URANIUM CHALCOGENIDES—II

HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF US_2 AND US_3 FROM 5 TO 350°K*

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Abstract—Heat capacity measurements and calculations of thermodynamic properties have been carried out for the compounds US_2 and US_3 from 5 to 350°K. The temperature dependence of the heat capacities is of normal sigmate type, except that for US_2 the rise in heat capacity in the region 10 to 20°K is more rapid than expected. Comparison of the US_2 data with those on US and US_3 indicates the presence of a Schottky-type transition in US_2 with a maximum of about 0·5 cal mole^{-1} °K^{-1} at 25°K.

Values of the heat capacity (C_p), entropy ($S° − S_0°$), and Gibbs energy function $[−(G° − H_0°)/T]$ at 298·15°K are 17·86, 26·42, and 14·01 for US_2 and 22·85, 33·09, and 17·45 for US_3, respectively, in cal mole^{-1}°K^{-1}.

URANIUM disulphide and uranium trisulphide are rather similar from a magnetic point of view in that they both formally contain quadrivalent uranium[1]. It therefore seemed of interest to compare their heat capacity behavior and also to explore to what extent they resembled uranium dioxide, in which a λ-type thermal anomaly[2, 3], associated with antiferromagnetic spin ordering[4, 5] has been observed at about 30°K.

The magnetic susceptibility of US_2 apparently follows the Curie-Weiss law down to 80°K, while for US_3 deviations are noticeable already at room temperature. Thus, the splitting of the $5f$ energy levels is probably larger in US_3 and the ground state reached at a higher temperature. For both compounds the Weiss constant is smaller than for UO_2 and the exchange interactions probably weaker. Non-cooperative transitions involving both spin and orbital states of uranium might therefore occur.

EXPERIMENTAL

The preparation of the US_2 and US_3 samples was carried out by reacting stoichiometric amounts of uranium and sulphur of earlier described purity in evacuated and sealed quartz tubes. In the case of the disulphide, the temperature of the mixture was slowly increased to 600°C, kept at this temp-

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erature for three days, and then increased to 800°C during two days and kept there for one week. After crushing the sample, it was homogenized at 800°C for another week, tempered at 500°C for one more week, and cooled to room temperature over two days. It was much easier to obtain a homogeneous sample of uranium trisulphide. This was achieved after slowly heating the mixture to 400°C, keeping it at this temperature for one day, and homogenizing it at 600°C for one week.

Measurements were made in the Mark III vacuum cryostat[6] provided with an electronic adiabatic shield control system consisting of three separate channels of recording circuitry with proportional, rate, and reset action. These kept the temperature differences between calorimeter and shield smaller than a millidegree and thereby reduced the heat exchange to a magnitude negligible in comparison with other sources of error. The gold-plated copper calorimeter (Laboratory designation W-29) had a capacity of 42·2 cm^3. The heat capacity of the empty calorimeter was determined separately and small corrections were applied for differences in the amounts of helium gas, indium-tin solder, and Apiezon-T grease for the loaded and empty calorimeter. The heat capacity of the US$_2$ sample, weighing 96·356 g, represented about 86 per cent of the total at 15°K and decreased to 57 per cent above 80°K. For the US$_3$ sample, weighing 79·123 g, the corresponding values were 82 per cent and 56 per cent respectively. All measurements of mass, temperature, resistance, potential and time were based upon calibration or standardizations made by the U.S. National Bureau of Standards.

RESULTS AND DISCUSSION

Experimental heat capacity values for the uranium disulphide and trisulphide samples are presented in Table 1 in chronological order for the mean temperatures of the determinations. The temperature increments employed in the measurements can usually be inferred from the adjacent mean temperatures. The values have been corrected for curvature of the heat capacities, and they are precise on the order of 1 per cent at 10°K, 0·1 per cent at 20°K, and a few hundredths of a per cent above 30°K. The thermodynamic functions might be considered reliable to better than 0·1 per cent at temperatures above 100°K making allowance for possible departures from the assumed compositions. The data are given in terms of the defined thermochemical calorie equal to 4·1840 J and an ice-point of 273·15°K.

The temperature dependence of the heat capacities is of the normal sigmate type, see Fig. 1, except that for US$_2$ the rise in heat capacity in the region 10 to 20°K is more rapid than expected.

The smoothed heat capacities and the thermodynamic functions derived from them by means of a digital computer using a previously described program[7] are given in Table 2 for selected temperatures. The thermodynamic function increments above 5°K may be considered reliable to better than 0·1 per cent at temperatures above 100°K, even taking possible departures from the assumed compositions into account. Since uncertainty exists with regard to the degree of order of the electron spins at 5°K, the entropy $(S_5^\circ - S_0^\circ)$, extrapolated by fitting a Debye function to the data, might not even be correct for chemical thermodynamic purposes, where nuclear spin and isotopic mixing contributions cancel. For this reason, the values of the thermodynamic functions must be used with caution.

Due to the lack of magnetic and other data below 80°K, it seems impossible at present to resolve the question of magnetic contributions unambiguously, but let us consider some of the problems involved.

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Table 1. Heat Capacity of US$_2$ and US$_3$*

Uranium disulphide (US$_2$, 1 mole = 303·16 g)

T	C_p	T	C_p	T	C_p
Series I		41·27	4·772	151·02	14·753
		45·82	5·336	160·11	15·14
5·73	0·011	51·05	5·983	169·28	15·50
6·39	0·016	56·60	6·670	178·54	15·79
7·14	0·037	62·37	7·383	180·04	16·07
7·95	0·062	68·46	8·112	197·88	16·31
8·75	0·101	75·00	8·859	207·56	16·55
9·57	0·162	82·14	9·687	216·62	16·74
10·56	0·251	89·72	10·485	225·56	16·91
11·74	0·367	85·57	10·057	234·51	17·08
13·06	0·543	93·36	10·815	243·41	17·22
14·49	0·759	101·22	11·494	252·31	17·34
15·95	0·999			260·31	17·44
17·48	1·262	Series II		269·26	17·56
19·17	1·555			277·26	17·66
21·17	1·900	85·45	10·047	285·87	17·77
23·54	2·301	92·70	10·759	294·38	17·78
26·30	2·739	100·26	11·417	302·95	17·90
29·30	3·182	108·18	12·081	311·49	17·98
32·51	3·637	116·27	12·706	320·11	18·01
36·01	4·106	124·58	13·282	328·93	18·10
39·37	4·536	133·16	13·816	337·86	18·16
42·68	4·948	141·97	14·304	346·50	18·25

Uranium trisulphide (US$_3$, 1 mole = 334·22 g)

| T	C_p	T	C_p	T	C_p
Series I		34·63	4·907	174·28	19·61
		38·41	5·609	183·46	20·01
5·54	0·031	42·26	6·273	192·53	20·36
6·12	0·052	52·37	7·885	201·61	20·69
6·77	0·072	57·66	8·679	210·63	20·99
7·50	0·108	63·40	9·538	219·59	21·26
8·38	0·153	69·40	10·382	228·67	21·51
9·29	0·227	75·55	11·208	237·82	21·76
10·14	0·303	82·28	12·147	246·87	21·97
11·07	0·386	89·51	13·061	255·87	22·13
12·18	0·499	90·73	13·203	264·99	22·31
13·45	0·670	98·25	14·018	274·27	22·49
14·89	0·882	105·82	14·782	283·54	22·62
16·47	1·444	113·44	15·53	292·69	22·76
18·23	1·469	121·36	16·24	301·80	22·90
20·22	1·869	129·71	16·92	299·34	22·87
22·50	2·351	138·29	17·56	308·47	22·99
25·02	2·901	146·96	18·14	317·78	23·13
27·87	3·526	155·87	18·67	327·21	23·26
31·12	4·221	165·03	19·18	336·76	23·37
				345·92	23·47

*Units: cal, mole, °K.
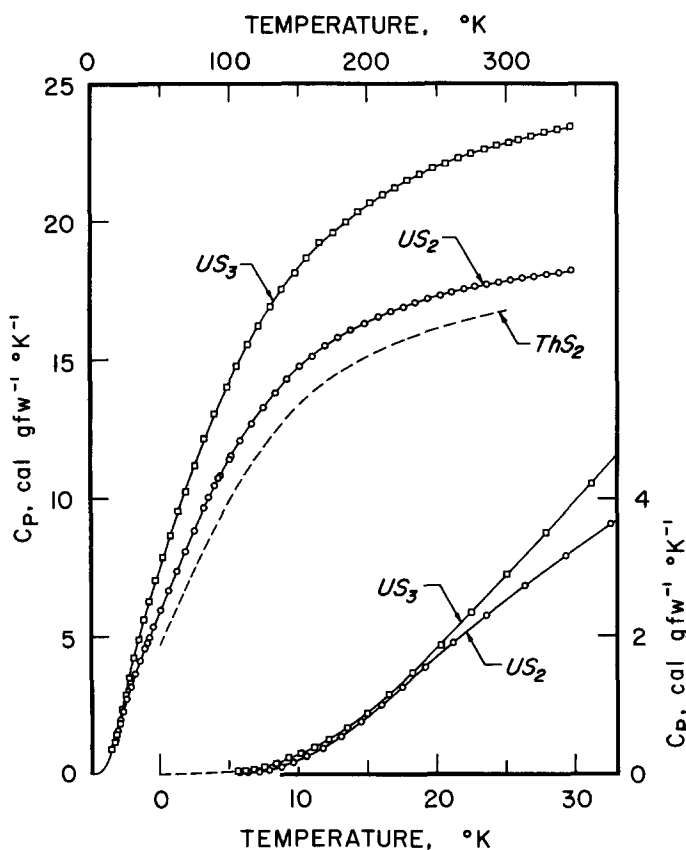
Fig. 1. Heat capacities of uranium sulphides. The ——O—— represents US_2, ——□——
represents US_3, and — — — ThS_2 [9].

It is apparent by comparing the low-temperature heat capacities of US_2
with those of US [8] and US_3 that an anomaly is present in US_2. Unfortunately,
heat capacity data on ThS_2 are reported [9] only over the range 53 to 297°K and
are of little assistance in resolving the lattice contribution in US_2. To get an
estimate of the lattice heat capacity of US_2 we approximate it as the arithmetic
mean of the heat capacities of US and US_3, after subtracting the spin wave and
conduction electron contributions in the former. On this basis the excess heat
capacity in US_2 has a maximum of about 0.5 cal $mole^{-1}°K^{-1}$ around 25°K see
Fig. 2. The cause of this non-cooperative heat capacity contribution is most
probably of electronic origin and related to zero-field splitting of the $5f$ energy
levels of the uranium atom. For U^{4+} with two unpaired $5f$ electrons the ground
state is triply degenerate if the orbital magnetic moment is completely quenched,
and ninefold degenerate for the free ion in the ground state $^3H_4$. Ligand field

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Table 2. Thermodynamic properties of US$_2$
US$_3$*

T	C_p	$S°$	$H°-H°_0$	$-(G°-H°_0)/T$	T	C_p	$S°$	$H°-H°_0$	$-(G°-H°_0)/T$
Uranium disulphide (US$_2$, 1 mole = 303·16 g)					Uranium trisulphide (US$_3$, 1 mole = 334·22 g)				
5	0·007	0·002	0·008	0·001	5	0·025	0·009	0·032	0·002
10	0·191	0·039	0·323	0·007	10	0·274	0·082	0·629	0·019
15	0·839	0·226	2·737	0·004	15	0·899	0·230	3·413	0·072
20	1·703	0·584	9·07	0·131	20	1·821	0·679	10·12	0·173
25	2·534	1·005	19·70	0·267	25	2·897	1·199	21·88	0·324
30	3·284	1·585	34·27	0·422	30	3·985	1·824	39·11	0·521
35	3·968	2·143	52·44	0·645	35	4·976	2·514	61·56	0·756
40	4·612	2·715	73·89	0·868	40	5·876	3·238	88·69	1·020
45	5·246	3·295	98·53	1·105	45	6·729	3·980	120·2	1·308
50	5·871	3·880	126·3	1·354	50	7·539	4·730	155·9	1·613
60	7·097	5·060	191·2	1·873	60	9·062	6·242	239·0	2·258
70	8·277	6·243	268·1	2·413	70	10·48	7·746	336·8	2·935
80	9·386	7·421	356·5	2·965	80	11·82	9·235	448·4	3·630
90	10·41	8·587	455·5	3·525	90	13·06	10·699	572·9	4·334
100	11·34	9·733	564·4	4·089	100	14·20	12·135	709·3	5·042
110	12·18	10·854	682·1	4·653	110	15·23	13·538	856·5	5·751
120	12·93	11·946	807·7	5·216	120	16·16	14·904	1013·6	6·457
130	13·60	13·009	940·5	5·774	130	16·97	16·230	1179·3	7·158
140	14·19	14·039	1079·5	6·328	140	17·69	17·515	1352·7	7·852
150	14·71	15·036	1224·1	6·876	150	18·33	18·757	1532·9	8·538
160	15·15	16·000	1373·5	7·416	160	18·89	19·958	1719·0	9·215
170	15·53	16·930	1526·9	7·948	170	19·39	21·118	1910·4	9·881
180	15·85	17·827	1683·9	8·472	180	19·84	22·240	2106·5	10·537
190	16·13	18·692	1843·8	8·988	190	20·25	23·323	2307·0	11·181
200	16·37	19·525	2006·3	9·494	200	20·63	24·372	2511·5	11·815
210	16·59	20·329	2171·1	9·991	210	20·98	25·387	2719·5	12·437
220	16·79	21·106	2338·0	10·479	220	21·29	26·370	2930·9	13·048
230	16·98	21·857	2506·9	10·957	230	21·57	27·323	3145·2	13·648
240	17·16	22·583	2677·6	11·426	240	21·82	28·246	3362·2	14·237
250	17·32	23·287	2850·0	11·887	250	22·03	29·141	3581·4	14·816
260	17·46	23·969	3024·0	12·338	260	22·22	30·009	3802·7	15·383
270	17·58	24·630	3199·2	12·781	270	22·40	30·851	4025·9	15·941
280	17·68	26·272	3375·6	13·216	280	22·56	31·669	4250·7	16·488
290	17·77	25·894	3552·9	13·643	290	22·73	32·463	4477·1	17·025
300	17·85	26·498	3731·0	14·061	300	22·88	33·236	4705·1	17·553
350	18·25	29·281	4634·0	16·041	350				
273·15	17·62	24·83	3255	12·92	273·15	22·45	31·11	4096	16·11
298·15	17·84	26·39	3698	13·98	298·15	22·85	33·10	4663	17·46

*Units: cal, mole, °K.

calculations [10–15] indicate that for a cubic point charge model the J = 4 multiplet splits into four states, one singlet (Γ_1), one doublet (Γ_3) and two triplets

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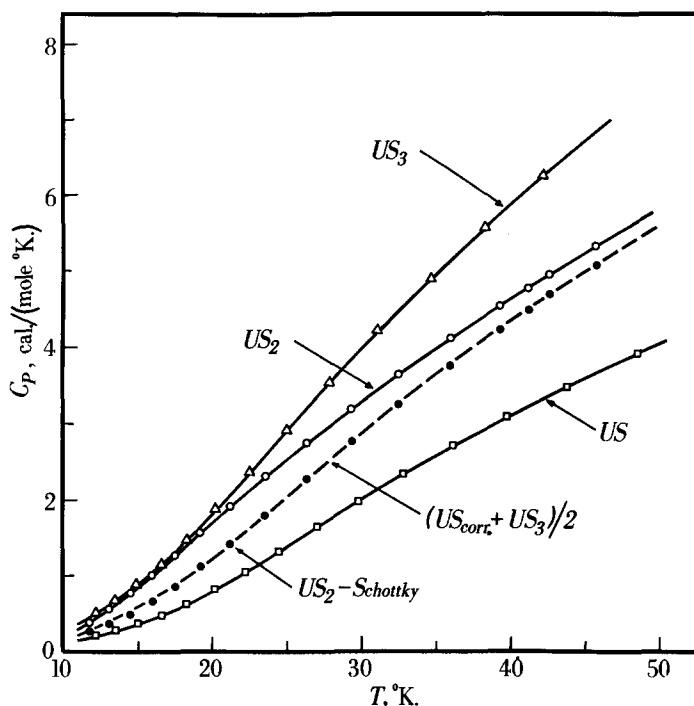
Fig. 2. Low-temperature heat capacity behavior of uranium sulphides. ——O—— represents US, ——O—— represents US_2, ——△—— represents US_3, — — — — represents $(US_{corr.} + US_3)/2$. The $US_{corr.}$ represents the lattice values (experimental values less magnetic and conduction electronic contributions). The solid circles represent the US_2 data less an adjustment for a Schottky contribution with $g_1 g_0 = 0.5$ and ΔE corresponds to $100\ cm^{-1}$.

(Γ_4 and Γ_5) of which the $^3\Gamma_5$ state is lowest in energy for the commonly assumed ratio between fourth and sixth order field parameters. Unfortunately, however, the resulting magnetic susceptibility for this state is not easily distinguishable from spin-only magnetism.

The low-symmetry field around the uranium atoms in US_2 occasions further splitting of the states, and one might expect either a singlet-singlet transition or a doublet-singlet transition to cause the excess heat capacity in US_2 around 25°K. For a Schottky type singlet-singlet transition the heat capacity maximum should amount to $0.87\ cal\ mole^{-1}°K^{-1}$, while for a lower doublet-singlet transition the value is $0.48\ cal\ mole^{-1}°K^{-1}$. Apparently, the latter alternative is in best agreement with the observations, but in view of the uncertainties in approximating the lattice heat capacity of US_2 the possibility of a singlet-singlet transition cannot be safely excluded.

Furthermore, the number of particles involved in the Schottky transition might well be smaller than assumed. Thus all uranium atoms might not be equivalent and other low-lying states might be present. In view of the sparseness of knowledge concerning electronic energy states in US_2 the possibilities of further electron spin ordering processes below 5°K cannot be excluded.

For US_3 the deviation from Curie-Weiss behaviour towards less temperature dependent magnetism is noticeable already at 300°K. The splitting of the $5f$ energy levels of uranium is therefore probably large and the ground state population high even at relatively high temperatures. Since no thermal anomalies are evident down to 5°K we are inclined to assume that ordered spin states have been reached at this temperature. Magnetic and other data at low temperatures are obviously needed to resolve the question.

The absence of cooperative phenomena in US_2 and US_3 might be discussed in terms of the theory proposed by Blume[16] for the transition in UO_2, in which he assumes that the non-magnetic singlet state Γ_1 lies below the magnetic triplet state Γ_5. For a sufficiently strong molecular field, one component of the triplet sinks below the singlet, and on increasing the temperature the field decreases due to depopulation of the lower magnetic level. Thus, when the ratio between ligand field splitting and exchange splitting falls within certain ranges the magnetic state is reached upon cooling either as a first-order or a second-order phase transition.

For US_2 and US_3 the coordination symmetry around the uranium atoms is lower and the degeneracies lifted further. The exchange splitting is apparently relatively small compared to the ligand field splitting and since no phase transition is observed the singlet state should not be lowest.

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