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THE HEAT CAPACITY OF $Cu_2Te(c)$, $CuTe(c)$, $Ag_2Te(c)$ AND $Ag_{1.64}Te(c)$

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ABSTRACT

The heat capacities and enthalpies of $Cu_2Te(c)$, $CuTe(c)$, $Ag_2Te(c)$ and $Ag_{1.64}Te(c)$ have been measured for the temperature range (280–800 K) using differential scanning calorimetry. Several transitions were observed in these substances and the enthalpies associated with these transitions have been determined.

INTRODUCTION

Copper and silver tellurides occur naturally as ores and are also major constituents of the slime produced in the electrolytic refining of copper. Recent interest in these substances arises from their potential use in semi-conductor devices. Heat capacities and enthalpies[1] of $Cu_2Te(c)$ over the temperature range (327–937 K) and enthalpies[2] of $Ag_2Te(c)$ for the range (288–663 K) have been measured. Low temperature heat capacities of $Ag_2Te(c)$[3] and $Ag_{1.88}Te(c)$[4] have also been reported. Values of $-\{G(T)-H(298)\}T^{-1}$ for $Cu_2Te(c)$, $Ag_2Te(c)$ and $Ag_{1.64}Te(c)$, reported by Mills[5] were calculated from the preliminary measurements of C_p obtained in this investigation. Standard thermodynamic properties of $Cu_2Te(c)$, $CuTe(c)$, $Ag_2Te(c)$ and $Ag_{1.64}Te(c)$ have been calculated from the heat capacities measured in this investigation.

EXPERIMENTAL

Materials

The preparation of $Cu_2Te(c)$, $Ag_2Te(c)$ and $Ag_{1.64}Te(c)$ has been described[5]. Copper telluride, $CuTe(c)$ was prepared from weighed stoichiometric amounts of tellurium (99.999 per cent purity) and copper powder (purity 99.9 per cent) reduced with hydrogen immediately prior to use. Pellets made from an intimate mixture of the elements were enclosed in silica capsules; the capsules were evacuated and heated at 500 K for one month and then slowly cooled. The product was crushed, mixed and encapsulated under vacuum. It was annealed at 500 K for one month and slowly cooled to room temperature.

Measurements

Measurements were made using a model 1B Perkin-Elmer differential scanning calorimeter (DSC). The calorimeter output was recorded as a voltage–time curve

(Fig. 1a); the voltage was proportional to the power required to maintain the sample pan at the same temperature as that of a reference pan. The calorimeter was always operated in the "specific heat mode"[6]. Readings were started with the calorimeter temperature, T_1, constant to define an isothermal baseline. The temperature was then raised at a linear rate to T_2 where readings were continued to give the isothermal baseline at this temperature. The calorimeter was first run empty, then filled with an inert calibrant and finally with the material under investigation. Calorimetry Conference synthetic sapphire was used as the calibrant.

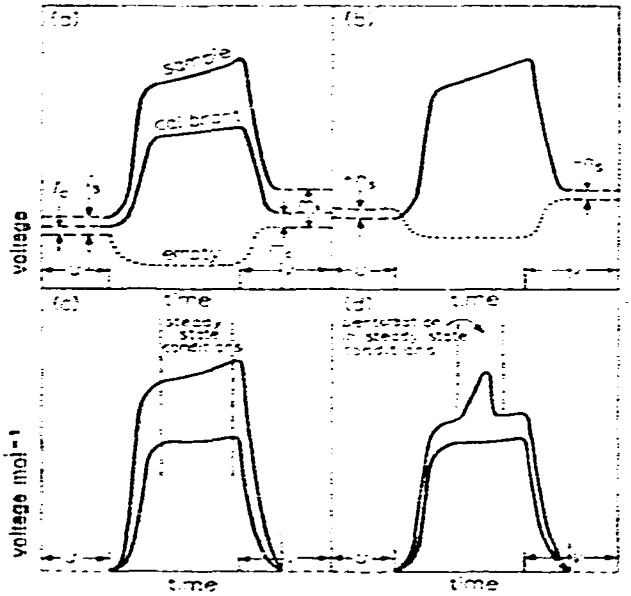

Fig. 1. Typical output data from DSC experiments and subsequent treatment of results. Programme temperatures (T_1 and T_2) are steady in the time regions *u* and *v* respectively. The vertical broken line on the abscissa is the time at which isothermal (T_2) conditions are attained in the calorimeter. a, Normal output of DSC; b, Treatment of data to superimpose "full" and "empty" curves (calibrant omitted for clarity); c, Composite "full minus empty" curves, reduced to unit molarity, for sample and calibrant; d, As (c) but showing deviations from "steady state" behaviour in sample.

The output signal from the DSC was measured with a digital voltmeter and recorded on paper tape. Data were treated using a method developed by Richardson, certain aspects of which have been described previously[7]. The primary aim of the data treatment was to construct composite "full minus empty" curves (Fig. 1c) by subtracting the curve for the empty calorimeter from those for the filled calorimeter. The areas enclosed by these are proportional to the enthalpy change, $H(T_2)-H(T_1)$, from T_1 to T_2. For clarity the curves of Fig. 1a are shown with the ordinate values displaced. This focuses attention on a major experimental problem, the poor reproducibility of the isothermal baselines. Ideally all isothermal portions should be coincident, that is, $l_i=m_i=0$, where i=c (calibrant) or s (sample). A constant displacement ($l_i=m_i$) is easily accommodated by adding the appropriate value to all points for the "empty" curve. In practice, however, it is usually found that $l_i \neq m_i \neq 0$ and additional data treatment is essential to obtain consistent results. In this work the "empty" curve was roughly superimposed on a "full" curve by adding the mean value of l_i and m_i to all points for the "empty" curve. The resulting curve had a constant error, $\pm n_i$, at the two isothermal ends (Fig. 1b). It was assumed that the mismatch, n_i, varied smoothly with temperature and a final correction $\pm n_i$ was added to all points in the isothermal regions with appropriately scaled values at intermediate temperatures.

The above procedure was completely justified experimentally. Thus it was very occasionally possible to obtain $l_i = m_i = 0$ and the resulting "full minus empty" areas were taken as reference values, A. Increasing the mismatch between l_i and m_i gave areas which deviated more and more from A after the initial approximate correction of $\frac{1}{2}(l_i + m_i)$. The second correction of $\pm n_i$, and proportions thereof, invariably brought these areas back to within ±1 per cent of A.

Accurate calibration of the dial temperature reading* was essential. The calibration was carried out by slow, stepwise ($\leqslant 0.1$ K increments) melting of eleven pure materials whose melting points had been determined using a platinum resistance thermometer calibrated in this laboratory. The factor for the conversion of areas to energies was then obtained from the results for synthetic sapphire. Data from two separate heating cycles are shown in Fig. 2. Least squares plots of the two are, fortuitously, identical. The scatter of the points gives a good idea of experimental reproducibility, most points are within ±1 per cent of the mean value. Although in principle the conversion factor should be independent of temperature, a slight

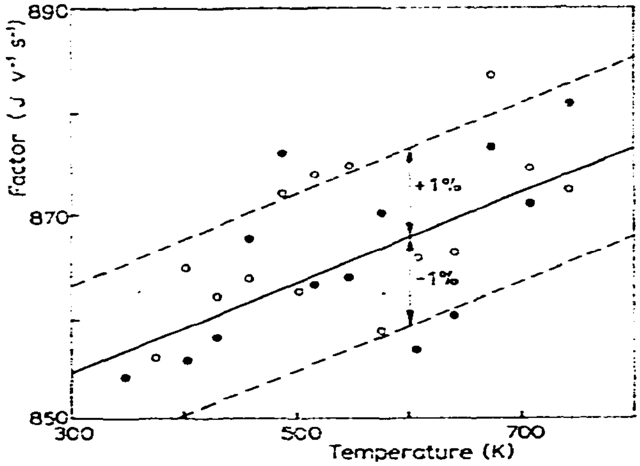

Fig. 2. The temperature dependence of the factor relating area and enthalpy of Al_2O_3: (———), linear least squares curve; (— — —), curves for error of +1 and −1 per cent; ○, experimental values for series 1; ●, experimental values for series 2.

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* Temperatures are based on IPTS-68.

increase (0.005 per cent K^{-1}) was always found in our experiments*. For temperatures above 730 K there is an uncertainty of ±1 K in the temperature calibration owing to the lack of well-defined melting points in the 723 to 800 K range. As both the reference material and the sample under investigation are run over the same temperature range, errors in the enthalpies, caused by uncertainties in the temperature, tend to cancel out.

There are no systematic deviations when reference materials other than synthetic sapphire are used, e.g. benzoic acid, at low temperatures where the vapour pressure is negligible, and well-characterized n-alkanes[8] gave factors indistinguishable from those in Fig. 2. It is therefore believed that the data treatment described enables enthalpy changes to be determined with a DSC to an accuracy of ±1 per cent. This is confirmed by the fact that values of $H(T)-H(298)$[9] obtained for ZnO(c), CdO(c) and Ga_2O_3(c) by DSC and by drop calorimetry agree within one per cent.

It is clearly a trivial operation to obtain the average heat capacity, C_p, for the temperature range T_1 to T_2 and where C_p varies slowly with temperature, this is the more accurate method of treating the output data to determine the heat capacity. However, the DSC, in principle, is capable of giving heat capacities at "point" temperatures since the ordinate is proportional to this quantity and the rate of heating. Maximum accuracy would therefore appear to be associated with the highest heating rates. This is not so, however, since in a dynamic experiment of this kind thermal lag between the specimen and the temperature sensors becomes of major importance. It is possible to correct for this effect when steady state conditions obtain but not when they are disturbed, for example in the vicinity of a phase transition, and here C_p values may be in error by several per cent. Thus in this paper when the curvature of the C_p–temperature curve is small, the data are believed to be accurate to ±1 per cent but uncertainties are much greater in the vicinity of phase changes.

An apparent transition temperature is a function of heating rate because of the dynamic nature of the method. Thus all transition temperatures quoted in the tables and related discussion are values obtained by extrapolating to zero heating rates and are therefore lower than the apparent values shown in Figs. 3, 5, 6 and 8.

It must be emphasized that the above comments relate to experimental difficulties in the definition of details of the path from T_1 to T_2 and do not affect the overall accuracy of the measurement of $H(T_2)-H(T_1)$.

Enthalpies of transition were obtained from enthalpy–temperature plots. Many of the transitions showed considerable "lattice loosening" prior to the major enthalpy increment and an unambiguous assignment of an isothermal enthalpy of transition is difficult. The DSC may be rapidly cooled and it was often possible to "supercool" a high-temperature form to a temperature low enough to determine the enthalpy of transition in a region where the lattice loosening is absent.

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* To our knowledge this is the only quantitative investigation of this effect. Conversion factors are normally obtained from the heat of fusion of one or two pure metals (usually including indium). We consider the thermodynamic properties of synthetic sapphire are much better defined.

RESULTS AND DISCUSSION

Throughout this paper the following values of molar mass were employed, $Cu_2Te(c) = 254.68$ g mol^{-1}, $CuTe(c) = 191.14$ g mol^{-1}, $Ag_2Te(c) = 343.34$ g mol^{-1} and $Ag_{1.64}Te(c) = 304.51$ g mol^{-1}.

$Cu_2Te(c)$

Values of the $Cu_2Te(c)$ heat capacity and enthalpy, $H(T) - H(298)$, for the temperature range (200–800 K) are plotted against temperature in Figs. 3 and 4 respectively. The values obtained by Kubaschewski[1] are also shown in these figures. The data recorded in the two investigations are in fair agreement. The five transitions reported by Kubaschewski[1] denoted I to V were all observed in this investigation but the enthalpies associated with transitions II and III were considerably different in the two studies and transition VI occurred at 750 K in this investigation compared with 850 K in Kubaschewski's experiments. The enthalpies of transition of $Cu_2Te(c)$ are compared in Table 1.

TABLE 1

THE TRANSITION TEMPERATURES AND ENTHALPY OF TRANSITIONS FOR $Cu_2Te(c)$

Transition	*This investigation*		*Kubaschewski*[1]	
	T_{trans} *(K)*	ΔH_{trans} *(kJ mol^{-1})*	T_{trans} *(K)*	ΔH_{trans} *(kJ mol^{-1})*
I	440	0.5	438	0.22
II	526	0.5	545	1.90
III	600	2.0	599	0.97
IV	625	2.6	631	2.50
V	750	2.0	850	1.97

The differences in the results of the two studies are probably due to small differences in the composition of the samples used in the different investigations. The thermodynamic properties listed in Table 2 were calculated from the heat capacity data recorded in this investigation and from the estimated entropy[10], $S°(298$ K, $Cu_2Te(c)) = 134.7$ J mol^{-1} K^{-1}.

$CuTe(c)$

Heat capacities were measured for the temperature range (266–605 K) and the experimental values are plotted against temperature in Fig. 5. Thermodynamic properties derived from these data and an estimated standard entropy[10], $S°(298$ K, $CuTe(c)) = 87.0$ J mol^{-1} K^{-1} are given in Table 3. A transition occurred at 610 K, confirming the observation by Stevels and Wiegers[11] that CuTe(c) disproportionates at 613 K into a tellurium-rich melt and the tellurium-rich limit of the $Cu_{3-x}Te_2(c)$ phase.

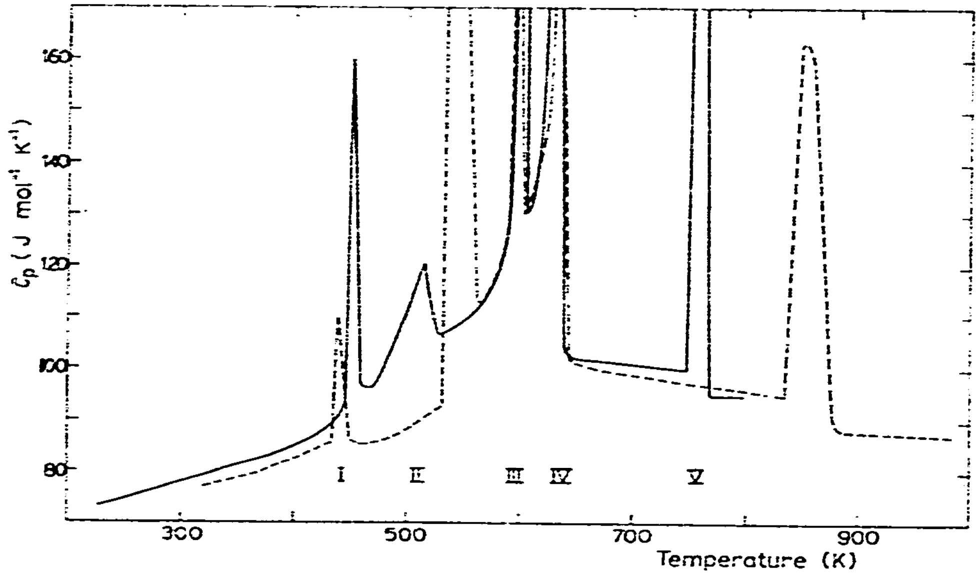

Fig. 3. The heat capacity of $Cu_2Te(c)$ as a function of temperature: (———), this investigation; (— — —), Kubaschewski[1].

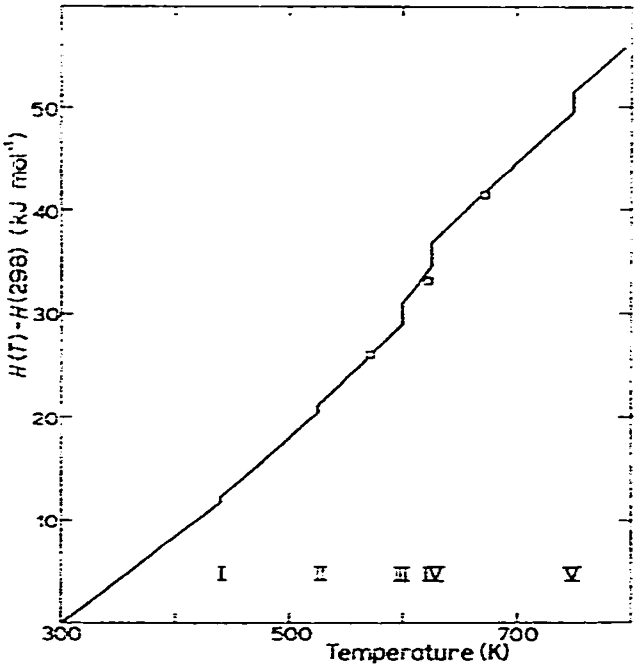

Fig. 4. The enthalpy of $Cu_2Te(c)$ as a function of temperature: (———), this investigation; ⊡ enthalpy values, taken from Kubaschewski[1].

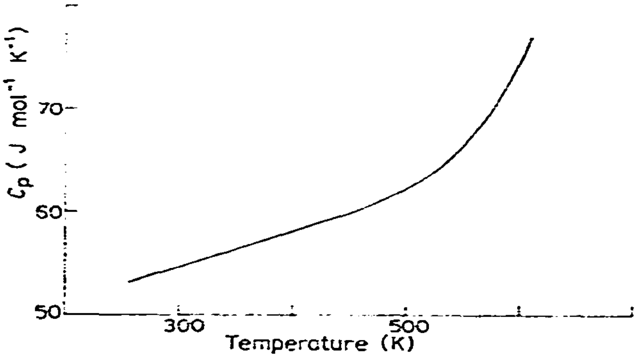

Fig. 5. The heat capacity of CuTe(c) as a function of temperature.

TABLE 2

THERMODYNAMIC PROPERTIES OF Cu_2Te(c)

T (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	$H(T)-H(298)$ ($J\ mol^{-1}$)	$S(T)-S(298)$ ($J\ mol^{-1}\ K^{-1}$)	$-\{G(T)-H(298)\}T^{-1}$ ($J\ mol^{-1}\ K^{-1}$)
298	77.63	0	0	134.70
350	81.17	4117	12.72	135.66
400	84.58	8261	23.78	137.83
440	87.31	11699	31.97	140.08
440	96.50[a]	12199	33.11	140.08
500	96.50[a]	17989	45.44	144.17
526	96.50[a]	20498	50.34	146.07
526	106.91	20997	51.29	146.07
550	107.90	23561	56.05	147.91
600	129.76	29404	66.21	151.90
600	130.50[a]	31404	69.54	151.90
625	130.50[a]	34666	74.87	154.10
625	102.50	37266	79.03	154.10
650	102.00	39822	83.04	156.47
700	101.00	44897	90.56	161.12
750	100.00	49922	97.49	165.63
750	95.00	51923	100.16	165.63
800	95.00	56673	106.29	170.15

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[a] For some transitions it is difficult to assign a temperature at which the transition first occurs, thus it becomes difficult to calculate accurate values of ΔH_{trans} from plots of C_p against temperature. More accurate values of ΔH_{trans} may be calculated for enthalpy-temperature plots. The thermodynamic properties listed in this table were derived from these more accurate values of ΔH_{trans} and by extrapolating the $C_p(T)$ equations to the temperature of transition, where the transition encompasses a large temperature range e.g. transition II for Cu_2Te(c), a constant value of C_p has been adopted. Thus the C_p values in the region of a transition are "extrapolated values" and do not represent the true values of C_p which can be obtained from the corresponding C_p–temperature plot (Fig. 3 for Cu_2Te).

TABLE 3

THE THERMODYNAMIC PROPERTIES OF CuTe(c)

T (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	$H(T)-H(298)$ ($J\ mol^{-1}$)	$S(T)-S(298)$ ($J\ mol^{-1}\ K^{-1}$)	$-\{G(T)-H(298)\}T^{-1}$ ($J\ mol^{-1}\ K^{-1}$)
298	54.44	0	0	87.00
350	56.25	2877	8.89	87.67
400	58.08	5735	16.52	89.18
450	59.98	8687	23.47	91.17
500	62.33	11734	29.89	93.42
550	66.29	14929	35.98	95.84
600	74.46	18433	42.07	98.35

$Ag_2Te(c)$

The heat capcity of $Ag_2Te(c)$ was measured over the temperature range (200–800 K); the heat capacity and enthalpy are plotted against temperature in Figs. 6 and 7, respectively. The transformation of orthorhombic $Ag_2Te(c)$ to cubic $Ag_2Te(c)$ occurred at 412 K.

Heat capacities in the temperature range (450–580 K) displayed a scatter of ±3 per cent which is much greater than the usual uncertainty of ±1 per cent. This behaviour was thought to be associated with the "thermal passage" of the sample through the transition. The heat capacity values with a quoted accuracy of ±5 per cent for $Ag_2Te(c)$ for the temperature range (80–300 K) reported by Gultyaev and Petrov[3] are 5 per cent greater than the values obtained in this investigation. Walsh, Art and White[4] have measured the heat capacity of $Ag_{1.88}Te(c)$ from 16 K

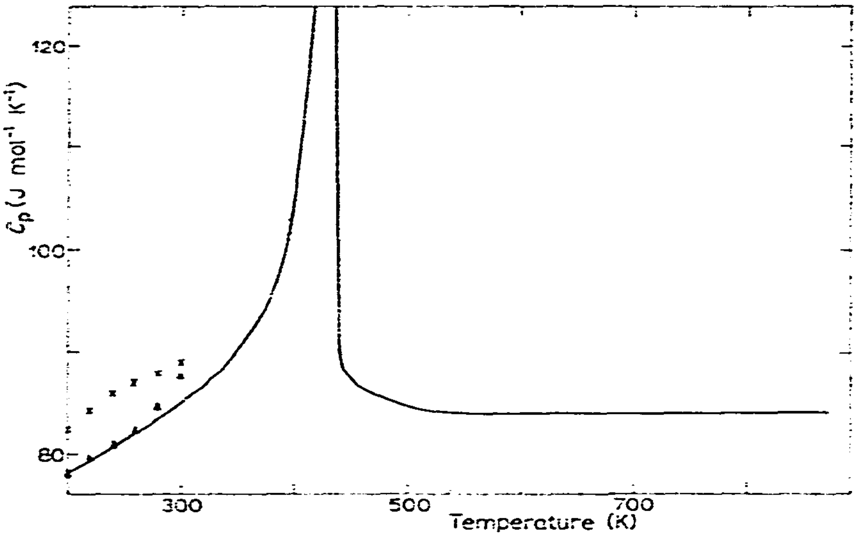

Fig. 6. The heat capacity of $Ag_2Te(c)$ as a function of temperature: (———), C_p values, this investigation; ×, C_p taken from ref. 3; △, $C_p(Ag_2Te)$ values calculated from data of ref. 4.

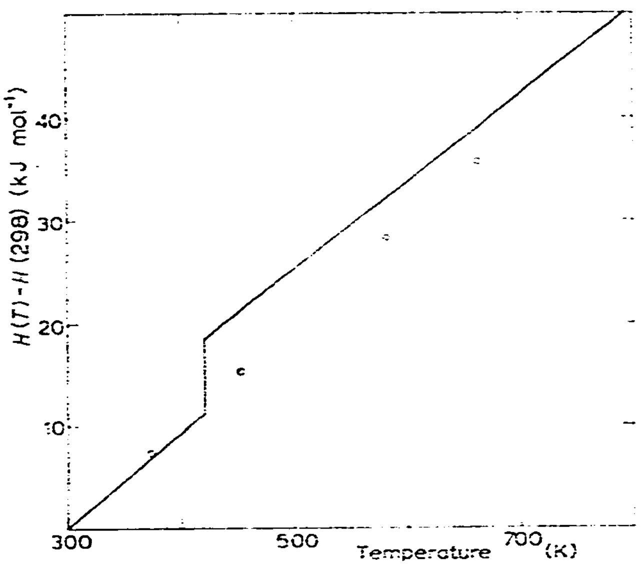

Fig. 7. The temperature dependence of the enthalpy, $H(T)-H(298)$, of $Ag_{1.64}Te(c)$: (———), this investigation; ○, enthalpy values due to Tilden[2].

to 296 K; in this range $Ag_{1.88}Te(c)$ consists of $(0.94\,Ag_2Te(c)+0.06\,Te(c))$ and values of $C_p(Ag_2Te(c))$ derived from these $C_p(Ag_{1.88}Te(c))$ and $C_p(Te(c))$[12] values are in good agreement with the values obtained in the present study. The enthalpy data for the temperature range (288–663 K) reported by Tilden[2] and evaluated by Kelley[13] are compared in Fig. 7 with enthalpy values obtained here. The values obtained for the enthalpy of transition are summarized in Table 4.

TABLE 4

THE TRANSITION TEMPERATURE AND ENTHALPY OF TRANSITION OF $Ag_2Te(c)$

Reference	*Method*	T_{trans} *(K)*	ΔH_{trans} *($Ag_2Te(c)$) (kJ mol^{-1})*
Kelley[13]	Evaluation of enthalpy measurements due to Tilden[2]	410	0.65
Kracek et al.[14]	Differential thermal analysis	418	12.2
This investigation	Differential scanning calorimeter—enthalpy measurements (Fig. 6)	421	7.4

Thermodynamic properties listed in Table 5 were derived from the present heat capacity data and a value, $S^\circ(298\text{ K}, Ag_2Te(c)) = 153.5\text{ J mol}^{-1}\text{ K}^{-1}$, obtained from Gibbs energy data[15–17] and the calorimetric value for $\Delta H_f^\circ(298\text{K}, Ag_2\,Te(c))$[18].

TABLE 5

THERMODYNAMIC PROPERTIES OF $Ag_2Te(c)$

T (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	$H(T)-H(298)$ ($J\ mol^{-1}$)	$S(T)-S(298)$ ($J\ mol^{-1}\ K^{-1}$)	$-\{G(T)-H(298)\}T^{-1}$ ($J\ mol^{-1}\ K^{-1}$)
298	85.02	0	0	153.50
300	85.20	170	0.56	153.50
350	89.88	4545	14.05	154.56
400	94.84	9163	26.37	156.96
421	96.98	11177	31.28	158.23
421	87.20	18577	48.85	158.23
460	85.98	21953	56.52	162.30
500	84.98	25371	63.65	166.41
550	84.00	29594	71.70	171.39
600	84.00	33794	79.01	176.18
650	84.00	37994	85.73	180.78
700	84.00	42194	91.96	185.18
750	84.00	46394	97.75	189.39
800	84.00	50594	103.17	193.43

$Ag_{1.64}Te(c)$

The heat capacity and enthalpy of $Ag_{1.64}Te(c)$ were measured over the temperature range (266–800 K) and are plotted against T(K) in Figs. 8 and 9, respectively. Five transitions were observed, denoted I to V, and the nature of some of these

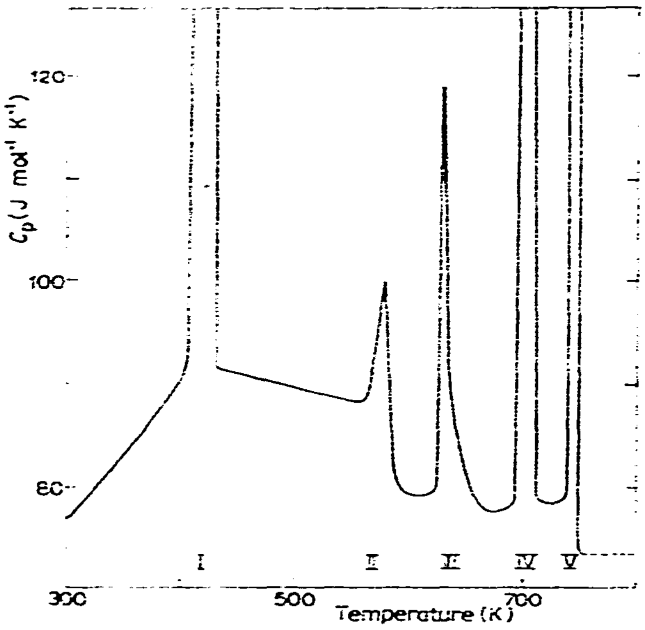

Fig. 8. The heat capacity of $Ag_{1.64}Te(c)$ as a function of temperature.

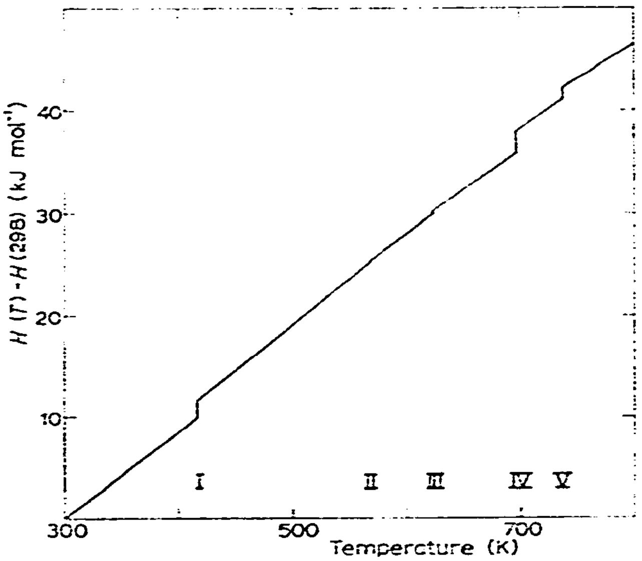

Fig. 9. The temperature dependence of the enthalpy, $H(T)-H(298)$, of $Ag_{1.64}Te(c)$.

transitions has been interpreted in Table 6 with the aid of the phase diagram recorded by Kracek et al.[14]. No other measurements of heat capacity have been reported; however, Kracek et al.[14] have listed enthalpy values for some of the transitions.

TABLE 6

THE TRANSITION TEMPERATURES AND ENTHALPIES OF TRANSITION FOR $Ag_{1.64}Te(c)$

Transition		*This investigation*		*Kracek et al.*[14]	
		T *(K)*	ΔH_{trans} *(kJ mol⁻¹)*	*T* *(K)*	ΔH_{trans} *(kJ mol⁻¹)*
?		418	1.85		
$Ag_{1.64}Te$ (low temp form)	= $Ag_{1.64}Te$ (high temp form)	569	0.2	568	2.5
$Ag_{1.64}Te$+(Te?)	= $Ag_{1.64}Te$+liquid 1[a]	625	0.25	628	—
$Ag_{1.64}Te$+liquid 1	= $Ag_{1.88}Te$+liquid 2[a]	697	2.2	693	3.4
$Ag_{1.88}Te$+liquid 2	= Ag_2Te+liquid 3[a]	737	1.2	733	3.0

[a] See Ag–Te phase diagram given in ref. 14.

The thermodynamic properties listed in Table 7 were derived from the data obtained in the present investigation and the estimated standard entropy, $S°(298\ K, Ag_{1.64}Te) = 133.9\ J\ mol^{-1}\ K^{-1}$, which was obtained by subtracting 0.24 of the Latimer contribution for Ag^{+} [19] from the value of $S°(298\ K, Ag_{1.88}Te(c))$ listed by Walsh et al.[4].

TABLE 7

THE THERMODYNAMIC PROPERTIES OF $Ag_{1.64}Te(c)$

T (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	$H(T)-H(298)$ ($J\ mol^{-1}$)	$S(T)-S(298)$ ($J\ mol^{-1}\ K^{-1}$)	$-\{G(T)-H(298)\}T^{-1}$ ($J\ mol^{-1}\ K^{-1}$)
298	76.97	0	0	133.90
350	83.40	4157	12.84	134.86
400	89.60	8482	24.38	137.07
418	91.83[a]	10115	28.37	138.07
418	91.94	11965	32.80	138.07
450	91.08	14894	39.55	140.35
500	89.73	19414	49.08	144.15
550	88.38	23867	57.57	148.07
569	87.87[a]	25541	60.56	149.57
569	79.00[a]	25741	60.91	149.57
600	79.00[a]	28190	65.10	152.02
625	79.00[a]	30165	68.33	153.96
625	77.50[a]	30415	68.73	153.96
650	77.50[a]	32352	71.76	155.89
697	77.50[a]	35995	77.18	159.43
697	78.50[a]	38195	80.33	159.43
700	78.50[a]	38430	80.67	159.67
737	78.50[a]	41335	84.71	162.53
737	73.00[a]	42535	86.34	162.53
750	73.00[a]	43484	87.62	163.54
800	73.00[a]	47134	92.33	167.31

[a] See footnote to Table 2 and Fig. 8.

REFERENCES

1 P. Kubaschewski, *Ph. D. Thesis*, Göttingen University, 1969.
2 W. A. Tilden, *Phil. Trans. Royal Soc.*, 203A (1904) 139.
3 P. V. Gultyaev and A. Petrov, *Sov. Phys. Solid State*, 1 (1959) 330.
4 P. N. Walsh, E. W. Art and D. White, *J. Phys. Chem.*, 66 (1962) 1546.
5 K. C. Mills, *J. Chem. Thermodynamics*, 4 (1972) 903.
6 B. Wunderlich, *J. Phys. Chem.*, 69 (1965) 2078.
7 M. J. Richardson, *J. Polym. Sci. C*, 38 (1972) 251.
8 C. M. L. Atkinson and M. J. Richardson, *Trans. Faraday Soc.*, 65 (1969) 1749.
9 K. C. Mills, Third European Conference on Thermophysical Properties at High Temperatures, Turin, Italy, June 20, 1972, published *High Temperatures–High Pressures* (1973).
10 K. C. Mills, *Selected Thermodynamic Values of Inorganic Sulphides, Selenides and Tellurides*, Butterworths, London, in press.
11 A. L. N. Stevels and G. A. Wiegers, *Rec. Trav. Chim.*, 90 (1970) 352.
12 C. W. Slansky and L. V. Coulter, *J. Amer. Chem. Soc.*, 61 (1939) 564.
13 K. K. Kelley, *U.S. Bur. Mines Bull.*, (1960) 584.
14 F. C. Kracek, C. J. Ksanda and L. J. Cabri, *Amer. Miner.*, 51 (1966) 14.
15 K. Kiukkola and C. Wagner, *J. Electrochem. Soc.*, 104 (1957) 379.
16 T. Takahashi and O. Yamamoto, *J. Electrochem. Soc.*, 117 (1970) 1.
17 H. Reinhold, *Z. Elektrochem.*, 40 (1934) 361.
18 M. J. Pool, *Trans. Amer. Inst. Mining Met. Eng.*, 23 (1965) 1711.
19 F. Grønvold and E. F. Westrum Jr, *Inorg. Chem.*, 1 (1962) 37.