M-2041

J. Chem. Thermodynamics 1987, 19, 369-375

Standard enthalpies of formation of tellurium compounds

I. Tellurium dioxide

E. H. P. CORDFUNKE, W. OUWELTJES, and G. PRINS

Netherlands Energy Research Foundation ECN. Petten, The Netherlands

(Received 29 May 1986; in final form 29 July 1986)

The enthalpy of formation of TeO₂(s) has been obtained by solution calorimetry using two independent thermochemical cycles: the first, in $\{3.0 \text{ mol} \cdot dm^{-3} \text{ H}_2\text{SO}_4 + 0.10 \text{ mol} \cdot dm^{-3} \text{ K}_2\text{Cr}_2\text{O}_7 + 0.010 \text{ mol} \cdot dm^{-3} \text{ MnSO}_4\}(aq)$, based on the standard enthalpies of formation of U₃O₈ and γ -UO₃, and the second, in $\{0.46 \text{ mol} \cdot dm^{-3} \text{ NaClO} + 0.5 \text{ mol} \cdot dm^{-3} \text{ NaOH}\}(aq)$, based on the standard enthalpies of formation of Ma_3CO_3 . The results are in good agreement: $\Delta_r H^{\circ}_m(\text{TeO}_2, \text{ s}, 298.15 \text{ K}) = -(318.74 \pm 7.35) \text{ kJ} \cdot \text{mol}^{-1}$ and $-(320.71 \pm 3.22) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The weighted mean is $-(320.4 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$. The enthalpy of formation of Na₂SO₃ was measured calorimetrically in $\{0.020 \text{ mol} \cdot dm^{-3} \text{ I}_2 + 0.090 \text{ mol} \cdot dm^{-3} \text{ KI}\}(aq)$. The result is: $\Delta_r H^{\circ}_m(\text{Na}_2\text{SO}_3, \text{ s}, 298.15 \text{ K}) = -(1101.8 \pm 0.7) \text{ kJ} \cdot \text{mol}^{-1}$.

1. Introduction

The enthalpy of formation of $TeO_2(s)$ is not known very well. When the National Bureau of Standards was evaluating in 1964 the then existing values for incorporation in the Technical Notes,⁽¹⁾ the selected value seemed to be a logical choice: of the two combustion values, (2,3) the value by Gadzhiev and Sharifov was apparently in error (table 1) as were Mixter's calorimetric measurements,⁽⁴⁾ whereas the e.m.f. value by Schuhmann⁽⁵⁾ could not be recalculated because the entropy of TeO₂(s) was lacking. Thus, Thomsen's value from enthalpy-of-solution measurements,⁽⁶⁾ and the value of Schneider and Zintl⁽²⁾ from combustion calorimetry, being in perfect agreement, provided the selected value: $\Delta_{\rm f} H^{\circ}_{\rm m}(298.15 {\rm K}) =$ -322.6 kJ mol⁻¹. However, shortly thereafter mass-spectrometric measurements by Muenow et al.⁽⁷⁾ yielded again a strongly deviating value which seemed to give some support to the rejected values of Mixter, and of Gadzhiev and Sharifov. Because TeO₂ is a key compound in tellurium chemistry we have redetermined the enthalpy of formation of TeO₂ by enthalpy-of-solution measurements. In view of the importance of this value as a reference for the other tellurium compounds we used two different dissolution cycles: one in acid solution and one in alkaline solution. both with elemental tellurium as a reference.

Author	$\Delta_{\rm f} H_{ m m}^{\circ}/({ m kJ})$	mol ⁻¹)	Method		
	Original	Recalculated			
Thomsen (1882)	- 322.9		Calorimetry		
Mixter (1910)	- 364.4		Calorimetry		
Schuhmann (1925)		-325.5	E.m.f. measurements		
Schneider and Zintl (1961)	-321.7 ± 5.0		Combustion calorimetry		
Gadzhiev and Sharifov (1962)	-379.1 ± 1.3		Combustion calorimetry		
NBS tables (1964)	- 322.6		Evaluation		
Muenow et al. (1969)	-351.9 ± 12.0		Mass spectrometry		

TABLE 1. The enthalpy of formation of $TeO_2(s)$ at 298.15 K

2. Experimental

TeO₂ was prepared by dissolving tellurium in nitric acid $\{n(HNO_3)/n(H_2O) = 1\}$ at room temperature. After washing the white precipitate with water, the resulting product was heated in oxygen at 775 K overnight. The Te content was determined by heating a sample in air at 875 K for 1 h and weighting as TeO₂. Two different preparations of TeO₂ were used: TeO₂-13-5 contained (0.7993±0.0007) mass fraction of Te and TeO₂-14-1 (0.7990±0.0004) mass fraction (calc. 0.7995).

Tellurium (CERAC) was purified from oxide contamination by melting it in hydrogen at 775 K; after cooling to room temperature the thin oxide layer could easily be removed from the surface. The resulting product was phase pure, according to X-ray analysis.

Reagent-grade Na₂SO₃, Na₂SO₄, I₂, and HI(aq) were used (Baker). Na₂SO₃ was purified further by repeated recrystallizations; its SO_3^{2-} content was determined iodometrically. The {NaClO + NaOH} solution was obtained by dilution of a commercial bleaching liquor and addition of the required amount of NaOH. The NaClO content of the diluted solution was determined iodometrically. The various compounds were characterized by X-ray diffraction.

The enthalpies of solution were measured in a calorimeter that has been described previously, together with the calorimetric procedure and calibration method.⁽⁸⁾ Corrections to the temperature rise in the calorimeter were based on a complete calculation of the pre- and post-period according to Newton's cooling law.

3. Results

Tellurium dioxide was dissolved in two different solvents so as to derive its standard enthalpy of formation from independent thermochemical cycles. In the first cycle TeO₂ was dissolved in {3.0 mol \cdot dm⁻³ H₂SO₄ + 0.10 mol \cdot dm⁻³ K₂Cr₂O₇ + 0.010 mol \cdot dm⁻³ MnSO₄}(aq) in which tellurium was quantitatively oxidized to the hexavalent state. In the second cycle TeO₂ was dissolved in {0.46 mol \cdot dm⁻³ NaClO + 0.5 mol \cdot dm⁻³ NaOH}(aq). Details of the measurements are given in table 2, where *m* denotes the mass of the sample dissolved, ε the energy equivalent of the calorimeter, $\Delta\Theta$ the temperature change, ΔH_m the molar enthalpy of solution, and Θ° an arbitrary temperature.

 $\Delta_{\rm f} H_{\rm m}^{\circ}({\rm TeO}_2,\,{\rm s})$

TABLE 2. Enthalpy of solution of a mass m of a specified solute in 200 cm³ of a specified aqueous solvent at 298.15 K

$\frac{m(\text{solute})}{g}$	$\frac{\varepsilon \Theta}{J}$	$\frac{\Delta \Theta}{\Theta^{\circ}}$	$\frac{\Delta H_{\rm m}}{\rm kJ\cdot mol^{-1}}$	$\frac{m(\text{solute})}{g}$	$\frac{\varepsilon \boldsymbol{\Theta}^{\circ}}{\mathbf{J}}$	$rac{\Delta oldsymbol{\Theta}}{oldsymbol{\Theta}^{\circ}}$	$\frac{\Delta H_{\rm m}}{\rm kJ\cdot mol^{-1}}$
(a) TeO ₂	solvent: {	3.0 mol · dn	1^{-3} H ₂ SO ₄ +0).10 mol · dm ^{- 3}	K,Cr,O	+0.010 mo	$1 \cdot dm^{-3} MnSO_4$ (aq)
0.13088 0.13653	89.415 89.700	1.4184 1.4906	-154.66 -156.30	0.1 328 1 0.1 259 5	90.407 89.004	1.4333 1.3717	
0.15145	90.185	1.42.52	- 150.08			average:	-155.49 ± 0.69
(b) Te s	olvent: {3.	0 mol·dm ⁻	$^{-3}$ H ₂ SO ₄ + 0.2	$10 \text{ mol} \cdot \text{dm}^{-3}$	$K_2Cr_2O_7$	+0.010 mol	dm^{-3} MnSO ₄ }(aq)
0.08172	75.508	4.7503	-560.06	0.07725	74.782	4.5588	- 563.12
0.07970	74.854	4.6986	- 563.09	0.07835	75.118	4.6046	- 563.31
0.07841	74.446	4.6360	- 561.65	0.07826	75.012	4.5967	- 562.20
0.07698	75.021	4.5168	- 561.68	0.07537	74.531	4.4342	- 559.51
						average:	-561.83 ± 1.01
(c) U_3O_8	solvent: {	3.0 mol · dn	$n^{-3} H_2 SO_4 + 0$).10 mol · dm ^{- 3}	$K_2Cr_2O_2$	+0.010 mo	$l \cdot dm^{-3} MnSO_4$ (aq)
1.36499	89.572	7.1561	- 395.43	1.36743	89.768	7.1591	- 395.76
1.38794	90.027	7.2340	- 395.13	1.37045	89,474	7.1766	- 394.55
						average:	-395.22 ± 0.51
	(d) γ-L	JO ₃ solve	nt: {3.0 mol · c	$lm^{-3}H_2SO_4 +$	0.10 mol·	$dm^{-3}K_2C$	r,0,+
			0.010 mol	dm ⁻³ MnSO	4}(aq)	-	-
1.38952	89.444	4.6064	- 84.81	1.39842	89.331	4.6595	-85.14
1.39435	89.186	4.6389	-84.87			average:	-84.94 ± 0.20
	(e) Te	O_2 solven	nt: {0.46 mol·c	lm⁻³ NaClO+	-0.5 mol·o	dm ⁻³ NaOI	H}(aq)
0.10987	74.872	1.9415	-211.16	0.14043	93.602	1.9846	-211.12
0.10643	89.623	1.5662	-210.49			average:	-210.92 + 0.43
	(f) T	e solvent	{0.46 mol dr	n^{-3} NaClO+() 5 mol · dr	n ⁻³ NaOH	- }(ag)
0.00040	76 5 61	5 0370	(0.10 mor un	0.06330		2 (400	(aq)
0.08810	76.001	5 9955	-055.55	0.05370	13.223	3.0488	- 652.19
0.00019	75 307	5.8033	- 030.39	0.05807	13.030	4,0394	- 052.07
0.00570	76 195	6 1823	-648 97	0.06088	79 587	3 9495	- 658 77
0.05911	74.706	4.0637	-655.34	0.00000	· /	average	$\frac{-652.71}{-652.73}$ + 2.50
			(0.44)			average.	052.75 <u>-</u> 2.50
	$(g) Na_2$	SO_4 solve	ent: {0.46 mol	dm ³ NaClO	+0.5 mol	·dm · NaC)H}(aq)
0.1/2/5	94.972	0.0752	-5.87	0.26/43	93.951	0.1169	-5.83
0.20362	93.003	0.1172	- 3.87			average:	-5.86 ± 0.03
	(h) Na ₂	SO ₃ solve	ent: {0.46 mol	· dm ⁻³ NaClO	+0.5 mol	·dm ⁻³ NaC	DH}(aq)
0.23236	93.144	6.9698	-352.14	0.23498	93.689	7.0126	-352.40
0.07851	94.078	2.3289	-351.73	0.23432	93.055	7.0195	- 351.35
0.07875	95.073	2.3058	- 350.86			average:	-351.70 + 0.55
			corrected f	or mass fractio	n 0.0022 c	of impurity:	-352.48 ± 0.55
	(i) N	la SO, so	ilvent: {0.020 r	nol·dm ⁻³ I. +	-0.090 mo		(ag)
0 12324	05 8 20	1 2223 30	-120.86	0 12780	Q5 144	1 2020	- 130 44
0.12524	95.449	1.2737	-120.80 -120.93	0.12/00	73.144	1.2030	120.75 + 0.20
			corrected f	ar man fractio	n 0 0022 -	average:	-120.75 ± 0.29
			corrected I	or mass tractio	u 0.0022 (я impurity:	-121.02 ± 0.29

m(solute)	ε Θ °	ΔΘ	$\Delta H_{\rm m}$	m(solute)	ε Θ °	$\Delta \Theta$	$\Delta H_{\rm m}$
g	J	Θ°	kJ · mol ^{−1}	g	J	$\overline{{oldsymbol{\Theta}}^{\circ}}$	$\overline{kJ \cdot mol^{-1}}$
	(j) N	Na ₂ SO ₄ s	olvent: {0.020 r	$nol \cdot dm^{-3} I_2 +$	⊦0.090 ma	ol · dm ⁻³ KI}(a	aq)
0.12639	94.073	0.0100	-1.06	0.15073	93.939	0.0118	-1.04
						average:	-1.05 ± 0.02
(k) HI \cdot 5.32H ₂ O solvent: {0.020 mol \cdot dm ⁻³ I ₂ + 0.090 mol \cdot dm ⁻³ KI}(aq)							
0.3333	77.641	0.1545	-8.05	0.3372	77.110	0.1485	- 7.60
0.33615	75.301	0.1533	- 7.68	0.3380	77.677	0.1524	7.84
						average:	-7.79 ± 0.20
	(1) I ₂ solve	ent: {0.020 mol	$dm^{-3}I_2 + 0.0$	090 mol·c	im ⁻³ KI}(aq)	
0.18739	77.224	-0.0630	6.59	0.18379	75.662	-0.0633	6.61
0.18597	74.865	-0.0685	7.00			average:	$\overline{6.73}\pm0.27$

TABLE 2-continued

THE $\{H_2SO_4 + K_2Cr_2O_7 + MnSO_4\}$ CYCLE

The reaction scheme to derive $\Delta_f H^{\circ}_m(\text{TeO}_2)$ is given in table 3. In this scheme the enthalpy of solution and oxidation of TeO₂(s), table 2(a), is combined with the enthalpies of solution of Te, U₃O₈, and γ -UO₃, table 2(b), (c), (d), and with the standard enthalpies of formation of U₃O₈,⁽⁹⁾ and γ -UO₃,⁽⁸⁾ which are key values in uranium thermochemistry. When we combine the values from table 2 with the auxiliary values according to the reaction scheme in table 3, the enthalpy of formation of TeO₂ can be calculated. We obtain $\Delta_f H^{\circ}_m(\text{TeO}_2, \text{ s}, 298.15 \text{ K}) = -(318.74 \pm 7.35) \text{ kJ} \cdot \text{mol}^{-1}$.

THE {NaClO + NaOH} CYCLE

The reaction scheme to derive $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm TeO}_2)$ from enthalpies of solution in $\{0.46 \text{ mol} \cdot {\rm dm}^{-3} \text{ NaClO} + 0.5 \text{ mol} \cdot {\rm dm}^{-3} \text{ NaOH}\}({\rm aq})$ is given in table 4. We used

TABLE 3. Reaction scheme for the enthalpy of formation of TeO₂; (soln) refers to { $3.0 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2 \text{SO}_4 + 0.10 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2 \text{Cr}_2 \text{O}_7 + 0.010 \text{ mol} \cdot \text{dm}^{-3} \text{ MnSO}_4$ } in water. $\Delta H_7 = -\Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6$

-	Reaction	$\Delta H_{\rm m}/(\rm kJ\cdot mol^{-4})$
1.	$TeO_{2}(s) + \{\frac{1}{4}K_{2}Cr_{2}O_{7} + \frac{4}{3}H_{2}SO_{4}\}(soln)$	
	$= \{H_2 \text{TeO}_4 + \frac{1}{3} \text{Cr}_2(\text{SO}_4)_3 + \frac{1}{3} \text{K}_2 \text{SO}_4 + \frac{1}{3} \text{H}_2 \text{O}\}(\text{soln})$	-155.49±0.69
2.	$Te(s) + \{K_2Cr_2O_7 + 4H_2SO_4\}(soln)$	
	$= \{H_2 TeO_4 + Cr_2(SO_4)_3 + K_2 SO_4 + 3H_2 O\}(soln)$	-561.83 ± 1.01
3.	$2U_3O_8(s) + {}_3^2K_2Cr_2O_7 + (26/3)H_2SO_4 (soln)$	
	$= \{6UO_2SO_4 + \frac{2}{3}Cr_2(SO_4)_3 + \frac{2}{3}K_2SO_4 + (26/3)H_2O\}(\text{soln})$	-790.44 ± 1.02
4.	$6U(s) + 8O_2(g) = 2U_3O_8(s)$	-7149.6 ± 5.0
5.	$6\gamma - UO_3(s) + 6H_2SO_4(soln) = \{6UO_2SO_4 + 6H_2O\}(soln)$	-509.64 ± 1.20
6.	$6\dot{U}(s) + 9\dot{O}_2(g) = 6\gamma \cdot UO_3(s)$	-7342.8 ± 5.0
7.	$Te(s) + O_2(g) = TeO_2(s)$	-318.74 ± 7.35

{0.46 mol·dm ⁻³ NaClO+0.5 mol·dm ⁻³ NaOH} in water. $\Delta H_7 = -\Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6$	
Reaction	$\Delta H_m/(kJ \cdot mol^-)$

Keaction	$\Delta \mathbf{n}_{m}/(\mathbf{k}\mathbf{j} \cdot \mathbf{m}(\mathbf{n}))$
1. $TeO_3(s) + \{NaClO + 2NaOH\}(soln) = \{Na_3 TeO_4 + NaCl + H_2O\}(soln)$	-210.92 ± 0.43
2. $Te(s) + {3NaClO + 2NaOH}(soln) = {Na_{2}TeO_{4} + 3NaCl + H_{2}O}(soln)$	-652.73 ± 2.50
3. $2Na_2SO_3(s) + 2NaClO(soln) = \{2Na_2SO_4 + 2NaCl\}(soln)$	-704.96 ± 1.10
4. $4Na(s) + 2S(s) + 3O_2(g) = 2Na_2SO_3(s)$	-2203.66 ± 1.44
5. $2Na_2SO_4(s) + (soln) = 2Na_2SO_4(soln)$	-11.72 ± 0.06
6. $4Na(s) + 2S(s) + 4O_2(g) = 2Na_2SO_4(s)$	-2775.8 ± 0.8
7. $Te(s) + O_2(g) = TeO_2(s)$	-320.71 ± 3.22

 $Na_2SO_3(s)$ as the reference reductant in the cycle. This salt always contains a few tenths mass per cent of impurity, probably sulphate, even after several recrystallizations. The Na₂SO₃ mass fraction in the sample used was 0.9978. Since the enthalpy of solution of $Na_2SO_4(s)$ is small, table 2(g), the contribution of this impurity to the enthalpy of solution of Na₂SO₃(s) was neglected when the last value was reduced to that of 100 mass per cent of $Na_2SO_3(s)$, table 2(h). In the scheme the enthalpy of solution and oxidation of TeO₂(s), table 2(e), is combined with the enthalpies of solution of Te, Na₂SO₄, and Na₂SO₃, table 2(f), (g), and (h), and with the standard enthalpies of formation of Na_2SO_4 ,⁽¹⁰⁾ and Na_2SO_3 . The last value was obtained from enthalpy-of-solution measurements in $\{0.020 \text{ mol} \text{ dm}^{-3} \text{ I}_2 +$ 0.090 mol dm^{-3} KI}(aq). The reaction scheme to obtain $\Delta_f H_m^{\circ}(Na_2SO_3)$ is given in table 5. In this scheme the enthalpy of solution and oxidation of Na₂SO₃, corrected for impurity, table 2(i), is combined with the enthalpies of solution of Na_2SO_4 , $(HI \cdot 5.32H_2O)(l)$, and I_2 , table 2(j), (k), (l), and with the enthalpies of formation of Na_2SO_4 ,⁽¹⁰⁾ $H_2O(l)$, and HI in 5.32 $H_2O(l)$. The last value was obtained by interpolation in the NBS table⁽¹¹⁾ after correction of this table with the new value of Sprengel.⁽¹²⁾ $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm I}^-, {\rm aq}, 298.15 {\rm K})$ by Vanderzee and We find $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm Na}_2{\rm SO}_3, \, {\rm s}, \, 298.15 \, {\rm K}) = -(1101.83 \pm 0.72) \, {\rm kJ} \cdot {\rm mol}^{-1}$. This value is in good

TABLE 5. Reaction scheme for the enthalpy of formation of Na₂SO₃; (soln) refers to {0.020 mol \cdot dm⁻³ I₂+0.090 mol \cdot dm⁻³ KI} in water. $\Delta H_9 = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 - \Delta H_6 - \Delta H_7 - \Delta H_8$

Reaction	$\Delta H_{\rm m}/({\rm kJ}\cdot{\rm mol}^{-1})$
1. $Na_{2}SO_{3}(s) + \{I_{2} + H_{2}O\}(soln) = \{Na_{2}SO_{4} + 2HI\}(soln)$	-121.02 ± 0.29
2. $\operatorname{Na}_{2}\operatorname{SO}_{4}(s) + (\operatorname{soln}) = \operatorname{Na}_{2}\operatorname{SO}_{4}(\operatorname{soln})$	-1.05 ± 0.02
3. $2Na(s) + S(s) + 2O_2(g) = Na_2SO_4(s)$	-1387.9 ± 0.4
4. $H_2(g) + I_2(s) + 10.64H_2O(1) = 2(HI \cdot 5.32H_2O)(1)$	-97.42 ± 0.20
5. $2(HI \cdot 5.32H_2O)(I) + (soln) = {2HI + 10.64H_2O}(soln)$	-15.58 ± 0.40
6. $I_2(s) + (soln) = I_2(soln)$	$+6.73\pm0.27$
7. $\tilde{H}_{2}(g) + \frac{1}{2}O_{2}(g) = H_{2}O(1)$	-285.830 ± 0.042
8. $11.64H_2O(1) + (soln) = 11.64H_2O(soln)$	0
9. $2Na(s) + S(s) + \frac{3}{2}O_2(g) = Na_2SO_3(s)$	-1101.83 ± 0.72

15

agreement with the value selected by the NBS: $-1100.8 \text{ kJ} \cdot \text{mol}^{-1}$.⁽¹³⁾ With our value for $\Delta_{\rm f} H^{\circ}_{\rm m}(\text{Na}_2\text{SO}_3)$ in the scheme of table 4 we obtain $\Delta_{\rm f} H^{\circ}_{\rm m}(\text{TeO}_2, \text{ s}, 298.15 \text{ K}) = -(320.71 \pm 3.22) \text{ kJ} \cdot \text{mol}^{-1}$.

We tried to replace Na_2SO_3 as the reference reductant in the {NaClO + NaOH} cycle by a compound that can easily be obtained in a state of high purity. Following clues given by Bigelow⁽¹⁴⁾ we tried KI, NaHS, and $Na_2S_2O_3$ as reductants, but in each case the temperature of the calorimeter did not fall regularly, not even after several hours. Probably slow consecutive reactions are involved. We also tried KBr, but this compound is not oxidized by NaClO in the concentration range used.

4. Discussion

The enthalpies of formation of TeO₂(s), derived from the two independent cycles, agree well. Taking the weighted mean of the two results we obtain $\Delta_{\rm f} H^{\circ}_{\rm m}$ (TeO₂, s, 298.15 K) = $-(320.4 \pm 3.0)$ kJ·mol⁻¹.

Note added to typescript

When the preceding article had been sent to the Journal, we learned that O'Hare *et al.*^(15,16) had submitted a paper on the enthalpy of formation of Na₂SO₃ and K₂SO₃. They find $\Delta_f H^{\circ}_m(Na_2SO_3) = -(1096.78 \pm 0.81) \text{ kJ} \cdot \text{mol}^{-1}$. If we use this value in our table 4, we obtain $\Delta_f H^{\circ}_m(TeO_2) = -(330.81 \pm 3.30) \text{ kJ} \cdot \text{mol}^{-1}$, which is no longer in agreement with the value obtained with our acid cycle (table 3), the difference in $\Delta_f H^{\circ}_m(TeO_2)$ being about 12 kJ · mol⁻¹. We cannot explain the discrepancy between our value for $\Delta_f H^{\circ}_m(Na_2SO_3)$ and that of O'Hare *et al.* The two investigations cannot be compared directly, since O'Hare *et al.* used an acid solution (iodine dissolved in hydriodic acid) and we a neutral solution (iodine dissolved in hydriodic acid) and we a neutral solution (iodine dissolved in compared different for the same substances. Since, as remarked earlier, our value for $\Delta_f H^{\circ}_m(Na_2SO_3)$ is in good agreement with the value of the NBS, and moreover gives a consistent value for $\Delta_f H^{\circ}_m(TeO_2)$, we prefer our own value for $\Delta_f H^{\circ}_m(Na_2SO_3)$.

REFERENCES

- Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS tables of chemical thermodynamic properties. J. Phys. Chem. Ref. Data 1982, 11, Suppl. No. 2, p. 2–62, table 16.
- 2. Schneider, A.; Zintl, G. Z. Anorg. Allg. Chem. 1961, 308, 290.
- 3. Gadzhiev, S. N.; Sharifov, K. A. Izv. Akad. Nauk Azerb. SSR, Ser. Fiz. Mat. i Tekhn. Nauk 1962, No. 1, 47 (Chem. Abstr. 1962, 57, 4114).
- 4. Mixter, W. G. Am. J. Sci., Ser. 4 1910, 29, 488.
- 5. Schuhmann, R. J. Am. Chem. Soc. 1925, 47, 356.
- 6. Thomsen, J. Thermochemische Untersuchungen. Vol. 2. A. Barth: Leipzig. 1882, pp. 278, 405.
- 7. Muenow, D. W.; Hastie, J. W.; Hauge, R.; Bautista, R.; Margrave, J. L. Trans. Faraday Soc. 1969, 65, 3210.
- 8. Cordfunke, E. H. P.; Ouweltjes, W.; Prins, G. J. Chem. Thermodynamics 1975, 7, 1137.
- 9. Huber, Jr., E. J.; Holley, Jr., C. E. J. Chem. Thermodynamics 1969, 1, 267.

 $\Delta_{\rm f} H_{\rm m}^{\circ}({\rm TeO}_2, {\rm s})$

- 10. Glushko, V. P.; Gurvich, L. V.; Bergman, G. A.; Veits, I. V.; Medvedev, V. A.; Kachkuruzov, G. A.; Yungman, V. S. Termodinamicheskie Svoistva Individual'nykh Veshchestv. Vol. IV, 1. Nauka: Moskva. 1982, p. 347.
- Reference I, pp. 2-52, table 12.
 Vanderzee, C. E.; Sprengel, M. E. J. Chem. Thermodynamics 1983, 15, 869.
- 13. Reference 1, pp. 2-306, table 99.
- 14. Bigelow, M. J. J. Chem. Education 1969, 46, 378.
- 15. O'Hare, P. A. G. Argonne National Laboratory, U.S.A. Personal communication.
- 16. O'Hare, P. A. G.; Jensen, K. J.; Johnson, G. K. J. Chem. Thermodynamics 1986, 18, 765.

Note added in proof

Mallika and Sreedharan (J. Chem. Thermodynamics 1986, 18, 727) have measured the standard enthalpy of formation of $TeO_2(s)$, using an e.m.f. method. Their result, $\Delta_{\rm f} H_{\rm m}^{\circ}({\rm TeO}_2, \, {\rm s}, \, 298.15 \, {\rm K}) = -(321.1 \pm 1.3) \, {\rm kJ \cdot mol^{-1}}$, is in excellent agreement with our value.