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The thermodynamic properties of six compounds in (tellurium + oxygen + hydrogen) from 10 to 1000 K

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The low-temperature (5 to 340 K) heat capacities of H_6TeO_6, H_2TeO_4, TeO_2, Te_4O_9, Te_2O_5, and β-TeO_3 have been determined by adiabatic calorimetry, and smoothed values of their thermodynamic functions $C^\circ_{p,m}(T)$, $S^\circ_m(T)$, and $\{H^\circ_m(T)-H^\circ_m(298.15\ K)\}$ have been computed. In addition high-temperature enthalpy increments of these compounds (with the exception of H_6TeO_6) have been measured by drop calorimetry. From the results smoothed thermodynamic functions of the compounds mentioned are given up to 1000 K.

1. Introduction

The system (tellurium + oxygen + hydrogen) is poorly known. The oxides TeO_2, Te_4O_9, Te_2O_5, and TeO_3 have been identified and, with the exception of TeO_3, their crystal structures have been solved.[(1–3)] However, their thermochemical properties have hardly been studied. The situation with respect to the hydrates, designated as the tellurium acids H_6TeO_6 and H_2TeO_4, is even worse.[(4–6)]

As part of our work on safety aspects of water-cooled nuclear reactors, where tellurium is one of the main volatile fission products of the "source term", we have been engaged in certain aspects of tellurium chemistry. As a contribution we here present the low-temperature heat capacities and the high-temperature enthalpy increments of the six main compounds in (tellurium + oxygen + hydrogen) from which their thermodynamic functions have been derived.

2. Experimental

H_6TeO_6 (Cerac) was recrystallized from water, and dried in air at 350 K. H_2TeO_4 was prepared by heating H_6TeO_6 in a closed silica ampoule at 525 K and under a water-vapour pressure of 2.8 MPa for about 90 h. The resulting product was crystalline; after drying in air at 525 K it had the proper composition. TeO_2 was prepared by dissolving tellurium (Cerac) in nitric acid $(HNO_3 + H_2O)$ at room

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temperature. After washing the white precipitate with water, the resulting product was heated in oxygen at 775 K overnight. β-TeO_3 was prepared by heating purified H_6TeO_6 in an autoclave at 625 to 675 K and 3 to 10 MPa water-vapour pressure. The ochre compound β-TeO_3 was analysed, after drying at 400 K, by heating it to TeO_2 at 825 K. Te_2O_5 and Te_4O_9 were prepared by heating mixtures of TeO_2 and H_6TeO_6 (or β-TeO_3) in the appropriate mole ratio in an autoclave at a water-vapour pressure of 8 to 11 MPa and 625 to 650 K. For Te_2O_5 relatively short heating times (15 to 20 h) had to be applied; for Te_4O_9 both temperature (670 K) and heating times (≈ 60 h) had to be increased somewhat. In most cases the resulting products were contaminated with Te_2O_5 and/or TeO_2; the degree of contamination depended to some extent on the heating time. Since both Te_2O_5 and Te_4O_9 are insoluble in dilute mineral acids, they could be easily purified from contaminations by TeO_2.

The tellurium content of the various compounds was determined indirectly from the mass loss when the compounds were heated in air at 875 K for about 2 h. Under these circumstances the resulting TeO_2 was not measurably volatile and was phase-pure. From a chemical analysis in this TeO_2, after dissolution in hydrochloric acid and titration of Te(IV) with Sn(II), it was found to have the correct composition. The results of the analyses are given in table 1.

LOW-TEMPERATURE HEAT CAPACITIES

The apparatus and the general measuring procedure have been described in detail.$^{(7)}$ About 9 to 14 g of the samples were used in the calorimeter which, except for Te_2O_5, was closed under vacuum after admission of about 1 kPa of helium. For Te_2O_5 the calorimeter could not be evacuated without almost emptying it due to a sudden eruption of locked air in the finely divided powder; for Te_2O_5 the calorimeter was closed after flushing it with helium at atmospheric pressure.

The heat-capacity measurements were made in calorimeter V which was tested with a standard sample of sapphire$^{(8)}$ and with *n*-heptane.$^{(9)}$

For standard sapphire we found a correspondence with the results of the N.B.S. from 80 to 340 K to within 0.1 per cent. Below 80 K the correspondence for *n*-heptane ranges from 0.1 per cent at 80 K to 2 per cent at 15 K.

TABLE 1. Analytical results; molar mass *M* and mass fraction *w*

Compound	$M/(g\cdot mol^{-1})$	10^2w(tellurium)		10^2w(impurities)
		expt	calc.	
H_6TeO_6	229.64	55.57 ± 0.03	55.59	
H_2TeO_4	193.61	65.76 ± 0.03	65.91	
β-TeO_3	175.60	72.66 ± 0.02	72.67	
Te_2O_5	335.20			
Te_4O_9 (a)	654.39			(1.3 ± 0.1) of TeO_2
Te_4O_9 (b)				0.65 of TeO_2 + 1.70 of Te_2O_5
TeO_2	159.60	79.96 ± 0.02	79.95	

Temperatures were determined with a 100 Ω platinum thermometer calibrated by Oxford Instruments to within 0.01 K. We used an automatic a.c. bridge; relative temperatures were read to 0.0002 K. The data collection and the timing of the runs were automated.

The thermal history of all samples was the same: after loading the calorimeter they were cooled to about 80 K, left overnight, then the cryostat was cooled using liquid helium, and the system was cooled to about 5 K in 20 h. That left us with a measuring period of about 30 h for the temperature range between 8 to 80 K. Below 30 K several runs were made; these runs are incorporated in the experimental values in order of increasing temperature. Two samples of Te_4O_9 were used: "Te_4O_9 (a)" contained a small impurity of TeO_2 $\{(1.3 \pm 0.1)$ mass per cent$\}$, whereas "Te_4O_9 (b)" contained small impurities of TeO_2 $\{(1.7 \pm 0.1)$ mass per cent$\}$ and of Te_2O_5 $\{(0.65 \pm 0.10)$ mass per cent$\}$. The experimental results given for Te_4O_9 in tables 2 and 3 have been corrected for these impurities. This correction is small, ranging from 1.5 per cent at 10 K to −0.15 per cent at 300 K. The experimental molar heat capacities are listed in table 2 in order of ascending temperature.

HIGH-TEMPERATURE ENTHALPY INCREMENTS

The measurements were done in a diphenyl-ether drop calorimeter described by Cordfunke *et al.*(10) The energy equivalent of the calorimeter was determined by means of calibrations with spherical pieces of α-quartz. A calibration factor of the ratio of energy input to the mass of mercury of $(79.977 \pm 0.063)\ \mathrm{J \cdot g^{-1}}$ was obtained.

For the drop-calorimetric studies, spherical vitreous silica ampoules with a 0.6 mm wall thickness and 20 mm diameter were used to contain the samples. The ampoules were about 4.2 $\mathrm{cm^3}$ in volume and weighed about 1.1 g empty. Energy from the sample and ampoule, when they were dropped into the calorimeter, melted solid diphenyl in equilibrium with its liquid in a closed system. The resulting volume increase of the ether was determined by weighing the displaced mercury. Temperature measurements in the furnace were made with calibrated Pt-to-(Pt + 10 mass per cent of Rh) thermocouples to within ±0.1 K. The enthalpy contributions of the vitreous silica were determined in separate experiments.

The empty ampoules had a mass of about 1.1 g of SiO_2, and contained 10.7954 g of TeO_2, 10.8221 g of Te_4O_9 (a), 5.1788 g of Te_2O_5, 9.1813 g of β-TeO_3, and 6.0974 g of H_2TeO_4, respectively. The H_6TeO_6 could not be measured, since the water-vapour pressure in the silica ampoules would be too high. The results of the measurements are listed in table 3. A correction was made for the difference in enthalpy between the final calorimeter temperature and the standard reference temperature, 298.15 K, using $C^{\circ}_{p,\mathrm{m}}(298.15\ \mathrm{K})$.

3. Results

Smoothed standard molar heat capacities $C^{\circ}_{p,\mathrm{m}}$ and values of $S^{\circ}_{\mathrm{m}}(T)$ and $\{H^{\circ}_{\mathrm{m}}(T) - H^{\circ}_{\mathrm{m}}(T_0)\}$ at regular temperature intervals are given in table 4. These values were calculated by first interpolating the experimental heat capacities (using the

TABLE 2. Molar heat capacity at constant pressure and at the mean temperature $\langle T \rangle$ of the measurements

$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C^{\circ}_{p,\mathrm{m}}}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C^{\circ}_{p,\mathrm{m}}}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C^{\circ}_{p,\mathrm{m}}}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{C^{\circ}_{p,\mathrm{m}}}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$
TeO_2							
7.97	0.154	38.66	8.35	98.69	28.51	229.79	53.86
8.63	0.166	40.07	8.86	102.17	29.59	234.79	54.45
8.75	0.190	41.38	9.34	105.56	30.56	239.75	55.03
9.37	0.223	42.62	9.79	108.86	31.48	244.68	55.59
9.77	0.235	45.44	10.79	112.09	32.37	249.58	56.12
9.87	0.259	47.52	11.51	115.25	33.22	254.45	56.62
10.29	0.288	49.45	12.16	118.35	34.04	259.29	57.12
10.50	0.305	51.25	13.01	121.40	34.81	264.11	57.62
10.63	0.311	54.58	14.15	124.39	35.55	268.90	58.09
10.66	0.323	56.15	14.48	127.34	36.25	273.67	58.53
11.06	0.372	57.65	15.01	130.25	36.94	278.42	58.97
11.55	0.401	59.08	15.52	133.11	37.60	283.15	59.43
11.96	0.480	60.47	16.03	135.94	38.24	287.85	59.81
12.00	0.487	61.81	16.50	138.74	38.86	292.53	60.29
12.14	0.527	63.11	16.96	141.50	39.46	297.21	60.52
13.20	0.635	64.27	17.39	148.61	40.95	301.87	61.11
13.86	0.626	65.60	17.84	154.58	42.16	305.46	61.35
13.97	0.550	66.79	18.26	160.42	43.30	306.51	61.40
15.26	1.07	67.96	18.67	166.17	44.39	310.63	61.74
16.31	1.24	69.10	19.05	171.82	45.41	311.12	61.18
17.17	1.39	70.22	19.46	177.39	46.39	315.72	62.10
18.95	1.66	71.32	19.83	182.89	47.32	315.78	62.13
19.95	2.18	72.39	20.17	188.31	48.18	320.31	62.55
20.00	2.35	73.45	20.50	193.67	49.01	320.91	62.43
21.54	2.57	74.48	20.81	198.98	49.78	326.03	62.74
22.18	3.05	79.20	22.47	204.23	50.53	331.13	63.08
25.92	3.97	83.46	23.81	209.43	51.25	336.21	63.38
33.61	6.55	87.51	25.13	214.58	52.02	341.28	63.65
35.47	7.21	91.37	26.35	219.69	52.60	346.33	63.93
37.13	7.81	95.09	27.47	224.76	53.24		
β-TeO_3							
8.35	0.036	64.59	10.93	151.01	40.55	298.58	71.51
9.92	0.041	66.02	11.42	156.28	42.10	301.21	71.77
11.01	0.095	67.41	11.92	161.45	43.61	303.84	72.22
11.77	0.090	68.75	12.38	166.52	45.02	306.45	72.54
12.01	0.114	70.06	12.89	171.51	46.42	309.06	72.92
12.77	0.200	71.33	13.33	176.42	47.71	311.65	73.40
13.18	0.272	72.57	13.77	181.25	48.97	311.65	73.46
13.44	0.280	73.79	14.18	186.02	50.19	314.22	73.52
14.78	0.364	74.98	14.51	190.73	51.34	314.24	73.56
14.93	0.428	76.15	15.02	195.37	52.44	316.78	73.89
15.26	0.410	77.30	15.45	199.97	53.50	316.82	73.91
15.64	0.456	78.42	15.82	204.51	54.53	319.11	74.06
15.73	0.410	79.53	16.24	209.01	55.51	319.34	74.26
16.21	0.430	80.62	16.63	213.47	56.48	319.39	74.19
16.53	0.466	81.69	17.01	217.88	57.45	321.15	74.28
16.89	0.444	82.74	17.39	222.25	58.37	321.89	74.48
18.52	0.552	83.78	17.71	226.59	59.22	321.96	74.64
20.34	0.780	84.81	18.09	230.89	60.07	323.19	74.66
23.03	0.950	85.82	18.45	235.15	60.92	324.44	74.78

TABLE 2—*continued*

$\langle T\rangle/\mathrm{K}$	$C^{\circ}_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\langle T\rangle/\mathrm{K}$	$C^{\circ}_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\langle T\rangle/\mathrm{K}$	$C^{\circ}_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\langle T\rangle/\mathrm{K}$	$C^{\circ}_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
25.13	1.24	86.81	18.78	239.39	61.73	325.22	74.84
30.35	2.01	87.00	19.24	243.60	62.51	326.99	75.16
36.10	3.06	88.77	19.52	247.77	63.28	327.25	75.09
42.48	4.52	89.73	19.94	251.93	64.03	329.28	75.32
45.49	5.27	95.09	21.83	256.05	64.79	329.52	75.38
48.11	5.97	102.57	24.53	260.16	65.16	331.30	75.59
50.48	6.78	109.55	27.05	264.25	66.12	332.05	75.69
52.64	7.42	116.16	29.39	268.30	66.92	334.58	75.94
54.64	7.98	122.47	31.55	272.33	67.40	337.10	76.24
56.52	8.29	128.54	33.57	276.34	68.06	339.62	76.47
58.28	8.84	134.40	35.45	280.33	68.73	342.14	76.81
59.97	9.39	140.08	37.23	284.30	69.33	344.64	76.96
61.57	9.94	145.61	38.93	295.94	71.19	347.15	77.32
63.11	10.44						
Te_2O_5							
8.08	0.623	41.68	14.39	117.65	62.74	231.54	113.17
9.08	0.730	44.80	16.28	121.31	64.79	234.18	114.11
9.49	0.993	47.53	17.99	124.90	66.80	236.81	115.00
9.86	0.985	49.99	19.30	128.42	78.69	239.44	115.94
10.02	0.890	52.25	21.48	131.88	70.53	242.06	116.75
10.42	1.10	54.35	22.65	135.29	72.32	247.62	118.58
10.81	1.26	56.31	23.20	138.64	74.03	250.87	118.19
11.02	1.25	58.18	24.42	141.95	75.72	254.10	120.19
11.51	1.34	59.95	25.67	145.21	77.40	257.30	121.19
12.00	1.60	61.64	26.79	148.44	78.99	260.49	122.07
12.16	1.34	63.26	27.90	151.62	80.61	263.67	123.04
12.49	1.58	64.83	28.99	154.78	82.16	266.84	123.98
12.87	2.19	66.35	29.98	157.89	83.65	270.00	124.78
12.94	2.15	67.81	31.07	160.98	85.17	273.14	125.62
13.33	1.90	69.24	31.97	164.04	86.62	276.28	126.44
13.68	1.95	70.63	33.02	167.07	88.05	279.40	127.53
13.73	2.24	71.98	33.84	170.08	89.46	282.52	128.10
14.73	2.26	73.30	34.77	173.06	90.84	285.62	129.36
14.74	2.79	74.60	35.68	176.01	92.15	288.71	129.85
15.78	2.95	75.86	36.52	178.95	93.45	291.78	131.05
16.59	2.52	77.10	37.30	181.86	94.72	294.86	131.64
17.26	2.87	78.32	38.12	184.75	95.93	297.92	132.61
18.81	3.71	79.52	38.94	187.63	97.06	300.98	133.08
19.99	3.22	80.70	39.70	190.48	98.36	304.03	133.50
20.87	3.68	81.86	40.40	193.32	99.47	307.08	134.41
21.61	4.44	83.00	40.95	196.14	100.60	310.12	135.09
22.18	4.83	84.13	41.84	198.94	101.59	313.15	135.71
22.71	4.35	85.24	42.49	201.73	102.69	316.18	136.51
23.19	4.50	86.34	43.28	204.51	103.69	319.19	137.08
24.93	5.69	87.43	43.85	207.27	104.77	322.20	137.82
27.67	6.65	88.50	44.65	210.01	105.73	325.21	138.54
29.86	7.62	89.56	45.34	212.74	106.66	328.20	139.65
31.70	8.61	93.51	47.92	215.46	107.63	331.19	139.62
33.33	9.41	97.88	50.68	218.17	109.66	334.18	140.14
34.78	10.22	102.08	53.50	220.86	109.76	337.16	140.45
36.11	11.00	106.14	55.95	223.55	110.43	340.13	142.08
37.34	11.66	110.08	58.26	226.22	111.33	343.10	141.86
38.48	12.40	113.91	60.56	228.88	112.32	346.06	142.55

TABLE 2—*continued*

$\langle T \rangle / \mathrm{K}$	$C^{\circ}_{p,\mathrm{m}} / \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\langle T \rangle / \mathrm{K}$	$C^{\circ}_{p,\mathrm{m}} / \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\langle T \rangle / \mathrm{K}$	$C^{\circ}_{p,\mathrm{m}} / \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\langle T \rangle / \mathrm{K}$	$C^{\circ}_{p,\mathrm{m}} / \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
			Te_4O_9				
6.10	0.845	55.21	49.66	112.44	120.21	184.84	187.11
6.45	0.942	56.87	51.78	115.28	123.29	186.99	188.68
7.26	0.861	58.45	53.85	118.07	126.33	189.12	190.29
7.94	1.14	59.96	55.91	120.81	129.30	191.24	191.86
8.76	1.17	61.42	57.79	123.51	132.11	193.35	193.64
8.90	1.16	62.83	59.57	126.17	134.81	199.56	197.65
9.29	1.49	64.20	61.47	128.80	137.48	205.64	201.71
10.19	1.67	65.52	63.33	131.39	140.12	211.65	205.66
10.53	1.72	66.81	64.98	133.94	142.57	217.58	209.37
10.64	1.87	68.07	66.58	136.47	145.10	223.46	212.99
11.98	2.48	69.30	68.45	138.97	147.48	229.29	216.38
12.92	3.31	70.50	70.05	141.45	149.82	235.05	219.61
13.72	2.43	71.67	71.42	143.90	152.16	240.77	222.99
14.54	4.43	72.82	72.73	146.33	154.38	246.44	226.04
15.74	5.15	73.95	74.21	148.73	156.60	252.07	228.89
16.57	5.89	75.06	75.66	151.11	158.79	257.65	231.77
18.70	7.21	76.16	76.65	153.47	160.97	263.20	234.69
21.19	9.20	77.23	78.10	155.82	163.06	268.70	238.28
23.08	11.00	78.29	79.83	158.14	165.14	274.18	238.83
24.63	13.06	79.33	81.29	160.45	167.14	279.63	242.07
28.61	16.73	80.36	82.98	162.74	169.30	285.04	244.76
32.08	20.41	83.52	86.45	165.01	171.14	290.41	247.02
34.82	23.70	87.16	90.78	167.27	173.00	295.76	249.04
39.79	30.05	90.66	95.08	169.51	174.88	301.08	251.19
42.71	34.00	94.04	99.02	171.74	176.71	306.39	252.97
45.27	36.99	97.31	102.71	173.96	178.59	311.67	255.57
47.57	40.15	100.48	106.41	176.16	180.37	316.93	256.53
49.68	42.66	103.58	110.16	178.35	182.12	322.18	258.61
51.64	46.21	106.60	113.64	180.52	183.78	327.40	259.97
53.48	48.50	109.55	116.92	182.69	185.46	332.60	261.35
			H_2TeO_4				
7.17	0.066	45.86	10.10	121.85	48.29	212.85	85.53
7.41	0.085	48.29	11.12	125.08	49.83	215.18	86.32
7.56	0.038	50.51	12.40	128.26	51.31	217.51	87.08
7.69	0.074	52.56	13.27	131.37	52.77	224.81	89.49
8.66	0.125	54.48	14.10	134.44	54.18	228.79	90.77
9.18	0.090	56.29	14.59	137.46	55.55	232.74	92.04
9.45	0.150	58.00	15.40	140.43	56.89	236.65	93.28
10.13	0.112	59.64	16.22	143.37	58.19	240.54	94.46
10.53	0.200	61.21	16.98	146.26	59.46	244.41	95.62
10.83	0.162	62.72	17.74	149.12	60.72	248.25	96.70
10.93	0.150	64.17	18.48	151.94	61.96	252.06	97.85
11.44	0.264	65.57	19.21	154.74	63.16	255.85	98.91
11.71	0.284	66.94	19.93	157.50	64.34	259.61	99.99
11.91	0.367	68.26	20.62	160.23	65.52	263.36	101.00
12.59	0.430	69.55	21.32	162.94	66.65	267.08	101.98
13.31	0.608	70.00	21.96	165.52	67.77	270.79	102.79
13.81	0.420	72.03	22.64	168.28	68.88	274.48	103.58
14.66	0.736	73.23	23.27	170.91	69.94	278.15	105.02
14.99	0.750	74.41	23.86	173.52	71.00	281.79	106.01
15.73	1.01	75.56	24.43	176.11	72.05	285.42	107.01
16.32	1.09	76.69	25.07	178.67	73.08	289.02	107.93

TABLE 2—*continued*

$\langle T \rangle / \mathrm{K}$	$C^{\circ}_{p,\mathrm{m}} / (\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	$\langle T \rangle / \mathrm{K}$	$C^{\circ}_{p,\mathrm{m}} / (\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	$\langle T \rangle / \mathrm{K}$	$C^{\circ}_{p,\mathrm{m}} / (\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	$\langle T \rangle / \mathrm{K}$	$C^{\circ}_{p,\mathrm{m}} / (\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$
16.84	1.05	77.80	25.63	181.22	74.12	292.61	108.80
17.38	1.26	78.89	26.24	183.75	75.06	296.18	109.64
17.89	1.30	79.97	26.76	186.26	76.01	299.74	110.53
18.37	1.37	84.02	28.86	188.75	76.95	303.28	111.33
19.43	1.64	88.51	31.25	191.23	77.90	306.81	112.14
22.84	2.37	92.77	33.49	193.69	78.79	310.33	112.98
25.18	2.90	96.84	35.56	196.13	79.68	313.84	113.76
27.03	3.38	100.74	37.59	198.56	80.55	317.33	114.54
30.63	4.42	104.51	39.63	200.98	81.40	320.81	115.33
32.99	5.17	108.17	41.46	203.38	82.26	324.27	116.12
34.98	5.87	111.71	43.26	205.77	83.10	327.73	116.89
36.74	6.50	115.17	45.01	208.14	83.91	331.17	117.55
38.31	7.09	118.55	46.68	210.50	84.72	334.61	118.21
43.13	9.02						
H_6TeO_6							
7.14	0.374	49.12	26.28	117.44	70.29	222.72	132.55
7.86	0.445	50.81	27.61	120.21	72.01	226.15	134.44
8.36	0.502	52.41	28.70	122.93	73.69	229.56	126.24
8.74	0.508	53.94	29.69	125.61	75.34	232.93	138.09
8.75	0.600	55.41	30.29	128.25	76.97	236.28	139.89
9.11	0.650	56.82	31.22	130.85	78.56	239.59	141.65
9.43	0.716	58.18	32.14	133.41	80.31	242.89	143.38
9.71	0.787	59.50	33.07	135.94	81.66	246.16	145.09
9.98	0.819	60.77	33.88	138.43	83.17	249.40	146.82
10.05	0.812	62.01	34.70	140.89	84.68	252.63	148.08
10.94	1.07	63.22	35.51	143.33	86.15	255.82	150.14
11.61	1.29	64.40	36.28	145.73	87.64	259.00	151.79
11.62	1.34	65.55	37.03	148.11	89.07	262.16	153.37
12.19	1.56	66.67	37.80	150.46	90.51	165.29	154.96
12.47	1.66	67.77	38.53	152.79	91.92	268.41	156.56
12.69	1.75	68.85	39.26	155.10	93.35	271.51	158.03
13.11	1.93	69.91	40.00	157.38	94.76	174.58	159.53
13.17	2.11	70.95	40.62	159.64	96.14	277.64	160.97
14.46	2.65	71.97	41.27	161.88	97.50	283.72	163.85
14.76	2.82	72.98	41.98	164.10	98.85	286.73	165.32
14.89	2.84	73.97	42.58	166.30	100.20	289.73	166.28
15.27	3.02	74.94	43.24	168.48	101.49	292.70	168.26
16.35	3.10	75.90	43.89	170.65	102.84	295.66	169.53
15.61	3.24	76.85	44.47	172.80	104.10	298.60	170.96
17.37	4.16	77.78	45.09	174.93	105.37	301.53	172.39
21.23	6.63	78.70	45.73	177.04	106.66	304.44	173.59
22.84	7.79	79.61	46.32	179.14	107.89	307.35	174.90
24.23	8.83	82.30	47.91	181.22	109.13	310.23	176.29
25.46	9.57	84.67	49.45	183.29	110.35	313.10	177.56
26.57	10.34	86.98	50.95	185.35	111.59	315.96	178.80
27.59	11.10	89.23	52.42	190.30	114.48	318.81	180.10
30.43	13.12	91.42	53.81	194.06	116.62	321.65	181.41
33.04	15.03	96.27	56.82	197.78	118.73	324.47	182.52
35.28	16.68	99.53	58.89	201.45	120.81	327.28	183.71
37.27	18.12	102.70	61.04	205.08	122.86	220.08	184.87
41.11	20.85	105.78	62.97	208.68	124.87	332.87	186.07
43.36	22.43	108.79	64.85	212.24	126.85	335.65	187.21
45.43	23.80	111.73	66.71	215.77	128.78	338.41	188.38
47.34	25.09	114.61	68.53	219.26	130.68	341.16	189.51

TABLE 3. Calorimetric enthalpy-increment measurements

$\frac{T}{\text{K}}$	$\frac{H^\circ_\text{m}(T)-H^\circ_\text{m}(298.15\text{ K})}{\text{J}\cdot\text{mol}^{-1}}$		$10^2\delta$	$\frac{T}{\text{K}}$	$\frac{H^\circ_\text{m}(T)-H^\circ_\text{m}(298.15\text{ K})}{\text{J}\cdot\text{mol}^{-1}}$		$10^2\delta$
	expt	calc.			expt	calc.	
(a) TeO_2							
382.3	5391	5352	0.73	533.1	15828	15804	0.15
411.1	7306	7276	0.41	586.8	19682	19721	−0.20
423.7	8124	8129	−0.06	633.5	23215	23197	0.08
441.9	9375	9374	0.01	684.5	27071	27064	0.03
462.2	10794	10779	0.14	732.8	30784	30792	−0.03
482.7	12168	12214	−0.38	753.3	32396	32392	0.01
(b) Te_4O_9							
394.9	25849	25745	0.40	511.5	59640	59691	−0.09
416.2	31757	31746	0.03	549.8	71430	71356	0.10
437.1	37857	37729	0.34	584.6	82233	82145	0.11
459.6	44085	44266	−0.41	621.8	94021	93866	0.17
483.1	51014	51193	−0.35	663.6	107120	107259	−0.13
(c) Te_2O_5							
438.6	20092	20069	0.11	540.9	36158	36144	0.04
453.2	22257	22296	−0.17	571.8	41184	41207	−0.06
464.2	23946	23988	−0.18	603.2	46515	46446	0.15
480.7	26563	26552	0.04	635.0	51952	51847	0.20
512.6	31535	31589	−0.17	674.0	58502	58598	−0.16
(d) β-TeO_3							
388.5	6861	6886	−0.36	508.8	17110	17092	0.11
401.8	7966	7963	0.04	535.6	19486	19497	−0.06
425.7	9954	9931	0.23	564.4	22110	22132	−0.10
446.4	11648	11670	0.19	589.0	24466	24421	0.18
471.7	13835	13837	−0.01	627.1	28017	28036	−0.07
(e) H_2TeO_4							
407.8	13110	13071	0.30	465.0	20817	26840	−0.11
422.9	14988	15053	−0.43	483.7	23554	23538	0.07
435.9	16843	16798	0.27	498.0	25649	25655	−0.02
454.9	19411	19416	−0.03	513.9	28067	28065	0.01

Newton algorithm) every 2 K; numerical integration of these values yielded the other functions. The low-temperature entropy and the enthalpy (below 15 K) were obtained by fitting the experimental results using a plot of T^2 against $C^\circ_{p,\text{m}}/T$ and extrapolating to $T = 0$ and $C^\circ_{p,\text{m}}/T = 0$.

The results of the drop-calorimeter measurements, as given in table 3, can be represented over the range of the experimental measurements as a function of temperature by a polynomial expression of the form: $\{H^\circ_\text{m}(T)-H^\circ_\text{m}(298.15\text{ K})\}/(\text{J}\cdot\text{mol}^{-1}) = a(T/\text{K})+b(T/\text{K})^2+c(\text{K}/T)+d$, the coefficients of which were obtained by least squares. The boundary conditions applied were $\{H^\circ_\text{m}(T)-H^\circ_\text{m}(298.15\text{ K})\} = 0$ and $C_{p,\text{m}}(T) = C_{p,\text{m}}(298.15\text{ K})$ at 298.15 K. The coefficients of the polynomials are listed in table 5, while the

TABLE 4. Thermodynamic functions

$\frac{T_0}{\mathrm{K}}$	$\frac{T}{\mathrm{K}}$	$\frac{C^\circ_{p,\mathrm{m}}}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{S^\circ_{\mathrm{m}}(T)}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{H^\circ_{\mathrm{m}}(T)-H^\circ_{\mathrm{m}}(T_0)}{\mathrm{J \cdot mol^{-1}}}$	$\frac{C^\circ_{p,\mathrm{m}}}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{S^\circ_{\mathrm{m}}(T)}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{H^\circ_{\mathrm{m}}(T)-H^\circ_{\mathrm{m}}(T_0)}{\mathrm{J \cdot mol^{-1}}}$
			TeO_2			β-TeO_3	
0	10	0.273	0.094	0.703	0.078	0.026	0.195
	50	12.41	6.54	223.8	6.62	2.66	96.20
	100	28.94	20.38	1270	23.60	12.19	833.0
	150	41.33	34.60	3045	40.25	25.03	2444
	200	49.94	47.73	5337	53.50	38.51	4803
	250	56.17	59.58	7997	63.69	51.59	7744
	298.15	60.67	69.88	10815	71.47	63.48	10999
298.15	298.15	60.67	69.88	0	71.47	63.48	0
	300	60.82	70.26	112	71.69	63.92	132
	400	66.96	88.67	6530	81.30	85.96	7816
	500	70.97	104.07	13436	88.36	104.89	16312
	600	74.15	117.30	20697	94.42	121.55	25456
	700	76.94	128.94	28254	100.00	136.52	35180
	(800)	79.52	139.39	36078	105.34	150.23	45449
	(900)	81.97	148.89	44153	110.52	162.93	56242
	(1000)	84.35	157.65	52470	115.61	174.84	67550
			Te_2O_5			Te_4O_9	
0	10	0.96	0.320	2.403	0.143	0.047	0.357
	50	19.31	10.70	350.5	43.23	23.52	788.7
	100	52.05	34.21	2140	105.8	73.20	4553
	150	79.79	60.18	5467	157.8	126.4	11204
	200	102.0	86.96	10038	197.9	177.6	20154
	250	118.6	111.6	15583	227.8	225.2	30831
	298.15	132.7	133.8	21645	250.1	267.3	42360
298.15	298.15	132.70	133.80	0	250.10	267.30	0
	300	133.02	134.62	246	250.84	268.85	463
	400	147.21	174.95	14299	280.54	345.48	27173
	500	158.25	209.02	29587	299.68	410.25	56234
	600	168.04	238.75	45908	314.67	466.26	86974
	(700)	177.25	265.35	63176	327.71	515.76	119105
	(800)	186.15	289.60	81349	339.70	560.31	152482
	(900)	194.87	312.03	100401	351.08	600.98	187025
	(1000)	203.47	333.01	120319	362.09	638.55	222686
			H_2TeO_4			H_6TeO_6	
0	10	0.175	0.058	0.438	0.86	0.287	2.16
	50	2.05	5.63	195.8	26.93	15.72	524.3
	100	37.19	21.43	1409	59.23	44.36	2683
	150	61.11	41.21	3888	90.22	74.31	6428
	200	81.05	61.62	7460	120.0	104.4	11694
	250	97.20	81.51	11931	147.1	134.1	18380
	298.15	110.2	99.76	16930	170.6	162.1	26042
298.15	298.15	110.20	99.76	0	170.6	162.1	0
	300	110.44	100.44	204	171.7	163.1	316
	400	128.02	134.45	12067			
	500	150.17	165.35	25955			
	(600)	174.12	194.82	42159			
	(700)	198.92	223.52	60806			
	(800)	224.16	251.72	81957			
	(900)	249.67	279.60	105648			
	(1000)	275.35	307.23	131897			

TABLE 5. Coefficients of the polynomial expression: $\{H^\circ_m(T)-H^\circ_m(298.15\ \mathrm{K})\}/(\mathrm{J\cdot mol^{-1}}) = a(T/\mathrm{K})+b(T/\mathrm{K})^2+c(\mathrm{K}/T)+d$, and standard deviations $s\{1-\Delta H(\mathrm{calc.})/\Delta H\}$

Compound	a	10^3b	$10^{-5}c$	d	$10^2s\{1-\Delta H(\mathrm{calc.})/\Delta H\}$	T/K
TeO_2	63.271	10.9465	8.1142	−22559	0.31	298 to 753
Te_4O_9	265.542	50.2927	40.3855	−97187	0.28	298 to 664
Te_2O_5	121.467	41.6067	12.0691	−43962	0.16	298 to 674
β-TeO_3	67.9412	24.3243	9.7568	−25691	0.19	298 to 627
H_2TeO_4	12.757	130.4211	−17.4884	−9531	0.25	298 to 514

smoothed values of the thermodynamic functions of the compounds are listed in table 4.

4. Discussion

Figure 1 shows that the high-temperature enthalpy increments fit the low-temperature heat capacities smoothly. Of the compounds dealt with in this study thermodynamic quantities of only TeO_2 have been measured, by Mezaki and Margrave(11) in the temperature range 446 to 1146 K and by Prescher and Schödter(12) in the range 352 to 1064 K. Whereas the former measurements agree fairly well with ours, the latter deviate considerably. Pashinkin *et al.*,(13) who published heat capacities of TeO_2 in the range 5 to 300 K very recently, arrived at the same conclusion. Their values, however, deviate systematically from our low-temperature heat capacities by about 1 per cent. At 298.15 K their values for $C^\circ_{p,\mathrm{m}}$ and S°_m are 61.38 and 70.40 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, compared with our values of 60.67 and

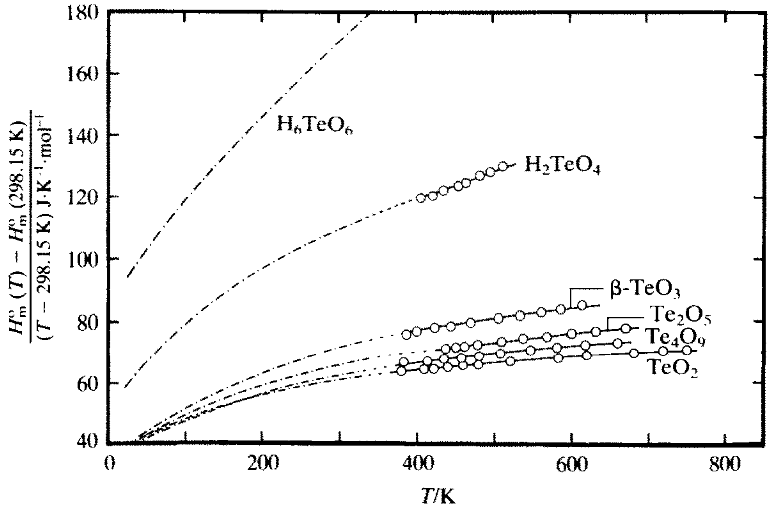

FIGURE 1. The function $\{H^\circ_m(T)-H^\circ_m(T_0)\}/(T-T_0)$ for $T_0 = 298.15$ K. — · —, Smoothed fit from low-temperature heat-capacity measurements (Utrecht); ○, experimental values from high-temperature enthalpy increments (ECN).

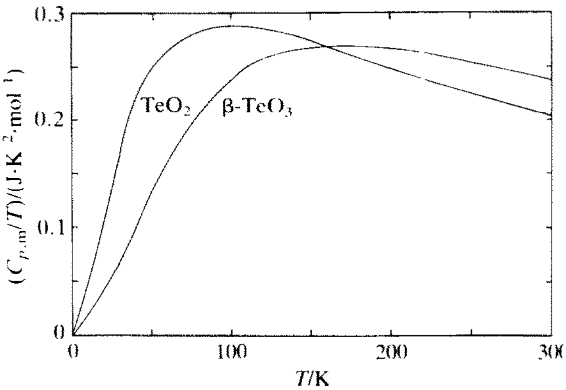

FIGURE 2. The $C^\circ_{p,\mathrm{m}}/T$ values as a function of temperature for TeO_2 and β-TeO_3.

69.88 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively. The high standard molar entropy of TeO_2, 79.5 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, selected by N.B.S.(14) does not fit our measurements.

The differences in thermodynamic behaviour between TeO_2 and β-TeO_3 are striking: whereas $C_{p,\mathrm{m}}$ of β-TeO_3 at 298.15 K is larger than the corresponding value for TeO_2, the entropy of β-TeO_3 at 298.15 K has a lower value. Analysis of the $C_{p,\mathrm{m}}$ and $C_{p,\mathrm{m}}/T$ curves as a function of temperature for both compounds (figure 2) shows a shift in the lattice contributions to the heat capacity near 170 K, and it is evident that the low-temperature contributions to the entropy of TeO_2 still dominate at 298.15 K. The same situation holds for MnO and MnO_2, having entropies of 59.71 and 53.05 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 298.15 K, respectively.(14) A detailed study of the structure of β-TeO_3 seems to be needed.

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