie (>99% at 753 K) and the activity of Te, can be defined as:

$$a_{\mathrm{Te}} = \sqrt{\frac{I_{\mathrm{Te}2}^+}{I_{\mathrm{Te}2}^{0+}}} \tag{3}$$

3. RESULTS

The results obtained are summarized in Table I. Columns 2 and 3 give the values of $\ln I_{\mathrm{Te}2}^+ . T$ determined at the eutectic level and at temperatures T (column 4) respectively.

TABLE I Activities, $a_{\mathrm{Te}}(\pm 0.03)$, of tellurium of Au-Te liquid alloy at 753 K. (*) derived from the work of [8]

x_{Te}	$(\ln I_{\mathrm{Te}_2}.T)$ *at the eutectic level*	$\ln I^{+}_{\mathrm{Te}_2}.\mathrm{T}$	$T(K)$	*Normalisation* $\ln I^{+}_{\mathrm{Te}_2}.T_{(753)}$	a_{Te}
0.485	11.50	12.67	782	12.25	0.325
0.530	11.55	12.80	772	12.59	0.385
0.570	11.79	13.20	763	12.95	0.460
0.600	11.68	12.97	755	12.94	0.460
0.610	12.00	13.12	741	13.25	0.535
0.615	11.85	13.13	763	12.84	0.435
0.623	11.92	13.44	766	12.90	0.470
0.635	11.80	13.08	754	13.05	0.485
0.645	11.97	13.48	756	13.25	0.535
0.667					0.560*

The normalized data (column 5) were compared to the mean value of the three measurements at the melting point of pure Te ($\ln I^{0+}_{\mathrm{Te}2}.T = 13.72$) and from the variation of P_{Te_2} between 723 and 753 K using the enthalpy of vaporization of Te of Hultgren *et al.* [13] i.e., 119.16 kJ . mol^{-1} of Te_2. The values of the activity of Te are given in Table I, column 6. The value of line 10 was derived from the work of Veale *et al.* [8] using the P_{Te_2} value of pure Te from Hultgren *et al.*

The activity of tellurium calculated as mentioned before are shown in Figure 3.

We calculated the excess partial free enthalpy of formation of Te in the whole range of concentration as:

$$g^{xs,f}_{\mathrm{Te}} = RT\ln(a_{\mathrm{Te}}/x_{\mathrm{Te}}) \tag{4}$$

$$\begin{aligned} g^{xs,f}_{\mathrm{Te}}/\mathrm{kJ.mol}^{-1} = {} & (1-x_{\mathrm{Te}})^2(-7.36 + 39.37x_{\mathrm{Te}}] \\ & - 63.88x^2_{\mathrm{Te}} + 3141.4x^3_{\mathrm{Te}} - 7384.7x^4_{\mathrm{Te}} \\ & + 7972.2x^5_{\mathrm{Te}} - 3232.7x^6_{\mathrm{Te}}) \end{aligned} \tag{5}$$

By the Gibbs-Duhem relation we also calculated the excess free integral enthalpy of formation by:

$$\begin{aligned} g^{xs,f}/\mathrm{kJ.mol}^{-1} = {} & x_{\mathrm{Te}}(1-x_{\mathrm{Te}})(-7.36 + 19.69x_{\mathrm{Te}} \\ & - 201.29x^2_{\mathrm{Te}} + 785.34\mathrm{x}^3_{\mathrm{Te}} - 1476.94x^4_{\mathrm{Te}} \\ & + 1328.69x^5_{\mathrm{Te}} - 451.82x^6_{\mathrm{Te}}) \end{aligned} \tag{6}$$

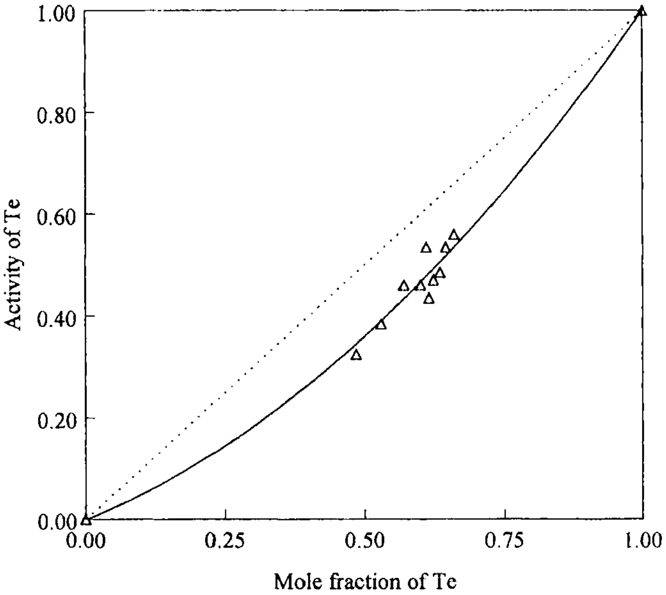

FIGURE 3 Activity of Te in the Au–Te melts at 753 K versus mole fraction of Te.

4. DISCUSSION

In order to check the validity of the results we calculated the phase diagram from the thermodynamic functions of the four phases i.e. pure Au, pure Te, liquid phase and $AuTe_2$ solid compound. The data corresponding to the pure components were taken from Hultgren *et al.* [13]

$$\Delta h_{Au}^{mel} = 12.55\ \text{kJ. mol}^{-1},\ T_{Au}^{mel} = 1337.3\ \text{K}$$

$$\Delta h_{Te}^{mel} = 17.49\ \text{kJ. mol}^{-1},\ T_{Te}^{mel} = 720.3\ \text{K}$$

We used for the enthalpy of formation of the liquid our calorimetric results published previously [5] which were fitted as follows:

$$\Delta h^{f}(751 < T/\text{K} < 819)/\text{kJ. mol}^{-1} = x_{Te}(1 - x_{Te})$$

$$(18.42 - 67.21 x_{Te} + 48.41 x_{Te}^{2})$$

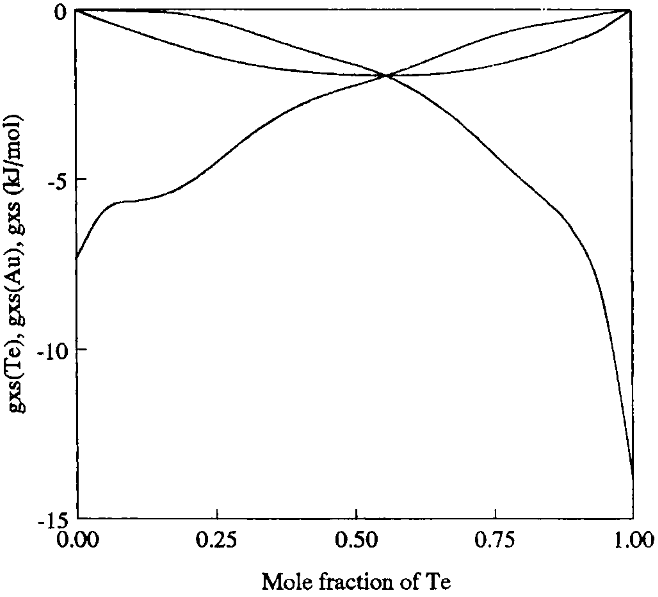

FIGURE 4 $g_{\mathrm{Te}}^{xs,f}$, $g_{\mathrm{Au}}^{xs,f}$ and $g^{xs,f}$ for liquid Au – Te alloys at 753 K versus mole fraction of Te.

$$\Delta h^f(872 < T/\mathrm{K} < 1000)/\mathrm{kJ.\,mol^{-1}} = x_{\mathrm{Te}}(1 - x_{\mathrm{Te}})$$
$$(12.45 - 39.16x_{\mathrm{Te}} + 24.44x_{\mathrm{Te}}^2)$$

The enthalpy of the formation of the solid compound was taken from Anres *et al.* [14] as

$$\Delta h^f(\mathrm{Au_{0.33}Te_{0.67}})/\mathrm{kJ.\,mol^{-1}} = -3.3$$

Its excess entropy of formation was calculated from the equilibrium between the solid and the liquid phases at its melting point (737 K). We found:

$$\Delta s^{f,xs}(\mathrm{Au_{0.33}Te_{0.67}})/\mathrm{J.mol^{-1}.K^{-1}} = -19.1$$

The phase diagram obtained in such a way is shown in Figure 5. The agreement between the calculated and experimental boundaries is good for

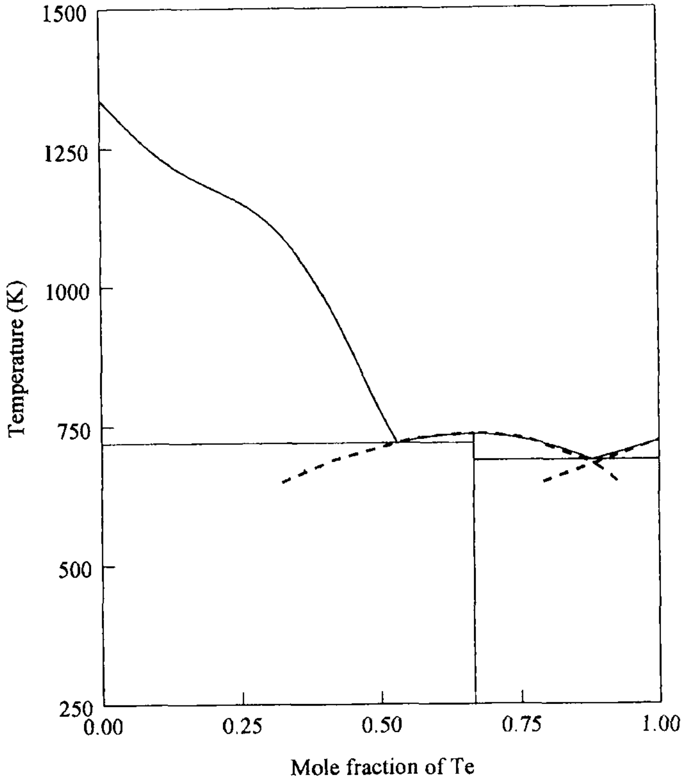

FIGURE 5 Phase diagram of the Au – Te binary system Full lines: according to [1]. Dotted lines: calculated from the thermodynamic functions of formation of phases.

the liquid-AuTe$_2$ equilibria and for the liquid-solid Te. We did not calculate the Au-rich liquidus since there is no experimental data for the enthalpy of formation nor for the Gibbs enthalpy of formation of the melt in this concentration range. Especially for the enthalpy of formation in the Au-rich side, any extrapolation should be very questionable since it depends strongly on the number of coefficients of the polynomial fitting.

5. CONCLUSION

Except in the Au-rich domain, the thermodynamic functions of formation of the different phases of the system are now well-known.

TABLE II Excess partial free enthalpy of formation of Te, $g^{xs,f}_{Te}$, of Au, $g^{xs,f}_{Au}$, and excess free enthalpy of formation, $g^{xs,f}$, of liquid Au – Te at 753K

x_{Te}	$g^{xs,f}_{Te}(J.mol^{-1})$	$g^{xs,f}_{Au}(J.mol^{-1})$	$g^{xs,f}(J.mol^{-1})$
0	−7358	0	0
0.05	−5911	−28	−322
0.10	−5653	−47	−608
0.15	−5496	−70	−884
0.20	−5107	−155	−1145
0.25	−4514	−328	−1375
0.30	−3861	−576	−1562
0.35	−3277	−857	−1704
0.40	−2822	−1129	−1806
0.45	−2488	−1374	−1876
0.50	−2225	−1612	−1919
0.55	−1972	−1892	−1936
0.60	−1691	−2274	−1924
0.65	−1377	−2800	−1875
0.70	−1056	−3467	−1780
0.75	−772	−4216	−1633
0.80	−555	−4961	−1436
0.85	−401	−5688	−1194
0.90	−267	−6645	−905
0.95	−111	−8672	−539
1.00	0	−13702	0

In a next paper we will describe the results of the critical assessment of the thermodynamic data of the binary including the experimental phase diagram. This assessment will lead to values of the excess free enthalpy of the melt on the Au-rich side in agreement with Au-rich boundary. Then it will be possible to use a model which describe the behavior of this system.

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