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THE THERMODYNAMIC PROPERTIES OF β-UO_3 AND γ-UO_3 *

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ABSTRACT

Heat capacities of carefully characterized samples of β-UO_3 and γ-UO_3 have been measured from 5 to 350 K using an adiabatic calorimeter, and from 350 to 700 K by enthalpy increment drop calorimetry. Values for the thermodynamic properties at 298.15 K, $C_p^\ominus(T)$, $S^\ominus(T)$, $\{H^\ominus(T)-H^\ominus(0)\}$ and $-\{G^\ominus(T)-H^\ominus(0)\}/T$, are for β-$UO_3$: 81.34 J K^{-1} mol^{-1}, 96.32 J K^{-1} mol^{-1}, 14682 J mol^{-1}, and 47.062 J K^{-1} mol^{-1}, respectively, and for γ-UO_3: 81.67 J K^{-1} mol^{-1}, 96.11 J K^{-1} mol^{-1}, 14585 J mol^{-1}, and 47.179 J K^{-1} mol^{-1}, respectively.

INTRODUCTION

At least six crystalline UO_3 phases as well as an amorphous form of oxides of this composition are known. A tentative phase diagram of this complicated system was presented by Cordfunke and Aling [1] in 1965. The relatively meager X-ray, infrared, and Raman spectroscopic data then available have been supplemented subsequently. The uniqueness of the UO_3 structure, in that the uranyl bond is present without the influence of other cations, has occasioned the comparison of the spectral features with those of other uranyl systems [2,3].

That the generally accepted hexagonal structure of α-UO_3 [4] is incorrect has been demonstrated by neutron diffraction [5]. The results have led to the conclusion that α-UO_3 is an imperfectly crystalline form of an orthorhombic modification of the oxide, in which twinning occurs on so small a scale that an average X-ray pattern is obtained. The structure of the orthorhombic cell

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is, however, unknown. The complexity of the α-UO_3 structure has also been shown by Siegel and Hoekstra [6], who used both spectroscopic and X-ray methods. The structure of β-UO_3 has been examined by Debets [7] and that of γ-UO_3 by Engmann and de Wolff [8], by Siegel and Hoekstra [9], and by Loopstra et al. [10]. In both structures, uranium atoms having six- and sevenfold coordination with oxygen atoms occur; however, the atomic arrangement in γ-UO_3 is markedly different from that in β-UO_3. In the latter, the uranium atoms possess six- and sevenfold coordination with the oxygen atoms. In γ-UO_3 the structure is made up of parallel chains of edge-fused uranium octahedra, cross-linked by uranium dodecahedra. The structure of ϵ-UO_3 (with a triclinic unit cell with eight molecules in the cell [11]) is complex but unknown. Only cubic δ-UO_3 contains a unique kind of uranium atom, at least if the simple proposed structure [12] is correct. In addition to these phases, all of which can be prepared at atmospheric pressure [13], a more dense orthorhombic polymorph ζ-UO_3 has been obtained in the 15–60 kbar pressure interval [14].

In contrast, rather few studies on the chemical thermodynamics of this interesting system have appeared. Wartime studies of a yellow sample of UO_3, presumed to be γ-UO_3, over the cryogenic [15] and elevated [16] temperature regions have been reported. Beketov and Vlasov [17] showed that the thermal stability of these phases increases in the sequence amorphous UO_3, β-UO_3, α-UO_3, and γ-UO_3 and, in agreement with these observations, Cordfunke and Aling [1] demonstrated that γ-UO_3 is obtained as the ultimate phase upon prolonged heating of α- or β-UO_3.

A concise summary of the cryogenic thermophysics of α-, β-, and γ-UO_3 from the present research has been made by Westrum [18], and values of the standard enthalpies of formation of β-UO_3 and γ-UO_3 have been published by Cordfunke et al. [19]. This determination has been selected as a key value by CODATA [20]. In the present presentation of the cryogenic heat capacities, the data for β-UO_3 and γ-UO_3 are combined with their standard enthalpies of formation and with higher-temperature enthalpy values on identical samples to provide more quantitative conclusions regarding the relative stabilities of these phases.

EXPERIMENTAL

Preparation of the UO_3 samples

Brick red β-UO_3 was prepared by heating uranyl nitrate hexahydrate (after drying first at 390 K) very rapidly to 725 K in platinum crucibles. Sufficiently crystalline β-UO_3 (i.e. with crystallite sizes $\sim$ 60 nm [21]) was thereby obtained. The sample had an average crystallite size of 58 nm, measured on the (040) reflection of the X-ray pattern [7]; the absence of γ-UO_3 was also established from the X-ray pattern.

TABLE 1

Molar mass and mass fraction for β-UO_3 and γ-UO_3

Compound	M (g mol^{-1})	$10^2\ w$(U)	
		Obs.	Calc.
β-UO_3	286.03	83.12 ± 0.02	83.22
γ-UO_3	286.03	83.17 ± 0.02	83.22

Yellow γ-UO_3 was prepared by heating uranyl nitrate first at 470 K until dry; thereafter it was powdered and heated very slowly to about 770 K to give a γ-UO_3 sample free from the β-phase as established by X-ray diffraction.

These UO_3 samples prepared at ECN had the isotopic distribution of natural uranium. The samples were handled in a glove box and characterized by X-ray diffraction and by chemical analysis. The uranium content was determined by automatic potentiometric titration [22]; the results are given in Table 1.

Low-temperature heat capacity measurements

Heat capacity data over the 5–350 K range were made in the University of Michigan's Mark II adiabatic cryostat by the usual intermittent heating technique [23]. All determinations of mass, potential current, time, and temperature were ultimately referenced to calibrations made by the National Bureau of Standards. Calorimeter W-42 was used with samples of β-UO_3 (~ 141 g) and γ-UO_3 (~ 272 g) and pressures of about 15 kPa of helium to provide thermal equilibration.

High-temperature enthalpy measurements

These drop calorimetric determinations were made at the Netherlands Energy Research Foundation ECN in an isothermal diphenylether calorimeter as described by Cordfunke et al. [24]. The calorimeter was immersed in a well-stirred water bath which maintained the solid diphenylether in equilibrium with its liquid (T_m = 300.06 K) The specimen was encapsulated in spherical silica ampules which were about 4.2 cm^3 in volume and weighed about 1.4 g empty. They contained about 6.78 g of β-UO_3 and about 9.84 g of γ-UO_3, respectively. The samples are heated to the desired temperature in a furnace which is separated from the calorimeter by means of a copper diaphragm in order to avoid heat leakage into the calorimeter. The whole apparatus (calorimeter and furnace) is operated under an argon pressure of about 13 kPa. When the temperature has reached a constant value, the sample is dropped into the calorimeter. Heat from the specimen melts the

TABLE 2

Low-temperature heat capacity data for uranium trioxide phases

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
β-UO_3							
Series I		*Series II*				*Series III*	
86.57	34.560	5.59	0.042	41.20	13.230	280.37	79.24
95.12	38.020	6.58	0.084	45.66	15.347	290.92	80.46
114.07	45.032	7.41	0.159	50.65	17.769	301.59	81.67
123.75	48.396	8.34	0.301	56.22	20.418	312.39	82.89
133.28	51.426	9.44	0.473	61.69	23.091	323.18	83.97
142.73	54.200	10.61	0.741	66.55	25.401	333.80	84.98
152.28	56.773	11.79	0.979	67.58	25.882	335.11	85.19
162.14	59.245	13.07	1.343	74.35	28.962 [a]	345.49	86.32
172.12	61.643	14.47	1.799	81.28	32.162		
182.17	63.85	16.03	2.356	89.19	35.669		
192.29	65.90	17.71	2.987	99.88	39.836		
202.61	67.82	19.58	3.682	109.89	43.585		
212.94	69.71	21.80	4.527				
223.11	71.42	24.39	5.565				
233.28	72.97	27.18	6.749				
243.42	74.43	30.20	8.083				
253.38	75.94	33.52	9.623				
263.45	77.28	37.16	11.339				
γ-UO_3							
Series I		*Series II*		*Series III*			
146.48	54.463	79.79	31.033	5.24	0.0820	46.13	15.928 [b]
157.17	57.266	84.09	32.941	5.98	0.0967	51.13	18.138
166.96	59.722	90.36	35.577	6.75	0.1544	56.67	20.610
176.18	61.865	97.37	38.258	7.70	0.2565	62.91	23.535
185.32	63.85	104.77	41.041	8.68	0.4803	69.73	26.573
194.75	65.73	113.33	44.124	9.75	0.7657	76.44	29.518 [b]
204.34	67.61	122.52	47.246	10.96	1.0309	83.25	32.572
213.97	69.33	131.48	50.133	12.31	1.3594		
223.70	71.00	140.32	52.785	13.76	1.8138		
233.47	72.63			15.25	2.3087	*Series IV*	
243.17	74.10			16.75	2.8493	259.61	76.38
252.98	75.60			18.38	3.4589	267.10	77.66
262.72	76.90			20.22	4.1802	275.97	78.83
282.04	79.58			22.34	5.0501	285.97	80.17
291.47	80.92 [b]			24.75	6.0902	296.03	81.34
300.94	81.84 [b]			27.42	7.280	306.43	82.63
310.53	83.26 [b]			30.34	8.598	317.29	83.89
320.11	84.18 [b]			33.55	10.088	328.37	84.64
329.73	84.81 [b]			37.35	11.837	339.57	85.35
339.57	85.35 [b]			41.62	13.807	347.36	85.77

[a] These runs were not used in integration because of poor shield control.

[b] These runs were not used in curve fitting and integration because of inexplicably irregular drifts.

diphenylether that is in equilibrium with the liquid ether in a closed vacuum system. The resulting volume increment is determined by mercury displacement. The ratio of heat input to mass of mercury making up the volume change is a constant for the apparatus (79.977 ± 0.063 J g^{-1}) and is obtained by calibration with α-SiO_2 and compared with the National Bureau of Standards standard reference material (No. 720) synthetic sapphire, Al_2O_3. Our results with sapphire all agree within 0.2% with the data given by NBS. Corrections were made for the small difference between the calorimeter temperature (300.06 ± 0.01) K and the standard reference temperature, 298.15 K, using C_p values at 298.15 K. Temperature measurements were made with calibrated Pt–(Pt + 10 mass% Rh) thermocouples to within ± 0.5 K.

RESULTS

Low-temperature data

The heat capacity data for both the samples given in Table 2 are based on a gram formula mass of 286.03 on the basis of 1961 international atomic weights [25] and presented in chronological sequence to permit deduction of the approximate temperature increments employed in the measurements from the differences in the adjacent mean temperature. The data have been adjusted for curvature (i.e., for the finite temperature increments used in the determination of the heat capacity). The data are also shown graphically in Fig. 1. The experimental heat capacities were curve-fitted to polynomials in reduced temperature by the method of least-squares, and then integrated by computer to yield the values of the thermal functions at regular temperature intervals presented in Table 3 for both phases. The uncertainty in the thermodynamic functions in this table is considered to be less than 0.1% from 100 to 350 K. Additional digits beyond those significant are occasionally given to facilitate interpolation and differentiation.

Values of the entropy and enthalpy increments below 5 K were obtained from plots of C_p/T vs. T^2. For both compounds, the magnitudes of these extrapolations are only minute fractions of the totals at 298.15 K. No attempt was made in the process of extrapolation to adjust for contributions due to isotopic mixing or nuclear spin; hence, the values tabulated are practical thermal functions for use in ordinary thermochemical calculations. It was assumed that the zero point entropies were zero and that for reasons discussed below no magnetic contribution is appropriate. As a test of the measurements (and integration procedures), several determinations over about 60-K ranges of temperature were made as indicated in Table 4. The enthalpy increment measured directly (fourth column) is compared with that obtained from heat capacity measurements in Table 2.

TABLE 3

Thermodynamic functions for uranium trioxide phases

T (K)	C_p (J K^{-1} mol^{-1})	$S^\ominus(T) - S_m^\ominus(0)$ (J K^{-1} mol^{-1})	$H^\ominus(T) - H^\ominus(0)$ (J mol^{-1})	$-[G^\ominus(T) - H^\ominus(0)]/T$ (J K^{-1} mol^{-1})
β-UO_3				
5	0.025	0.008	0.033	0.004
10	0.590	0.138	1.125	0.025
15	1.975	0.611	7.184	0.134
20	3.824	1.431	21.669	0.351
25	5.828	2.498	45.719	0.669
30	8.008	3.749	80.25	1.075
35	10.309	5.155	126.02	1.556
40	12.665	6.686	183.43	2.100
45	15.037	8.314	252.67	2.699
50	17.435	10.025	333.84	3.347
60	22.263	13.627	532.33	4.757
70	27.037	17.422	779.1	6.293
80	31.627	21.334	1072.4	7.929
90	35.936	25.309	1410.4	9.640
100	39.940	29.305	1790.3	11.406
110	43.656	33.288	2208.3	13.213
120	47.112	37.238	2662.3	15.050
130	50.350	41.137	3149.7	16.908
140	53.371	44.982	3668.5	18.778
150	56.183	48.760	4216.6	20.652
160	58.781	52.472	4791.5	22.522
170	61.170	56.107	5391.5	24.393
180	63.39	59.668	6014.5	26.255
190	65.40	63.149	6658.4	28.104
200	67.32	66.551	7322.4	29.941
210	69.16	69.881	8004.8	31.388
220	70.88	73.141	8704.8	33.572
230	72.51	76.325	9421.9	35.363
240	74.06	79.446	10155.0	37.133
250	75.44	82.496	10902.2	38.886
260	76.78	85.483	11663.7	40.622
270	77.99	88.404	12437.4	42.338
280	79.20	91.261	13223.5	44.032
290	80.37	94.061	14021.4	45.710
300	81.55	96.805	14831.0	47.367
325	84.14	103.437	16902.5	51.430
350	86.65	109.767	19038.5	55.371
273.15	78.37	89.33	12682	42.873
298.15	81.34	96.32	14682	47.062
γ-UO_3				
5	0.067	0.021	0.084	0.004
10	0.828	0.213	1.674	0.046
15	2.226	0.787	8.962	0.188
20	4.092	1.674	24.644	0.444

TABLE 3 (continued)

T (K)	C_p (J K^{-1} mol^{-1})	$S^{\ominus}(T) - S_m^{\ominus}(0)$ (J K^{-1} mol^{-1})	$H^{\ominus}(T) - H^{\ominus}(0)$ (J mol^{-1})	$-[G^{\ominus}(T) - H^{\ominus}(0)]/T$ (J K^{-1} mol^{-1})
25	6.201	2.812	50.300	0.799
30	8.447	4.138	86.86	1.243
35	10.753	5.615	134.85	1.761
40	13.058	7.201	194.39	2.339
45	15.347	8.870	265.43	2.971
50	17.615	10.606	347.82	3.648
60	22.192	14.221	546.85	5.104
70	26.732	17.983	791.6	6.678
80	31.146	21.845	1081.1	8.330
90	35.355	25.757	1413.8	10.050
100	39.309	29.690	1787.4	11.816
110	42.999	33.610	2199.1	13.619
120	46.438	37.501	2646.4	15.447
130	49.639	41.346	3127.1	17.292
140	52.626	45.137	3638.4	19.146
150	55.413	48.861	4179.0	21.004
160	58.015	52.522	4746.3	22.861
170	60.442	56.116	5338.8	24.711
180	62.701	59.635	5954.7	26.552
190	64.81	63.082	6592.3	28.384
200	66.78	66.454	7250.0	30.204
210	68.62	69.760	7927.4	32.008
220	70.37	72.994	8622.4	33.798
230	72.05	76.157	9334.5	35.572
240	73.60	79.258	10062.9	37.330
250	75.14	82.295	10806.9	39.066
260	76.57	85.270	11565.4	40.786
270	77.99	88.186	12338.2	42.489
280	79.37	91.048	13125.2	44.170
290	80.67	93.855	13925.2	45.836
300	81.92	96.609	14738.1	47.484
325	84.47	103.274	16819.7	51.522
350	85.90	109.587	18950.6	55.446
273.15	78.41	89.03	12585	43.020
298.15	81.67	96.11	14585	47.179

High-temperature enthalpies

The results of the drop calorimetric measurements (shown in Table 5) can be represented over the range of the experimental measurements as a function of temperature by a polynomial expression of the form $H^{\ominus}(T) - H^{\ominus}(298.15\ \mathrm{K}) = aT + bT^2 + cT^{-1} + d$, the coefficients of which have been obtained by least-squares. The boundary conditions applied were $H^{\ominus}(T) -$

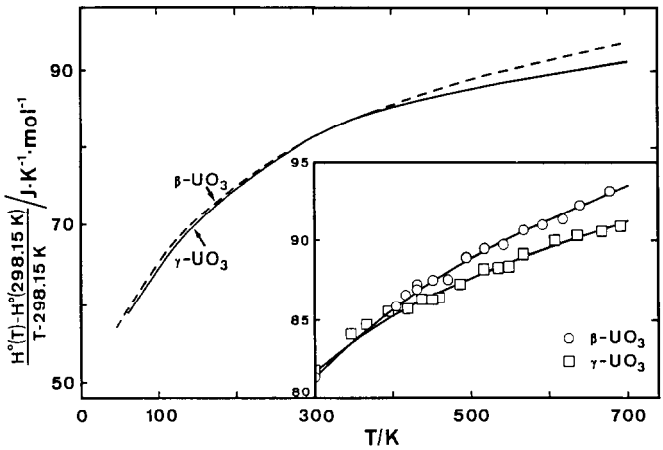

Fig. 1. The reduced and smoothed enthalpy increments of β-UO_3 and γ-UO_3 (insert, experimental values).

$H^{\ominus}(298.15\ \mathrm{K}) = 0$ and $C_p(T) = C_p(298.15\ \mathrm{K})$ at $T = 298.15$ K. The values of $C_p(298.15\ \mathrm{K})$ are taken from Table 3. The drop calorimetric measurements for β-UO_3 can be represented (298–678 K) by the equation

$$H^{\ominus}(T) - H^{\ominus}(298.15\ \mathrm{K}) = 86.170T + (12.4922 \times 10^{-3})T^2 + (10.9151 \times 10^{5})T^{-1} - 30463$$

The standard deviation is 0.32%.

For γ-UO_3 we obtain (298–693 K)

$$H^{\ominus}(T) - H^{\ominus}(298.15\ \mathrm{K}) = 88.701T + (7.2448 \times 10^{-3})T^2 + (10.0903 \times 10^{5})T^{-1} - 30475$$

The standard deviation is 0.35%.

At temperatures below 300 K the differences in C_p between β-UO_3 and γ-UO_3 are very small; between 300 and 360 K the C_p value of γ-UO_3 is, judging from the precision with which the values have been measured, even somewhat higher than that of β-UO_3. Above 360 K the C_p values of the

TABLE 4

Comparison of enthalpy determinations of γ-UO_3 with smoothed heat capacity curve

Detn.	T_1 (K)	T_2 (K)	$H^{\ominus}(T) - H^{\ominus}(0)$ (J mol^{-1})	
			Expt.	Calc.
A	140.93	198.18	3443.9	3443.4
B	198.18	256.04	4138.0	4134.6

TABLE 5

High-temperature enthalpy increments for uranium trioxide phases

T (K)	$H^{\ominus}(T)-H^{\ominus}$(298.15 K) (J mol^{-1})		δ (J mol^{-1})	T (K)	$H^{\ominus}(T)-H^{\ominus}$(298.15 K) (J mol^{-1})		δ (J mol^{-1})
	Expt.	Calc.			Expt.	Calc.	
β-UO_3							
404.9	9172	9171	1	517.9	19663	19623	40
417.2	10316	10278	38	542.7	21952	21992	−40
432.2	11701	11639	62	568.2	24471	24453	18
432.3	11678	11648	30	593.0	26822	26869	−47
452.4	13507	13490	17	617.9	29199	29317	−118
471.6	15190	15268	−78	640.5	31582	31558	24
494.4	17461	17401	60	678.4	35421	35353	68
γ-UO_3							
347.1	4118	4093	25	516.9	19308	19263	45
366.3	5773	5743	30	536.0	21009	21033	−24
394.6	8258	8212	46	548.3	22108	22179	−71
419.6	10416	10425	−9	568.6	24117	24078	39
438.6	12134	12124	10	608.4	27916	27831	85
452.5	13321	13376	−55	636.8	30584	30533	51
460.8	14068	14127	−59	668.1	33499	33531	−32
486.3	16426	16449	−23	693.1	35902	35940	−38

oxides diverge, resulting in a more pronounced stability of γ-UO_3 vs. β-UO_3.

Thermochemical values

Combination of the data of the present research with literature data permits the evaluation of the chemical thermodynamics of formation for the phases noted. Utilizing values for the enthalpies of formation at 298.15 K of β-UO_3, -1220.1 ± 0.8 [19] and γ-UO_3, -1223.8 ± 2.0 kJ mol^{-1} [26], the entropies at 298.15 K of uranium, 50.20 ± 0.20 [26], and oxygen gas, 205.037 ± 0.033 J K^{-1} mol^{-1} [26], we concluded that the standard thermochemical values for the formation process are those given in Table 6.

DISCUSSION

An impression of the accuracy of the measurements as well as of the deviation of the samples from each other is given in Fig. 1.

There is only one prior determination of the low-temperature heat capacity of UO_3 by Jones et al. [15] (which is believed to be the γ-phase because

TABLE 6

Thermodynamic properties of β-UO_3 and γ-UO_3

T (K)	$C_P^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-[G^\ominus(T)-H^\ominus(298)]/T$ (J K^{-1} mol^{-1})	$H^\ominus(T)-H^\ominus(298)$ (J mol^{-1})	$\Delta_f H^\ominus(T)$ (J mol^{-1})	$\Delta_f G^\ominus(T)$ (J mol^{-1})
β-UO_3						
298	81.340	96.320	96.320	0	−1220100	−1142151
300	81.537	96.824	96.324	150	−1220083	−1141668
400	89.342	121.459	99.629	8732	−1218826	−1115707
500	94.296	141.958	106.102	17928	−1217298	−1090100
600	98.129	159.500	113.575	27555	−1215745	−1064808
700	101.432	174.879	121.256	37536	−1214282	−1039770
800	104.452	188.623	128.833	47832	−1212978	−1014931
900	107.308	201.092	136.179	58421	−1211887	−990243
1000	110.063	212.541	143.251	69290	−1213469	−965500
γ-UO_3						
298	81.670	96.110	96.110	0	−1223800	−1145788
300	81.836	96.616	96.116	150	−1223783	−1145306
400	88.190	121.130	99.412	8687	−1222571	−1119321
500	91.910	141.237	105.829	17704	−1221222	−1093664
600	94.592	158.241	113.183	27035	−1219965	−1068273
700	96.784	172.992	120.696	36607	−1218911	−1043078
800	98.716	186.044	128.065	46383	−1218127	−1018016
900	100.496	197.775	135.169	56345	−1217663	−993034
1000	102.182	208.451	141.972	66479	−1219980	−967921

of its preparation and color). Although the trend of our data is the same, the data of Jones et al. are somewhat higher than those of the present sample, possibly due to poor crystallinity, non-stoichiometry or impurities. These authors report having exposed their finely ground oxide to the atmosphere, and noted that water had been taken up. In the hope of removing this absorbed water, they heated the sample in an oven at 373 K for 3 h immediately before sealing it into the calorimeter. Their data show a small anomaly just below the ice point indicating a free water content of about 0.04 mol%. The sample was subsequently used by Moore and Kelley [16] who reported that the sample as received from Jones et al. contained 1.17% by weight of water which was not removable at 393 K. An analysis made by Moore and Kelley [16] on their final material indicated only 83.02 mass% of uranium compared with the theoretical value of 83.22 mass%. Jones et al. [15] considered that any significant amount of water contained in their sample was bound in such a manner as to give an almost normal heat capacity at the ice point, and made no correction.

Unpublished measurements on the susceptibility by the Gouy method [27] indicated both UO_3 phases to be very weakly paramagnetic, probably due to the presence of different oxygen atom environments of uranium atoms. No anomalies were found between 1.3 and 5 K.

The relative stabilities of β-UO_3 and γ-UO_3 can be seen in Table 6. These are clearly in accord with previous observations of Cordfunke and Aling [1]. The small differences in the $\Delta G^{\ominus}$ values as compared with significant differences in structure are interesting and emphasize the need for precise data in correlating phase behavior.

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