Thermochimica Acta, 126 (1988) 385–391
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOCHEMICAL PROPERTIES OF URANYL ARSENATES.
II. DERIVATIONS OF STANDARD ENTROPIES

H. BARTEN *

Netherlands Energy Research Foundation ECN, Petten (The Netherlands)

(Received 19 November 1987)

ABSTRACT

Standard entropies of uranyl arsenates have been derived by combining their standard enthalpies of formation and high-temperature data. As a result the high-temperature molar thermodynamic values of these compounds have been calculated.

INTRODUCTION

Part I of this series [1] gave the results of the arsenic oxide vapour pressure measurements of the uranyl arsenates. Furthermore, their enthalpies of formation have been determined [2,3]. In addition to this, the high-temperature enthalpy increment functions have only recently been determined by means of drop calorimetry [4].

No low-temperature enthalpy increment measurements have been performed, which would reveal the standard entropies. These values are necessary to enable calculations of high-temperature thermodynamic data of the uranyl arsenates.

The aim of this paper is to report the derivations of the standard entropies of the uranyl arsenates by using interrelations of the mentioned available data. Also, use will be made of the newly derived thermodynamic data of $As_4O_{10}(g)$ [5].

RESULT AND DISCUSSIONS

Additional data

As indicated in the introduction, enthalpy content functions of the uranyl arsenates have recently been measured [4]. The results became available for these derivations, and are summarized in Table 1.

---

* Present address: KEMA Laboratories, Arnhem, The Netherlands.

0040-6031/88/$03.50

TABLE 1

Uranyl arsenates. Parameters of the enthalpy content functions $H^\ominus(T) - H^\ominus(298.15\ \mathrm{K}) = AT + BT^2 + CT^{-1} + D$, measured by Cordfunke et al. [4] in the given temperature regions. The value are in J K^{-1} mol^{-1}

Compound	A	$B \times 10^3$	$C \times 10^{-5}$	D	Temperature range (K)
$(UO_2)_3(AsO_4)_2$	331.151	105.680	26.818	−117121.7	375.7–867.1
$(UO_2)_2As_2O_7$	307.411	52.907	58.513	−115983.0	397.8–868.2
$UO_2(AsO_3)_2$	208.461	44.455	30.346	−76282.5	377.8–781.3

Differentiation of these functions gives the respective heat capacity functions. In some cases of the derivations, the functions have to be used outside the indicated temperature regions. This is expected not to cause large errors in the derived entropy values.

$As_4O_{10}(g)$

The high-temperature specific heat function of $As_4O_{10}(g)$ and its standard entropy have been estimated from assumed similarities of the thermodynamics of gaseous phosphorus oxides and arsenic oxides. These data have been used to derive the standard enthalpy of formation of $As_4O_{10}(g)$ from the pressures measured of the non-dissociative evaporation of $As_2O_5(s)$ [6].

The estimated heat capacity function for $As_4O_{10}(g)$ has been found [5]

$$C_p(T) = 344.33 - 20.37 \times 10^{-3}T - 257.56 \times 10^5 T^{-2} + 45.158 \times 10^8 T^{-3} + 11.91 \times 10^{-6} T^2\ (\mathrm{J\ K^{-1}\ mol^{-1}})$$

It is expected that this function gives heat capacity values with an accuracy better than 10%.

In this way, the standard enthalpy of formation $\Delta H_f^\ominus(As_4O_{10}$, g, 298.15 K) = −1514 ± 12.0 kJ mol^{-1} has been obtained.

Standard entropies of uranyl arsenates

The standard entropies will be separately derived in the next parts; in the case of the ortho-arsenate an additional independent estimation will be done for comparison.

$(UO_2)_3(AsO_4)_2$

The entropy of this compound can be estimated by using the method of Latimer [7]. On the basis of the known entropies of $Ca_3(AsO_4)_2$ and $Sr_3(AsO_4)_2$, which are 225.94 and 255.22 J K^{-1} mol^{-1} [8], and taking 87.86

J K^{-1} mol^{-1} for $S^\ominus(UO_2^{2+})$ [7], we obtain $S^\ominus_{298\,K}((UO_2)_3(AsO_4)_2) = 372 \pm 20$ J K^{-1} mol^{-1}.

The measured vapour pressures [1] can serve as a source of a more reliable value, since these pressures could be related to the reaction

$$(UO_2)_3(AsO_4)_2(s) \rightleftharpoons U_3O_8(s) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}As_4O_{10}(g) \qquad (1)$$

in which the thermodynamic data of all components except the entropy of the ortho-arsenate are known. Thus, using the relation

$$\Delta G_r^\ominus = -RT \ln K_p = \Delta H^\ominus_{r,T} - T\Delta S^\ominus_T$$

in which

$$\Delta H^\ominus_{r,T} = \Delta H^\ominus_{r,298\,K} + \int \Delta C_p(T)\,dT$$

and

$$\Delta S^\ominus_T = \Delta S^\ominus_{298\,K} + \int \frac{\Delta C_p(T)}{T}\,dT$$

the value of $S^\ominus_{298\,K}((UO_2)_3(AsO_4)_2)$ can be derived from individual pressures by a reversed "third law" procedure expressed by the relation

$$\begin{aligned} S^\ominus_{298\,K}((UO_2)_3(AsO_4)_2) = -\frac{1}{T}\Big[& RT \ln K_p + \Delta H^\ominus_{r,298\,K} - TS^\ominus_{298\,K}(U_3O_8) \\ & + \tfrac{1}{2}S^\ominus_{298\,K}(O_2) + \tfrac{1}{2}S^\ominus_{298\,K}(As_4O_{10}) \\ & + \int \Delta C_p(T)\,dT - T\int \frac{\Delta C_p(T)}{T}\,dT \Big] \end{aligned}$$

The results of the calculations are given in Table 2, where it is shown that the resulting entropy values slightly vary with temperature. No further discussion is given on this phenomenon because the deviations are relatively small, whilst a rather extended temperature range has been studied. The average value is $S^\ominus_{298\,K}((UO_2)_3(AsO_4)_2) = 366.6 \pm 3.0$ J K^{-1} mol^{-1}. Uncertainties in the thermodynamic data used lower the reliability of this value to about 8.0 J K^{-1} mol^{-1}.

The experimental and the estimated values support each other nicely: of course the experimental value and its uncertainty will be adopted.

$(UO_2)_2As_2O_7$

The vaporization reaction of this compound has been discussed extensively in our paper [1]. As a result, we can use the individual pressures measured at 1 atm oxygen for the derivation of the entropy of the pyroarsenate. Under these circumstances the vaporization reaction is

$$3(UO_2)_2As_2O_7(s) \rightleftharpoons 2(UO_2)_3(AsO_4)_2(s) + \tfrac{1}{2}As_4O_{10}(g) \qquad (2)$$

TABLE 2

Calculations of the standard entropy of uranyl ortho-arsenate from the arsenic oxide pressures at 1 atm oxygen given in ref. 1. Additional thermodynamic data are taken from refs. 8–13

Exp. nr.	P_i	Temperature (K)	$S^{\ominus}_{298\ \mathrm{K}}((\mathrm{UO_2})_3(\mathrm{AsO_4})_2)$ (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)
1	3.18×10^{-5}	1273.0	370.83
2	1.32×10^{-5}	1252.1	370.39
3	9.84×10^{-6}	1252.7	371.72
4	4.81×10^{-6}	1235.1	370.55
5	3.22×10^{-6}	1209.0	367.22
6	1.98×10^{-6}	1199.3	367.11
7	7.32×10^{-7}	1169.1	364.32
8	1.17×10^{-7}	1141.1	365.12
9	6.79×10^{-8}	1125.6	363.43
10	5.15×10^{-8}	1111.9	361.01
11	6.78×10^{-9}	1080.7	360.89
			average value: 366.6 ± 3.0

Using the same procedure as was used for the ortho-arsenate, the standard entropy of the pyro-arsenate can be derived using the relation

$$S^{\ominus}_{298\ \mathrm{K}}\big((\mathrm{UO_2})_2\mathrm{As_2O_7}\big) = -\frac{1}{3T}\Big[RT\ln K_\mathrm{p} + \Delta H^{\ominus}_{\mathrm{r},298\ \mathrm{K}} - T\big(2S^{\ominus}_{298\ \mathrm{K}}\big((\mathrm{UO_2})_3(\mathrm{AsO_4})_2\big) + \tfrac{1}{2}S^{\ominus}_{298\ \mathrm{K}}(\mathrm{As_4O_{10}})\big) + \int \Delta C_\mathrm{p}(T)\,\mathrm{d}T - T\int \frac{\Delta C_\mathrm{p}(T)}{T}\,\mathrm{d}T\Big]$$

TABLE 3

The standard entropy of uranyl pyro-arsenate

Exp. nr.	P_i	Temperature (K)	$S^{\ominus}_{298\ \mathrm{K}}((\mathrm{UO_2})_2\mathrm{As_2O_7})$ (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)
1	2.91×10^{-4}	1026.7	285.07
2	6.89×10^{-5}	989.1	285.44
3	5.34×10^{-5}	986.9	285.70
4	4.50×10^{-5}	983.1	285.77
5	3.68×10^{-5}	978.3	285.84
6	2.98×10^{-5}	996.5	286.94
7	1.26×10^{-5}	965.6	286.70
8	3.73×10^{-6}	951.7	287.75
9	1.41×10^{-7}	899.8	289.66
			average value: 286.5 ± 1.7

TABLE 4

Calculations of the standard entropy of uranyl meta-arsenate from the arsenic oxide pressures at 1 atm oxygen

Exp. nr.	P_i	Temperature (K)	$S^{\ominus}_{298\ \mathrm{K}}(\mathrm{UO_2(AsO_3)_2})$ (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)
1	7.06×10^{-5}	985.3	210.45
2	4.01×10^{-5}	970.2	210.71
3	4.05×10^{-5}	971.6	210.76
4	3.49×10^{-5}	969.9	210.98
5	2.70×10^{-5}	960.9	210.94
6	1.99×10^{-5}	954.5	211.17
7	1.05×10^{-5}	939.4	211.53
8	2.77×10^{-6}	907.4	212.09
9	9.87×10^{-7}	892.0	213.12
			average value: 211.3 ± 1.7

in which only the $\mathrm{As_4O_{10}}$ pressure and the temperature measured must be applied to give the entropy wanted. The results of such calculations are given in Table 3. The average value obtained is $S^{\ominus}_{298\ \mathrm{K}}((\mathrm{UO_2})_2\mathrm{As_2O_7}) = 286.5 \pm 1.7$ J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$. The uncertainty of this value rises to about 8.0 as a result of the uncertainties in the thermodynamic data used in the calculations.

TABLE 5

Thermodynamic functions of solid $(\mathrm{UO_2})_3(\mathrm{AsO_4})_2$

T (K)	$C^{\ominus}_p(T)$ (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)	$S^{\ominus}(T)$ (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)	−GEF [a] (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)	$H^{\ominus}(T)-H^{\ominus}(298\ \mathrm{K})$ (kJ $\mathrm{mol^{-1}}$)	$\Delta H^{\ominus}_f(T)$ (kJ $\mathrm{mol^{-1}}$)	$\Delta G^{\ominus}_f(T)$ (kJ $\mathrm{mol^{-1}}$)	log $K^{\ominus}_p$
298.15	364.00	366.60	366.60	0.00	−4710.10	−4325.28	757.76
300	364.76	368.85	366.62	0.67	−4709.98	−4322.89	752.67
400	398.93	478.74	381.37	38.95	−4702.52	−4194.93	547.79
500	426.10	570.75	410.27	80.24	−4693.41	−4069.05	425.08
600	450.52	650.62	443.82	124.08	−4683.00	−3945.14	343.45
700	472.52	721.82	478.53	170.30	−4671.57	−3823.06	285.28
800	496.05	786.53	513.04	218.79	−4659.30	−3702.67	241.76
876	512.81	832.30	538.78	257.12	−4649.54	−3612.23	215.39
876	512.81	832.30	538.78	257.12	−4742.32	−3612.23	215.39
900	518.06	846.23	546.80	269.49	−4739.84	−3581.31	207.85
942	527.23	870.07	560.68	291.45	−4735.43	−3527.34	195.59
942	527.23	870.07	560.68	291.45	−4743.80	−3527.34	195.59
1000	539.83	901.94	579.55	322.39	−4736.46	−3452.66	180.35

[a] −GEF is the Gibbs energy function $[G^{\ominus}_T - H^{\ominus}_{298\ \mathrm{K}}]/T$.

TABLE 6

Thermodynamic functions of solid $(UO_2)_2As_2O_7$

T (K)	$C_p^\ominus(T)$ ($J\,K^{-1}\,mol^{-1}$)	$S^\ominus(T)$ ($J\,K^{-1}\,mol^{-1}$)	$-$GEF ($J\,K^{-1}\,mol^{-1}$)	$H^\ominus(T)-H^\ominus(298\,K)$ ($kJ\,mol^{-1}$)	$\Delta H_f^\ominus(T)$ ($kJ\,mol^{-1}$)	$\Delta G_f^\ominus(T)$ ($kJ\,mol^{-1}$)	$\log K_p^\ominus$
298.15	273.14	286.50	286.50	0.00	−3446.70	−3144.66	550.92
300	274.14	288.19	286.49	0.51	−3446.60	−3142.79	547.20
400	313.17	300.12	224.92	30.08	−3439.50	−3042.51	397.31
500	336.92	445.59	320.29	62.65	−3430.38	−2944.29	307.58
600	354.65	508.64	346.54	97.26	−3420.14	−2848.02	247.94
700	369.54	564.45	373.75	133.49	−3409.24	−2753.52	205.47
800	382.92	614.68	400.78	171.12	−3397.94	−2660.62	173.72
876	392.48	649.87	420.89	200.59	−3389.22	−2590.97	154.49
876	392.48	649.87	420.89	200.59	−3481.99	−2590.97	154.49
900	395.42	660.51	427.12	210.05	−3479.90	−2566.59	148.96
942	400.50	678.67	437.95	226.76	−3476.22	−2524.06	139.96
942	400.50	678.67	437.95	226.76	−3481.80	−2524.06	139.96
1000	407.38	702.80	452.61	250.19	−3475.97	−2465.27	128.77

$UO_2(AsO_3)_2$

A similar treatment can be carried out for the meta-arsenate. The reaction considered is

$$2UO_2(AsO_3)_2(s) \rightleftharpoons (UO_2)_2As_2O_7(s) + \tfrac{1}{2}As_4O_{10}(g) \qquad (3)$$

TABLE 7

Thermodynamic functions of solid $UO_2(AsO_3)_2$

T (K)	$C_p^\ominus(T)$ ($J\,K^{-1}\,mol^{-1}$)	$S^\ominus(T)$ ($J\,K^{-1}\,mol^{-1}$)	$-$GEF ($J\,K^{-1}\,mol^{-1}$)	$H^\ominus(T)-H^\ominus(298\,K)$ ($kJ\,mol^{-1}$)	$\Delta H_f^\ominus(T)$ ($kJ\,mol^{-1}$)	$\Delta G_f^\ominus(T)$ ($kJ\,mol^{-1}$)	$\log K_p^\ominus$
298.15	200.83	211.30	211.30	0.00	−2177.30	−1959.51	343.29
300	201.42	212.54	211.31	0.37	−2177.22	−1958.16	340.94
400	225.06	274.03	219.53	21.80	−2171.86	−1885.90	246.27
500	240.78	326.02	235.76	45.13	−2165.24	−1815.15	189.62
600	253.38	371.07	254.64	69.86	−2157.78	−1745.83	151.99
700	264.50	410.97	274.17	95.76	−2149.71	−1677.80	125.20
800	274.85	446.98	293.57	122.73	−2141.14	−1610.96	105.18
876	282.39	472.26	307.98	143.91	−2134.38	−1560.91	93.07
876	282.39	472.26	307.98	143.91	−2227.15	−1560.91	93.07
900	284.73	479.92	312.46	150.71	−2225.64	−1542.68	89.53
942	288.79	493.00	320.23	162.76	−2222.95	−1510.87	83.78
942	288.79	493.00	320.23	162.76	−2225.74	−1510.87	83.78
988	293.20	506.87	328.59	176.14	−2222.45	−1476.04	78.04

Calculations are performed in which the entropy is obtained from a relation essentially the same as for the pyro-arsenate in the previous section. The results of such calculations are given in Table 4; the value $S^{\ominus}_{298\,K}$-$(UO_2(AsO_3)_2) = 211.3 \pm 1.7$ J K^{-1} mol^{-1} is obtained.

Also in this case the uncertainty will increase to about 9.0 J. K^{-1} mol^{-1} because of the uncertainties in the constituent thermodynamic data.

Thermochemistry of uranyl arsenates

As a result of the above given derivations, the high-temperature thermodynamic data of the uranyl arsenates can be calculated. This was done for a number of temperatures, and the results are shown in Tables 5–7.

REFERENCES

1 H. Barten and E.H.P. Cordfunke, Thermochim. Acta, 90 (1985) 177.
2 E.H.P. Cordfunke, W. Ouweltjes and H. Barten, J. Chem. Thermodyn., 14 (1982) 883.
3 E.H.P. Cordfunke and G. Prins, J. Chem. Thermodyn., Revised values, to be published.
4 E.H.P. Cordfunke et al., J. Chem. Thermodyn., to be published.
5 H. Barten, Thesis, University of Amsterdam, 1986.
6 H. Barten and E.H.P. Cordfunke, Thermochim. Acta, 80 (1984) 221.
7 W.M. Latimer, The Oxidation States of The Elements and Their Potentials in Aqueous Solutions, Pretence-Hall, New York, 1952.
8 V.B. Parker, D.D. Wagman, and W.H. Evans, Natl. Bur. Stand. U.S. Tech. Note 270-6, 1971.
9 E.J. Huber and C.E. Holley, J. Chem. Thermodyn., 1 (1969) 267.
10 E.F. Westrum, and F.J. Grønvold, Am. Chem. Soc., 81 (1959) 1777.
11 E.H.P. Cordfunke, W. Ouweltjes, and G. Prins, J. Chem. Thermodyn., 7 (1975) 1137.
12 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey, and R.H. Schumm, Natl. Bur. Stand. U.S. Tech. Note 270-3, 1968.
13 C.E. Wicks and F.E. Block, Bulletin 605. Bureau of Mines, 1963.