P 05384

24375

PDF

DIFFRACTION OF SELENIUM WITH SULFIDE SOLUTION AND OF SULFUR WITH SELENIDE SOLUTIONS

T. N. Greiver and I. G. Zaitseva

UDC 546.22

It is known that selenium dissolves in solutions of alkali and alkaline-earth sulfides to form compounds with mixed anions [1]. The solubility of selenium in sodium sulfide solutions is utilized in technology. For example, sodium sulfide is used for extraction of selenium from sludge by-products in the sulfuric acid and pulp and paper industries [2]. Several variants have been devised for smelting of dusts from lead-manufacturing plants with formation of polysulfide slags containing selenium, which are then subjected to further hydrometallurgical treatment [3, 4]. There are also other possibilities for effective utilization of the properties of solutions of sodium selenosulfides. This makes it all the more necessary to study the interaction of selenium with sodium sulfides and of sulfur with solutions of sodium selenides, as the information on the subject in the literature is very limited.

Table 1 contains data on the solubility of selenium in solutions of sodium mono- and polysulfides, and on the main reactions occurring in the dissolution process.

Selenium and sulfur were dissolved in the various solutions in closed flasks, agitated by magnetic stirrers. In order to avoid oxidation of the sulfides and selenides, the samples were withdrawn with the aid of rubber bulb in a mechanical sampling device through an inverted Schott funnel contained in the reaction flask. Control experiments were conducted in an atmosphere of technical nitrogen additionally treated with pyrogallol to remove oxygen.

Sodium sulfide of analytical grade, sulfur containing 99.9% S, and selenium containing 99.99% Se were used in the experiments.

The potentials were measured with an R-300 potentiometer with the aid of a platinum electrode, within ± 0.001 V. A saturated calomel electrode was used as the reference electrode.

The results show that selenium dissolves in mono-, di-, and trisulfide to form diselenosulfide when the solution is saturated with selenium.* The solubility of selenium in tetrasulfide is very limited. Dissolution of selenium is accompanied by color changes of the colorless sulfide and yellow polysulfides to intense red-brown, characteristic of polyselenide solutions.

Analogous color changes occur when elemental sulfur is introduced into colorless monoselenide solution. In this case a mixed anion and sodium monosulfide are formed first, by the reaction

$$2Se^{2-} + 2S = SSe_2^{2-} + S^{2-}. \tag{4}$$

On further addition of sulfur polysulfides appear. So long as mono-, di-, and trisulfides are present in the solution, selenium is not displaced by sulfur from the selenosulfide, as selenium is soluble in lower polysulfides with formation of tetrasulfide [see Table 1, reactions (2) and (3)]. Accordingly, the reaction when sulfur dissolves in monoselenide without displacement of selenium is

$$2Se^{2-} + 2S = SSe_2^{2-} + S_4^{2-}. \tag{5}$$

---

* Polysulfide solutions contain ions with different numbers of sulfur atoms simultaneously [5]. In this paper we describe solutions with average S/Na ratio of 2 as disulfides, with ratio of 3 as trisulfides, etc.

Leningrad Mining Institute. Translated from Zhurnal Prikladnoi Khimii, Vol. 40, No. 8, pp. 1683-1686, August, 1967. Original article submitted October 1, 1965.

TABLE 1. Dissolution of Selenium in Sodium Sulfide Solutions

Original sodium sulfide	Concentration		[Se (g-atom/liter)]/[Na_2S_n (mole/liter)] ratio	Average [Se (g-atom/liter)]/[Na_2S_n (mole/liter)] ratio	Presumed reactions between sulfides and selenium	Theoretical [Se (g-atom/liter)]/[Na_2S_n (mole/liter)] ratio
	sulfide (M)	dissolved selenium (g-atom per liter)				
Na_2S	0.96	2.22	2.30	2.05	$Na_2S + 2Se = Na_2SSe_2$ (1)	2.00
	1.09	1.82	1.67			
	1.46	3.00	2.05			
	1.46	3.20	2.20			
Na_2S_2	0.97	1.20	1.26	1.23	$3Na_2S_2 + 4Se = 2Na_2SSe_2 + Na_2S_4$ (2)	1.33
	0.98	1.22	1.25			
	0.99	1.17	1.20			
Na_2S_3	0.83	0.51	0.62	0.57	$3Na_2S_3 + 2Se = Na_2SSe_2 + Na_2S_4$ (3)	0.66
	0.92	0.51	0.56			
	0.96	0.50	0.52			
Na_2S_4	0.88	0.11	0.12	0.12	$4Na_2S_4 + 2Se = Na_2SSe_2 + 3Na_2S_5$	0.50
	1.23	0.11	0.09			
	1.40	0.22	0.15		$Na_2S_4 + 2Se = Na_2SSe_2 + 3S$	2.00

Addition of fresh portions of sulfur is accompanied by displacement of selenium from sodium selenosulfide by the reaction

$$SSe_2^{2-} + 3S = S_4^{2-} + 2Se. \qquad (6)$$

Further dissolution of sulfur merely leads to increased S/Na ratio.

The above suggestions are confirmed by the good agreement between experimental data (see Fig. 1, curves 2 and 4) and the theoretical curves (curves 1, 3) plotted in accordance with the equations for reactions (5) and (6) for solutions with different initial selenium contents. Complete precipitation of selenium cannot be achieved in practice, because equilibrium between polysulfide and diselenosulfide ions becomes established in the final solution.

If one starts with polyselenide solutions, then the following is to be expected (by analogy with the foregoing) when sulfur is introduced into them:

$$\begin{array}{rl} Na_2Se_n + S = Na_2SSe_2 + (n-2)\,Se & (7) \\ Na_2SSe_2 + 3S = Na_2S_4 + 3Se & (8) \\ \hline Na_2Se_n + 4S = Na_2S_4 + n\,Se & (9) \end{array}$$

Thus, it is possible to dissolve 1 mole of sulfur per mole of diselenide without displacement of selenium, while further additions of sulfur, as in the case of monoselenide solution, lead to precipitation of sulfur and formation of tetrasulfide. In original tri- and tetraselenide solutions dissolution of sulfur proceeds right from the start only by displacement of selenium from the diselenosulfide.

Figure 1 (on the right) shows the results of an experiment in which sulfur was introduced into sodium selenide solution saturated with selenium. Apart from the last few points, the experimental results fit satisfactorily on the theoretical straight line corresponding to the tetraselenide.

It is evident from the above that the same compound, Na_2SSe_2, is formed when selenium dissolves in solutions of sodium sulfides and when sulfur dissolves in solutions of sodium selenides. Some properties of aqueous solutions of this compound were investigated.

Diselenosulfide solutions are relatively stable. During prolonged contact with air they are slowly oxidized with formation of the gray crystalline form of elemental selenium.

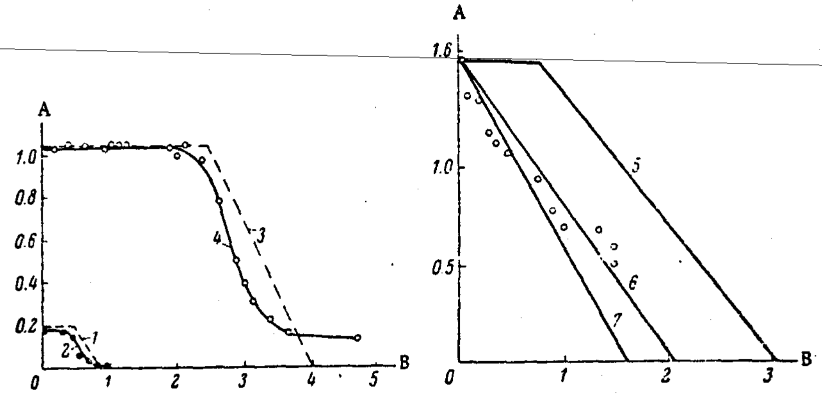

Fig. 1. Displacement of selenium by sulfur from sodium selenide solutions. A) Selenium concentration (g-atom/liter); B) sulfur concentration (g-atom/liter). 1-4) Monoselenide; 5-7) polyselenide. Curves: 1,3) theoretical, from Eqs. (5) and (6) respectively; 2,4) experimental; 5) Na_2Se_2 + 4S; 6) Na_2Se_3 + 4S; 7) Na_2Se_4 + 4S.

When air is passed through the solution, selenium is precipitated without any substantial separation of sulfur, which is oxidized predominantly to thiosulfate by the reaction

$$2Na_2SSe_2 + 2O_2 + H_2O = 2Se + Na_2S_2O_3 + 2NaOH. \tag{10}$$

In electrolysis of diselenosulfide solution the gray crystalline form of elemental selenium is formed at the anode; the selenium is deposited in a compact layer and rapidly makes the anode passive; separation of elemental sulfur was not observed.

When the solution is acidified, elemental sulfur is precipitated and hydrogen sulfide is evolved.

In each of the cases studied sulfur acts as an ion having a charge of —2, while selenium behaves like a neutral ligand which enters the complex anion and is liberated when the ion is decomposed. Grinberg [6] referred to the possibility of such a structure.

The change of free energy in formation of the SSe_2^{-2} ion can be approximately estimated from data on dissolution of selenium in polysulfides.

Since selenium dissolves only in mon-, di-, and trisulfide, the following inequality holds:

$$\Delta Z^0_{S_4^{2-}} < \Delta Z^0_{SSe_2^{2-}} < 3\Delta Z^0_{S_3^{2-}} - 2\Delta Z^0_{S_4^{2-}}.$$

Taking the values given by Maronny and Valensi [5] for $\Delta Z^0_{S_4^{-2}}$ and $\Delta Z^0_{SSe_2^{-2}}$ we have

$$16.6 < \Delta Z^0_{SSe_2^{2-}} < 20.6.$$

For refinement of this value, we measured the emf of the following cell at various Na_2SSe_2 concentrations:

$$Pt(Se) \mid Na_2SSe_2 \parallel KCl \mid Hg_2Cl_2 \mid Hg.$$

The standard potential of Se/SSe_2^{-2} was calculated from the results; it was found to be —0.383 V at t = 25°.

Assuming that the primary anode reaction is

$$SSe_2^{2-} = 2Se + S^* + 2\bar{e}, \tag{11}$$

we obtain the value ΔZ^0_{298}° = 17.6 kcal/mole for the SSe_2^{-2} ion; this fits into the range indicated above. Hence the instability constant of the complex SSe_2^{-2} anion is $10^{-3.2}$.

CONCLUSIONS

1. Selenium dissolves in sodium mono-, di-, and trisulfide to form the diselenosulfide Na_2SSe_2. The solubility of selenium in tetrasulfide is slight.

2. Dissolution of sulfur in sodium selenides is accompanied by primary formation of the diselenosulfide. Further additions of sulfur lead to displacement of selenium and formation of polysulfides.

3. The change of free energy in formation of the SSe_2^{-2} ion was found to be 17.6 kcal/mole.

LITERATURE CITED

1. J. W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Selenium. Longmans, London, 10 (1930).
2. B. F. Ostand and I. I. Kazarnovskii, Authors' certif. No. 15340, March 23, 1928.
3. Z. A. Serikov and V. G. Ageenkov, Izv. vuzov, Tsvet. metallurg., 5, 69 (1959).
4. Z. A. Serikov and S. M. Anisimov, Izv. vuzov, Tsvet. metallurg., 6, 65 (1960).
5. G. Maronny and G. Valensi, International Committee of Electrochemical Thermodynamics and Kinetics. Ninth Meeting, London, Butterworths Scientific Publications, 155 (1959).
6. A. A. Grinberg, Introduction to the Chemistry of Complex Compounds [in Russian], Izd. "Khimiya," Moscow—Leningrad (1966).