Thermochimica Acta, 181 (1991) 337–339
Elsevier Science Publishers B.V., Amsterdam

Note

DETERMINATION OF THE THERMODYNAMIC PARAMETERS OF SOME SLIGHTLY SOLUBLE SELENITES

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(Received 4 September 1990)

With the rapid development of a number of new branches of industry such as electronics, telemechanics, the atomic industry and the industries of semiconductors and luminophores etc., selenium and its compounds have acquired an increasing importance from the practical and theoretical points of view. The compounds of four-valent selenium also have a variety of practical applications. The salts of selenious acid, the selenites, are used in the glass industry for colouring and discolouring of glass, in organic synthesis as catalysts and in analytical methods for the quantitative determination of many metal ions. They are the starting compounds from which pure selenides used as semiconductors and luminophores are obtained. The selenites are important intermediate products in the technology of the extraction and purification of selenium.

The thermodynamic parameters of selenites have not been sufficiently studied and this makes it impossible to determine their behaviour in chemical reactions of practical importance. The aim of this research is to determine the unknown thermodynamic data of some slightly soluble selenites.

Some of our previous papers contain data concerning the solubility products of a number of slightly soluble selenites at 25°C [1,2]. These as well as literature data [3–5] were used to calculate the standard isobaric potential, ΔZ_{298}. The values available in the literature concern the concentration solubility product and therefore should be corrected by the corresponding activity coefficients.

The standard isobaric potential of formation of the selenite of a given metal is the sum of the isobaric potential of formation of that selenite from its cations and anions and the isobaric potential of the ions in its saturated solution. If we designate the selenite as K_mA_n, the following equation is used to calculate the standard isobaric potential

$$\Delta Z_{298} = m\left(\Delta Z_{298}^{\ominus}\right)K^{n+} + n\left(\Delta Z_{298}^{\ominus}\right)A^{m-} + RT \ln K_s \qquad (1)$$

where K_s is the thermodynamic solubility product of K_mA_n at 25°C.

0040-6031/91/$03.50

TABLE 1

Data for calculating the standard isobaric potential of some selenites

Compound	Solubility product	Isobaric potential (kcal mol^{-1}) [6]	
		Cations	Anions
$CuSeO_3$	1.41×10^{-8}	+15.53	−89.33
Cu_2SeO_3	3.29×10^{-14}	+12.00	−89.33
Ag_2SeO_3	1.72×10^{-16}	(+18.43)×2	−89.33
$ZnSeO_3$	2.7×10^{-7}	−35.18	−89.33
$CdSeO_3$	9.33×10^{-9}	−18.58	−89.33
$HgSeO_3$	1.75×10^{-14}	+33.38	−89.33
Hg_2SeO_3	1.49×10^{-19}	+36.85	−89.33
$Al_2(SeO_3)_3$	7.86×10^{-32}	−117.59	−89.33
$Ga_2(SeO_3)_3$	6.65×10^{-38}	(−38.7)×2	(−89.33)×3
$In_2(SeO_3)_3$	7.70×10^{-40}	(−23.52)×2	(−89.33)×3
$Tl_2(SeO_3)_3$	2.02×10^{-47}	(+51.33)×2	(−89.33)×3
$Ge(SeO_3)_2$	3.38×10^{-26}		(−89.33)×2
$Sn(SeO_3)_2$	2.80×10^{-31}	+0.59	(−89.33)×2
$PbSeO_3$	3.121×10^{-13}	−5.81	−89.33
$BeSeO_3$	1.07×10^{-8}	−91.1	−89.33
$Fe_2(SeO_3)_3$	2×10^{-31}	(−1.08)×2	(−89.33)×3
$Th(SeO_3)_2$	1.35×10^{-20}	−175.00	(−89.33)×2
Co_2SeO_3	3.8×10^{-11}	−246.4	−89.33
$MnSeO_3$	1.2×10^{-7}	−53.4	−89.33
$Ce_2(SeO_3)_3$	3.7×10^{-29}	(−162.0)×2	(−89.33)×3

TABLE 2

Thermodynamic parameters of some slightly soluble selenites

Compound	$\Delta H^{\ominus}_{298}$ (kJ mol^{-1})	$S^{\ominus}_{298}$ (J mol^{-1})	$\Delta Z^{\ominus}_{298}$ (kJ mol^{-1})
$CuSeO_3$	392.7	253.2	353.8
Cu_2SeO_3			350.5
Ag_2SeO_3	341.2	315.9	309.7
$ZnSeO_3$	623.0	176.6	558.8
$CdSeO_3$	575.7	139.9	497.7
$HgSeO_3$	358.0	190.6	287.7
Hg_2SeO_3	2385		327.2
$Al_2(SeO_3)_3$			2284
$Ga_2(SeO_3)_3$			1658
$In_2(SeO_3)_3$	1794	320.3	1542
$Tl_2(SeO_3)_3$	534.3		958.8
$Ge(SeO_3)_2$			
$Sn(SeO_3)_2$	981.8		919.9
$PbSeO_3$	533.4	194.5	469.7
$BeSeO_3$	848.3	201.1	801.0
$Fe_2(SeO_3)_3$			1306
$Th(SeO_3)_2$	529.7	111.3	1594
			1465
$MnSeO_3$	694.6	189.8	637.1
$Ce_2(SeO_3)_3$			2641

In a number of cases, the values for $\Delta Z^{\ominus}_{298}$ of cations and anions are known with great accuracy. Therefore, the accuracy of the calculated value of the standard isobaric potential of the corresponding selenite depends on the error made in determining its solubility product. The initial data for calculating $\Delta Z^{\ominus}_{298}$ are given in Table 1, and the free energy values are shown in Table 2.

The data obtained here, together with the literature data [7] for the standard isobaric potential of formation of the selenites, were used to determine the heats of formation of the selenites and to calculate the absolute entropy of the crystalline selenites. The change in the entropy of reaction can be found by using the Gibbs–Helmholtz equation:

$$\Delta S^{\ominus}_{298} = \frac{\Delta H_{298} - \Delta Z^{\ominus}_{298}}{T} \qquad (2)$$

Using the values of absolute entropy of selenium, oxygen and the corresponding metal, the absolute entropy of the crystalline metal selenites was calculated. The lack of data concerning standard enthalpies of some of the selenites given in Table 2 did not allow us to calculate their enthalpy.

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