from run k at 370°C) with carbon in Cl_2, and no exothermic peak at 200~300°C is observed. Curve (m) is the result for the hematite-carbon system in Cl_2.

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References

1) T. Ishii, R. Furuichi, Y. Kobayashi, *Thermochim. Acta* 9, 39 (1974)
2) JIS M 8361 - 1968, "Methods for chemical analysis of bauxite ores", Japan (1968)

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Thermochemical Studies of Au + Te

Takao Ishida, Takashi Maekawa and Toshio Yokokawa

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Enthalpies of mixing of gold + tellurium have been measured at 769 K by a high temperature calorimeter. The results are in agreement with the values by Castanet *et al.*, but differ from those by Predel and Piehl. The enthalpy of fusion of $AuTe_2$ was also determined. These allow to evaluate the enthalpy of formation of $AuTe_2(s)$.

Introduction

In the previous papers we have reported a series of enthalpies of liquid solution of B-metal + chalcogen systems.[1-4] The results indicated that these systems show large negative enthalpies of mixing in the liquid state, and the minima in the enthalpy – composition diagram appear at the compositions of the solid compounds at lower temperature. Both Castanet *et al.*[5] and Predel and Piehl[6] have measured the enthalpies of mixing in gold + tellurium system. Their values disagree each other, partly because of quite different experimental temperatures. In this paper the results obtained in our laboratory and the enthalpy of fusion of $AuTe_2$ are reported and are discussed in terms of bond formation in the liquid state.

Experimental

The calorimeter and the experimental procedure are the same as described in the previous paper.[1] For the determination of the enthalpy of fusion of the compound, the solution calorimetry method with the same experimental procedure as in the above mixing was applied. The $AuTe_2$ was dissolved in liquid tin both below and above the melting point. The concentrations of $AuTe_2$ in tin solvent after the dissolution were 1.2 and 1.5 mol per cent. In order to prepare the compound, the mixture of the nominal composition was sealed in an evacuated quartz tube and heated up to 775 K for 24 h. The purities of gold and tellurium were better than 99.99 mass per cent and that of tin was 99.96 mass per cent.

Results and Discussion

The observed enthalpies of mixing are shown in Table 1 and are plotted in Fig. 1 with the data of the previous authors. The present results are in good agreement with the values at 737 K by Castanet *et al.* and are much more endothermic than those of Predel and Piehl at 1281 K. In the second column of the Table 1, $H^E(s)$ is the raw value with solid gold. Subtracting the enthalpy of fusion times mole fraction of gold from $H^E(s)$, $H^E(l)$ is evaluated. The difference of heat capacities of liquid and solid was neglected. In Fig. 2 are plotted $H^E(l)$ referred to the pure liquid metals and the partial molar enthalpy of tellurium evaluated by derivative of $H^E(l)$ equation of fourth order of composition:

Department of Chemistry, Faculty of Science,
Hokkaido University, Sapporo 060

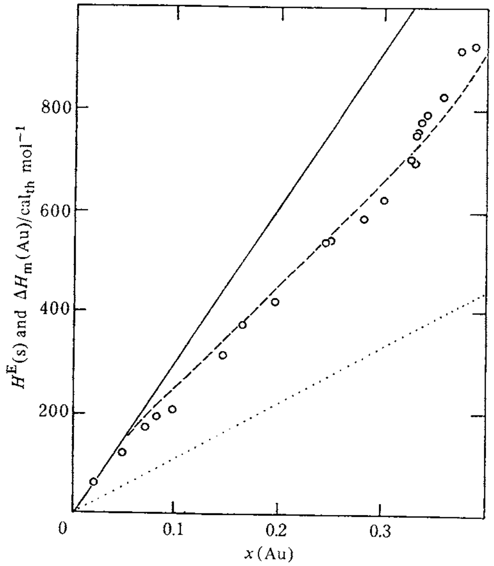

Fig. 1. Enthalpies of mixing of gold + tellurium. ○ ; this work, Dashed line; Castanet *et al.* by 737 K, Dotted line; Predel and Piehl by 1281 K, Solid line; enthalpy of fusion of gold.

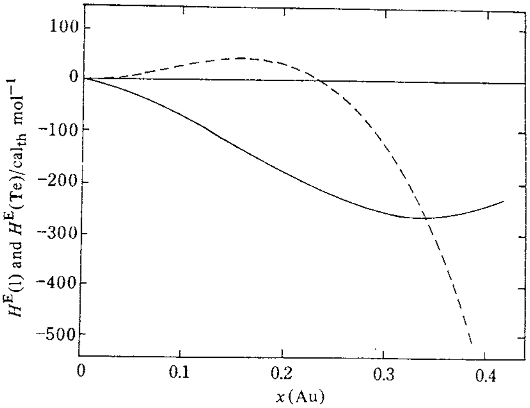

Fig. 2. Enthalpy of mixing of gold + tellurium (solid curve) and the partial molar enthalpy of tellurium (dashed curve) referred to the liquid state expressed by a fourth order equation.

Table 1. Molar excess enthalpies of gold + tellurium at 769 K.

x(Au)	$H^E(s)^{\dagger}$/cal$_{th}$ mol^{-1}	$H^E(l)^{\dagger\dagger}$/cal$_{th}$ mol^{-1}
0.024	65.3	−8.3
0.048	121.3	−26.1
0.072	173.3	−47.5
0.081	199.3	−47.1
0.095	210.6	−79.5
0.145	317.9	−125.6
0.165	377.5	−127.0
0.194	424.1	−168.2
0.244	541.7	−202.2
0.249	541.9	−218.5
0.280	592.3	−261.5
0.299	625.1	−285.3
0.325	708.7	−282.2
0.331	699.8	−308.9
0.333	782.9	−232.8
0.333	754.0	$-249.4^{\dagger\dagger\dagger}$
0.333	766.9	−262.4
0.341	795.3	−245.6
0.356	832.9	−251.7
0.380	894.0	−265.3
0.394	953.4	−248.6

† Au(s) + Te(l)

†† Au(l) + Te(l)

††† Measured at 761 K

$$H^E(l)/\mathrm{cal}_{th}^{\dagger}\ \mathrm{mol}^{-1} = 15340x^4 - 478x^3 - 2600x^2 - 461x$$

and

$$\sigma/\mathrm{cal}_{th}\ \mathrm{mol}^{-1} = 17.7\ ,$$

where x is an atomic fraction of gold and σ is a root mean square deviation. Further addition of higher order term on it did not improve curve fitting. In a similar way as the other homologous systems, the minimum appears at the composition of $AuTe_2$ which is only one compound known in this system.[7] The partial molar enthalpy of tellurium derived from the equation is positive in the range of low gold concentration and turns to negative with increase of gold content.

The results for the solution calorimetry are given in Table 2. If we use the linear relation between the enthalpy of solution and temperature, the gap between higher and lower lines corresponds to the enthalpy of fusion of $AuTe_2$. The two sets of enthalpies of solution lead to $\Delta H_m(AuTe_2) = (15.3 \pm 2.5)$ kcal$_{th}$ mol^{-1}. The reported melting point ranges 725 to 747 K.[7] Our own experiment shows $T_m(AuTe_2) = (733 \pm 2)$K. The entropy of fusion derived to be 20.9 cal$_{th}$ K^{-1} mol^{-1}. The data above permits evaluation of the enthalpy of formation of $AuTe_2$,

$$Au(s) + 2Te(s) = AuTe_2(s)$$

$$\Delta H_f(AuTe_2, 733K) = -4.69\ \mathrm{kcal}_{th}\ \mathrm{mol}^{-1}.$$

In Table 3 are listed the entropies of fusion of some tellurides.

The entropy of fusion classifies the liquids into two groups, one is order(solid)→order(liquid) type and the other is order(solid)→disorder(liquid) type.[8] In the former case the entropy of fusion can be well approximated by the sum of the entropy of fusion of individual element. On the other hand in the latter case an

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† Throughout this paper cal$_{th}$ = 4.184 J

Table 2. Enthalpies of solution of $AuTe_2$ in liquid tin.

$x(AuTe_2)$	T/K	ΔH_{soln}/$kcal_{th}$ mol^{-1}
0.0121	704	−28.93
0.0118	712	−26.99
0.0121	722	−26.94
0.0119	742	−37.37
0.0119	748	−34.95
0.0119	767	−32.29
0.0120	788	−32.73†
0.0154	704	−30.69
0.0153	712	−28.57
0.0155	716	−28.43
0.0153	723	−28.04
0.0153	734	−41.91
0.0154	742	−41.30
0.0153	748	−39.30
0.0152	767	−35.87
0.0150	788	−34.29†

† These values are excluded when the enthalpies are expressed as a linear function of temperature, because these temperatures are far apart from the other points.

additional term corresponding to the entropy of random mixing should be taken in account. Thus, Sb_2Te_3 and In_2Te_3 seem not to change in chemical bonding on fusion, while Bi_2Te_3 and the present $AuTe_2$ behave like liquid alloys where the compounds dissociate into atoms on fusion and they mixed randomly.

Table 3. The entropy of fusion of some tellurides.

Compounds	ΔS_m / cal_{th} K^{-1} mol^{-1}	$\{\Delta S_m - \sum_i \Delta S_{m,i}\}$† / cal_{th} K^{-1} mol^{-1}
In_2Te_3	20.6††	−0.4
Sb_2Te_3	26.6†††	−1.3
Bi_2Te_3	32.9†††	+6.0
$AuTe_2$	20.9	+7.1

† $\sum_i \Delta S_{m,i}$ is the sum of the entropy of fusion of individual element

†† Reference 9

††† Reference 10

References

1) T. Maekawa, T. Yokokawa and K. Niwa, *J. Chem. Thermodyn.*, 3, 143 (1971)
2) T. Maekawa, T. Yokokawa and K. Niwa, *J. Chem. Thermodyn.*, 3, 707 (1971)
3) T. Maekawa, T. Yokokawa and K. Niwa, *J. Chem. Thermodyn.*, 4, 153 (1972)
4) T. Maekawa, T. Yokokawa and K. Niwa, *J. Chem. Thermodyn.*, 4, 873 (1972)
5) R. Castanet, Y. Claire and M. Laffitte, *J. Chim. Phys. Phys.-chim. Biol.*, 68, 1133 (1971)
6) B. Predel and J. Piehl, *Z. Metallkd.*, 66, 33 (1975)
7) M. Hansen and K. Anderko, "Constitution of Binary Alloys", McGraw-Hill, New York (1958)
8) O. Kubaschewski, E. LL. Evans and C. B. Alcock, "Metallurgical Thermochemistry", Pergamon Press, Oxford (1967)
9) B. W. Howlett, S. Misra and M. B. Bever, *Trans. Met. Soc. AIME.*, 230, 1367 (1964)
10) P. M. Robinson and M. B. Bever, *Trans. Met. Soc. AIME.*, 236, 814 (1966)