

THERMODYNAMIC EQUILIBRIA IN THE SYSTEMS S-H₂O, Se-H₂O, AND Te-H₂ IN THE 25-300°C TEMPERATURE RANGE AND THEIR GEOCHEMICAL INTERPRETATIONS*

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(ABSTRACT)

On the basis of the latest values of thermodynamic quantities of compounds in the systems S - H₂O, Se - H₂O, Te - H₂O and an improved method of their calculation at elevated temperatures, Eh - pH diagrams of the stability fields of various forms of sulfur, selenium and tellurium were plotted for 25, 150 and 300°C.

Comparative analysis of the diagrams shows that the separation of sulfur, selenium and tellurium in processes involving the participation of aqueous solutions may be determined by a change in the oxidation-reduction potential, acidity, and temperature of these solutions. The most significant of these factors is the oxidation-reduction potential of the medium. The maximum separation of sulfur, selenium and tellurium in hydrothermal processes should be observed under oxidation conditions at low temperatures and weakly alkaline values of the pH.

The authors are grateful to V. V. Shcherbina for a number of useful comments during his review of the paper. —Authors' summary

Sulfur, selenium and tellurium, which are elements of the 6b subgroup of the periodic system having similar chemical properties, display a close relationship to one another in natural processes. The concentration or dispersion of the rare elements selenium and tellurium largely depends on the behavior of their fairly commonly distributed analog, sulfur.

Along with their common geochemical properties, there are also certain differences in the behavior of sulfur, selenium and tellurium which separate these three elements, differences which contrast particularly in processes involving the participation of aqueous solutions.

In hypogenic mineral formation, selenium becomes dispersed mainly in sulfides, in which it replaces sulfur isomorphously, whereas tellurium more often separates in the form of its own minerals. Selenium and tellurium are characterized by accumulation at later stages of the hydrothermal process relative to sulfur. Whereas sulfides are formed under the most diverse temperature conditions, tellurides and especially selenides are comparatively low-temperature minerals. In the hypergene zone, in addition to a significant migration of sulfur, there is observed only a slight mobility of selenium and tellurium.

An important factor affecting the behavior of sulfur, selenium and tellurium under hypogenic and hypergenic conditions is the oxidation-reduction potential of the medium. Thus, selenium minerals, which practically

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do not occur in sulfide deposits, are frequently observed in hematite, carbonate and barite veins in associations formed under clearly oxidizing conditions. Studies published in the last few years indicate that tellurium has the "ability to accumulate in the presence of a high oxygen potential" [1, 2].

The influence of the change of the oxidation potential, temperature and acidity of solutions on the behavior of elements of variable valence is conveniently analyzed by means of Eh - pH diagrams.

The fields of stability of various forms of sulfur in Eh - pH coordinates were first examined by G. Valensi [3], who placed special emphasis on the identification of the relationships between stable and metastable forms of sulfur. Later, diagrams of the fields of stability of selenium in the Se - H₂O system [4] and tellurium in the Te - H₂O system [5] were published.

The Eh - pH diagrams calculated by metallurgists soon attracted the attention of geochemists. R. M. Garrels and C. P. Naeser [6] analyzed and further studied the diagram of the stability fields of sulfur. They showed that, of all the many forms of sulfur, only H₂S, HS⁻, HSO₄⁻, SO₄²⁻ and elemental sulfur play a substantial part under natural conditions, and of the others, only S²⁻ is present in concentrations slightly greater than 10⁻⁶. The authors came to the conclusion that native sulfur is formed under restricted conditions in natural processes and that sulfides are unstable in oxidizing conditions. The diagram of the stability fields of various forms of selenium in Eh - pH coordinates was examined from the geochemical point of view by R. G. Coleman and M. Delevaux [7] and also by N. D. Sindeyeva [8]. G. Thishendorf and H. Ungethum [9] carried out a comparative analysis of the diagrams of the stability fields of sulfur and selenium.

Many of the thermodynamic constants used in the above-mentioned studies [3 - 5, 9] for plotting Eh - pH diagrams of the stability fields of sulfur, selenium and tellurium have now largely become obsolescent. Thus, in particular, the magnitude of the free energy of formation of H₂Se_{aq} has been almost doubled, so that on the Eh - pH diagram of the stability fields of selenium, the selenide-elemental selenium boundary should pass above the line of stability of water instead of below it. Thus, W. M. Latimer's conclusion [10] that "soluble selenides are unstable with respect to the process of oxidation by

hydrogen ions" has turned out to be erroneous.

Until recently, the lack of necessary data on the thermodynamic properties of dissolved substances at elevated temperatures had not permitted the calculation of the Eh - pH diagram for conditions close to those of a hydrothermal process. The use for the temperature extrapolation of the Van't Hoff equation, by means of which certain authors (J. Verhoogen [11], H. L. Barunes and G. Kullerud [12], G. Thishendorf and H. Ungethum [9]) studied the influence of temperature on the position of the stability fields of the dissolved substances, may lead to substantial errors.

An accurate calculation of the free energy changes of the reactions requires the knowledge of the temperature dependence of the heat capacities of the dissolved substances (ions, neutral molecules) participating in the reactions. In the present study, the equation $\bar{C}_p^0 = bT$, where b is a constant and T is the temperature in °K, was used to press the temperature dependence of the heat capacity of the substances dissolved in water. In calculating coefficient b , standard values (at 298°K) of the partial molar heat capacity of the substances dissolved in water were used [14]. In cases where experimental values of \bar{C}_p^0 were lacking, they were estimated approximately by using empirical relations relating the partial molar heat capacities of the substances dissolved in water with their entropies at 298°K [14].

Table 1 shows values of the free energy of formation of ions from the elements at elevated temperatures, necessary for plotting the stability fields of various forms of sulfur, selenium and tellurium in Eh - pH coordinates. Table 2 lists values of the dissociation constants of acids (pK) in the systems S - H₂O, Se - H₂O, Te - H₂O at various temperatures, calculated from the equation

$$\log K = -\frac{A^*}{T} + D^* - C^*T. \quad (1)$$

Within the limits of experimental values, this equation adequately describes the temperature dependences of the dissociation constants of weak acids [13, 14]. The same table shows coefficients A*, D*, C*, calculated from the data of Table 1 by using the equations

$$A^* = \frac{2\Delta H^0 - \Delta C_p^0 T}{4.606R},$$

Table 1

Thermodynamic Constants of Substances Dissolved in Water
in the Systems S - H₂O, Se - H₂O, Te - H₂O

Component	ΔH_{298}°	S_{298}°	\bar{C}_p°	$b \cdot 10^3$	ΔG_f°		
					25° C	150° C	300° C
H ₂ S	-9.5 [43]	29.0	31.5 ²³	106	-6.66 [43]	-5.9	-6.4
HS ⁻	-4.2 [43]	15.0	-33.6 ²³	-113	2.88 [43]	7.1	15.2
S ²⁻	7.9 [43]	-3.5	-95.7 ²³	-321.0	20.5 [43]	28.6	45.8
HSO ₄ ⁻	-221.08 [43]	31.5	-17.0	-57.0	-180.69 [43]	-166.4	-146.5
SO ₄ ²⁻	-217.32 [43]	4.8	-71.6	-240.1	-177.97 [43]	-158.9	-129.5
H ₂ SO ₃	-153.2 [43]	55.5	43.0 ²³	144	-128.56 [43]	—	—
HSO ₃ ⁻	-149.67 [43]	33.4	-16.7 ²³	-56.0	-126.15 [43]	—	—
SO ₃ ²⁻	-151.9 [43]	-7.0	-64.1 ²³	-215.0	-116.3 [43]	-99.1	-72.7
H ₂ S ₂ O ₃	-144.45	57.9 ²⁴	41.3 ²³	139	-125.97 ⁰	—	—
HS ₂ O ₃ ⁻	-149.3	38.9 ²⁴	-20.3 ²³	-68.1	-125.15 ¹	—	—
S ₂ O ₃ ²⁻	-155.9 ²	8.9	-71.8 ²³	-241	-122.8 ²	-106.3	-79.6
H ₂ Se	4.6 ³	39.1	24.7 ²³	82.8	5.3 ³	5.3	4.4
HSe ⁻	3.8	19.0	-36.3 ²³	-121.7	10.5 ⁴	14.6	22.9
Se ²⁻	15.3	-11.0 ²⁴	-90.7 ²³	-304.41	30.9 ⁵	40.1	58.4
Se ₃ ²⁻	15.4	11.5	-76.4 ²³	-256.4	27.3 ⁶	32.3	50.6
H ₂ SeO ₃	-121.29 [43]	49.7	46.9 ²³	157.2	-101.87 ⁷	-94.3	-87.0
HSeO ₃ ⁻	-122.98 [43]	32.1	-15.8 ²³	-52.9	-98.30 ⁸	-87.0	-70.7
SeO ₃ ²⁻	-121.7 [43]	-1.7	-67.7 ²³	-227.0	-86.9 ⁹	-70.1	-43.5
HSeO ₄ ⁻	-137.7 ¹⁰	38.9	-20.3 ²³	-68.2	-107.76 ¹⁰	-94.0	-74.5
SeO ₄ ²⁻	-143.2 [43]	12.9	-77.4 ²³	-260.0	-105.5 [43]	-87.0	-58.5
SeO ₂ cryst (selenolite)	-53.86 [43]	12.2	—	—	-39.86	—	—
H ₂ Te	18.6	33.7 ²⁵	28.4 ²³	95.2	21.4 ¹¹	22.1	21.7
HTe ⁻	16.6	14.7 ²⁴	-33.4 ²³	-112	26.0 ¹²	29.7	38.4
Te ²⁻	24.2	-15.3 ²⁴	-87.8 ²³	-294.5	41.59 ¹³	51.5	70.1
Te ₃ ²⁻	27.2	15.4	-79.1	-256.2	38.97 ¹⁴	46.4	61.8
TeOOH ⁺	-75.6	13.5	12.0 ²³	40.2	61.4 ¹⁵	-55.6	-48.6
H ₂ TeO ₃	-132.6	52.2 ²⁴	45.2 ²³	151.6	-113.4 ¹⁶	-105.9	-98.9
HTeO ₃ ⁻	-133.0	33.2 ²⁴	-16.53 ²³	-55.4	-108.1 ¹⁷	-96.7	-80.6
TeO ₃ ²⁻	-127.3 [58]	3.2	-70.9 ²³	-237.9	-93.5 ¹⁸	-76.9	-50.9
H ₄ TeO ₆	282.5	84.3 ¹⁹	23.9 ²³	80.1	-232.4 ²⁰	-210.9	-184.3
H ₆ TeO ₆ ⁻	-276.7	68.5 ²⁴	-40.0 ²³	-134	-221.9 ²¹	-196.7	-161.3
H ₄ TeO ₆ ²⁻	-269.5	42.5 ²⁴	-97.1 ²³	-325.7	-206.9 ²²	-177.0	-131.9
TeO ₂ cryst (tellurite)	-76.9 [58]	14.0 [58]	15.3 [58]	—	-63.236	—	—
H O ₁	-68.315 [43]	16.71 [43]	17.995 [43]	—	-56.687	-52.02	-46.86

- From $pK = 0.60$ of the reaction $H_2S_2O_3 = HS_2O_3^- + H^+$ [44].
- From $pK = 1.72$ of the reaction $HS_2O_3 = S_2O_3^{2-} + H^+$ [44].
- From $\Delta H^{\circ} = -167.07$ kcal/mole of the reaction $S_2O_3^{2-} + 4Br_2(sol.) + 5H_2O = 2SO_4^{2-} + 8Br^- + 10H^+$ [45] and $pK = -1.86$ of the reaction $2Ag(c) + S_2O_3^{2-} = \alpha AgS + SO_3^{2-}$ [45].
- From $pB^{\circ} = 1.1$ and $\Delta H^{\circ} = -2.43$ kcal/mole of the process of dissolution of H_2Se_{gas} in water [46].
- From the average value from $pK = 3.73$ [47] and $pK = 3.89$ [48] of the reaction $H_2Se(sol.) = HSe(sol.) + H^+$.
- From $pK = 15.0$ of the reaction $HSe(sol.) = Se(sol.) + H^+$ [49].
- Obtained by method of comparative calculation from the correlation curve ΔG_{298}° of the ions S_2^{2-} , Se_2^{2-} , Te_2^{2-} as functions ΔG_{298}° of the gases H_2S , H_2Se , H_2Te .
- From $pK = 18.5$ of the reaction $Se(hex) + 2I_2(c) + 3H_2O = H_2SeO_3 + 4H^+ + 4I^-$ [50].
- From $pK = 2.62$ of the reaction $H_2SeO_3(sol.) = HSeO_3(sol.) + H^+$ [51].

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Table 1 (Continued)

9. From pK = 8.32 of the reaction $\text{HSeO}_3^-(\text{sol.}) = \text{SeO}_3^{2-}(\text{sol.}) + \text{H}^+$ [51].
10. From pK = 1.657 and $\Delta H_{298}^\circ = -5.57$ kcal/mole of the reaction $\text{HSeO}_4^-(\text{sol.}) = \text{SeO}_4^{2-} + \text{H}^+$ [25].
11. From $\Delta G^\circ = 1$ kcal/mole of the reaction $\text{H}_2\text{Te}(\text{g}) \rightarrow \text{H}_2\text{Te}(\text{sol.})$ [10].
12. From pK = 2.64 of the reaction $\text{H}_2\text{Te}(\text{sol.}) = \text{HTe}^-(\text{sol.}) + \text{H}^+$ [47].
13. From pK = 12.2 of the reaction $\text{HTe}^-(\text{sol.}) = \text{Te}^{2-}(\text{sol.}) + \text{H}^+$ [52].
14. From $E^\circ = -0.845$ V of the reaction $\text{Te}_2^{2-}/2\text{Te}(\text{c})$ [53].
15. From pK = 15.32 of the reaction $\text{TeO}_2(\text{c}) + \text{H}_2\text{O} = \text{HTeO}_2^+ + \text{OH}^-$ [54].
16. From pK = 10.5 of the reaction $\text{H}_2\text{TeO}_3(\text{sol.}) = \text{HTeO}_3^+ + \text{OH}^-$ [54].
17. From pK = 3.88 of the reaction $\text{H}_2\text{TeO}_3(\text{sol.}) = \text{HTeO}_3^- + \text{H}^+$ [54].
18. From $E^\circ = 0.412 \pm 0.007$ V of the reaction $\text{TeO}_3^{2-} + 3\text{H}_2\text{O}/\text{Te}(\text{c}) + 6\text{OH}^-$ [55].
19. From $\Delta S^\circ = 9.4$ e. u. (from the temperature dependence of pK) of the reaction $\text{TeO}_3(\text{c}) + 3\text{H}_2\text{O}(\text{l}) = \text{H}_6\text{TeO}_6(\text{sol.})$ [56].
20. From pK = 7.70 of the reaction $\text{H}_6\text{TeO}_6(\text{sol.}) = \text{H}_5\text{TeO}_6^-(\text{sol.}) + \text{H}^+$ [57].
21. From pK = 10.95 of the reaction $\text{H}_5\text{TeO}_6^- = \text{H}_4\text{TeO}_6^{2-} + \text{H}^+$ [57].
22. From $E^\circ = 0.4$ V of the reaction $\text{H}_4\text{TeO}_6^{2-}(\text{sol.})/\text{TeO}_3^{2-}(\text{sol.}) + 2\text{OH}^- + \text{H}_2\text{O}$ [10].
23. Values of C_p° were obtained from correlation equations relating the partial molar heat capacity and entropy of ions in solution [14]. The heat capacities of elemental sulfur, selenium and tellurium were taken from the handbook of Kelley and King [59].
24. The values of S° were calculated assuming ΔS° of the dissociation reactions of all the acids to be an average of 19 e. u. for the first step and 30 e. u. for the second step.
25. The value of S° was calculated assuming ΔS° of the reactions of dissolution of gases in water to be an average of 19 ± 3 e. u.

Table 2

Dissociation Constants of Acids (pK) in the Systems S - H₂O, Se - H₂O, Te - H₂O in the 25 - 300°C Temperature Range and Constants of Eq. (1)

Acid	T, °C							Constants of Eq. (1)			
	25	50	100	150	200	250	300	A°	D°	C°	
H ₂ S	pK ₁	6.94	6.69	6.50	6.70	7.05	7.6	8.2	3279	11.17	0.02386
	pK ₂	12.91	12.27	11.45	11.15	11.1	11.3	11.7	4668	9.53	0.02276
H ₂ SO ₃	pK ₁	1.78	2.06	2.72	3.49	4.30	5.2	6.1	1036	8.22	0.02188
	pK ₂	7.20	7.36	7.75	8.30	8.90	9.6	10.3	1057	1.53	0.01737
H ₂ S ₂ O ₃	pK ₁	0.60	0.92	1.65	2.5	3.4	4.3	5.3	947	9.31	0.02257
	pK ₂	1.72	2.13	2.98	3.8	4.7	5.6	6.5	235	4.70	0.01887
H ₂ SO ₄	pK ₂	1.99	2.33	3.07	3.85	4.70	5.5	6.5	633.6	6.10	0.02001
H ₂ Se	pK ₁	3.81	3.89	4.25	4.80	5.45	6.2	7.0	1809	8.92	0.02232
	pK ₂	15.0	14.3	13.6	13.2	13.1	13.3	13.5	4263	5.24	0.01978
H ₂ SeO ₃	pK ₁	2.61	2.74	3.20	3.80	4.50	5.4	6.2	1672	9.85	0.02296
	pK ₂	8.32	8.28	8.40	8.75	9.20	9.8	10.4	1969	3.95	0.01901
H ₂ SeO ₄	pK ₂	1.66	2.01	2.78	3.60	4.50	5.4	6.4	658.0	6.79	0.02093
H ₂ Te	pK ₁	2.64	2.80	3.30	3.90	4.65	5.5	6.4	1560	9.33	0.02261
	pK ₂	11.80	11.21	11.3	11.4	11.7	12.1	12.6	3444	5.33	0.01993
H ₂ TeO ₃	pK ₁	3.87	3.93	4.25	4.70	5.40	6.2	7.0	1932	9.353	0.02260
	pK ₂	10.70	10.42	10.15	10.20	10.50	10.9	11.4	3009	5.333	0.01994
H ₂ TeO ₄	pK ₁	7.72	7.41	7.2	7.3	7.6	8.1	8.8	3336	10.47	0.02338
	pK ₂	10.96	10.59	10.2	10.2	10.3	10.7	11.2	3442	6.86	0.02104

$$D^* = \frac{\Delta S^0 - \Delta C_p^0}{2.303R}, \quad C^* = \frac{\Delta C_p^0}{4.606RT},$$

where R is the gas constant.

As is evident from Fig. 1, a and b, the theoretically calculated dissociation constants of acids are in good agreement with those determined experimentally, indicating that the calculations made were reliable.

Figure 2 (a, b, c) shows diagrams of the stability fields of sulfur, selenium and tellurium at 25°C, P = 1 atm, $\Sigma S = 10^{-1}$; $\Sigma Se = 10^{-6}$ and $\Sigma Te = 10^{-7}$. Comparison of these Eh - pH diagrams explains certain characteristics of the behavior of sulfur, selenium and tellurium in low-temperature geochemical processes. Attention is drawn to the fact that the size of the fields of the elemental forms of selenium and tellurium surpasses the size of the fields of elemental sulfur. The field of elemental sulfur occupies a narrow area which rapidly shrinks toward lower pH values. In this connection, R. M. Garrels and C. P. Naeser correctly observed that the formation of native sulfur under natural conditions requires either low solution pH's or unusually high sulfur concentrations in the solutions.

The considerable size of the fields of elemental forms of selenium and tellurium indicate the variety of conditions in which native selenium and tellurium can form in nature. The literature frequently gives accounts of findings of native selenium [7, 8, 26, 27]. Native hypergenic tellurium has been described by P. Ramdor in deposits of Cripple Creek and Porcupine. The enrichment of covellite and quartz-sulfur "sypuchkas"* with tellurium in zones of secondary sulfide ores of Ural pyrite deposits is apparently due to the presence of native tellurium [28]. The scarcity of data on native tellurium in low-temperature formations is accounted for, in our view, not so much by the rarity of this form in nature [8], but by the difficulty of detecting native tellurium in hypergenic products.

As follows from the illustrated diagrams, native tellurium should oxidize at lower pH values of the medium than native selenium. The value of the oxidation potential of

Te \rightarrow Te⁴⁺ is anomalous in the series S, Se, Te, since the lowest oxidation potential of R \rightarrow R⁴⁺ is that of sulfur, and the highest that of selenium, and not that of tellurium. Apparently, this anomaly does indeed exist in nature. Thus, in the oxidation of artificial selenides and tellurides [29], cases were observed in which the maintained oxidation potential of the medium was insufficient to oxidize selenium and make it go into solution, but turned out to be favorable for the oxidation and dissolution of tellurium. Hence it is possible to postulate that under certain oxidizing conditions, tellurium should have a greater migration capacity than selenium. Studies of the distribution of selenium and tellurium in the oxidation zone of copper-pyrite deposits of southern Urals have shown that tellurium produces more substantial dispersion aureoles around oxidizing sulfite ores than does selenium [28].

In oxidation to the hexavalent state, the potential gradually increases from sulfur to tellurium, and on Eh - pH diagrams, the line separating tellurite from tellurate runs the highest. Oxidation of sulfur to sulfate occurs at the lowest pH values, so that its broad migration in the form of sulfate is observed under natural conditions [8, 30, 31].

On the Eh - pH diagrams of the stability fields of selenium and tellurium, the fields of the solid phases SeO₂ and TeO₂ cease to exist even at 25°C. This indicates that the deposition of selenite and tellurite under natural conditions requires higher concentrations of selenium and tellurium than 10⁻⁶ and 10⁻⁷ mole/kg of H₂O respectively.

Analysis of Eh - pH diagrams of sulfur, selenium and tellurium at 150, 300°C and pressures of 5 and 85 atm respectively (Fig. 2 d-i) shows that an increase in temperature leads to an expansion of the areas of stability of the less dissociated forms of sulfur, selenium and tellurium, this being due to the change of the dissociation constants of the acids (see Table 2). The field of TeOOH⁺ decreases (150°C), then disappears (300°C) on the diagram, so that there is less reason to consider TeOOH⁺ as one of the important forms of transport of tellurium under hydrothermal conditions [8]. There is just as little reason to consider the sulfite and thiosulfate forms as important forms of transport of sulfur, as was indicated earlier by V. V. Shcherbina [32].

*Editor's note: friable sand containing barite, quartz, or pyrite.

In order to evaluate the equilibrium concentrations of sulfite and thiosulfate forms of

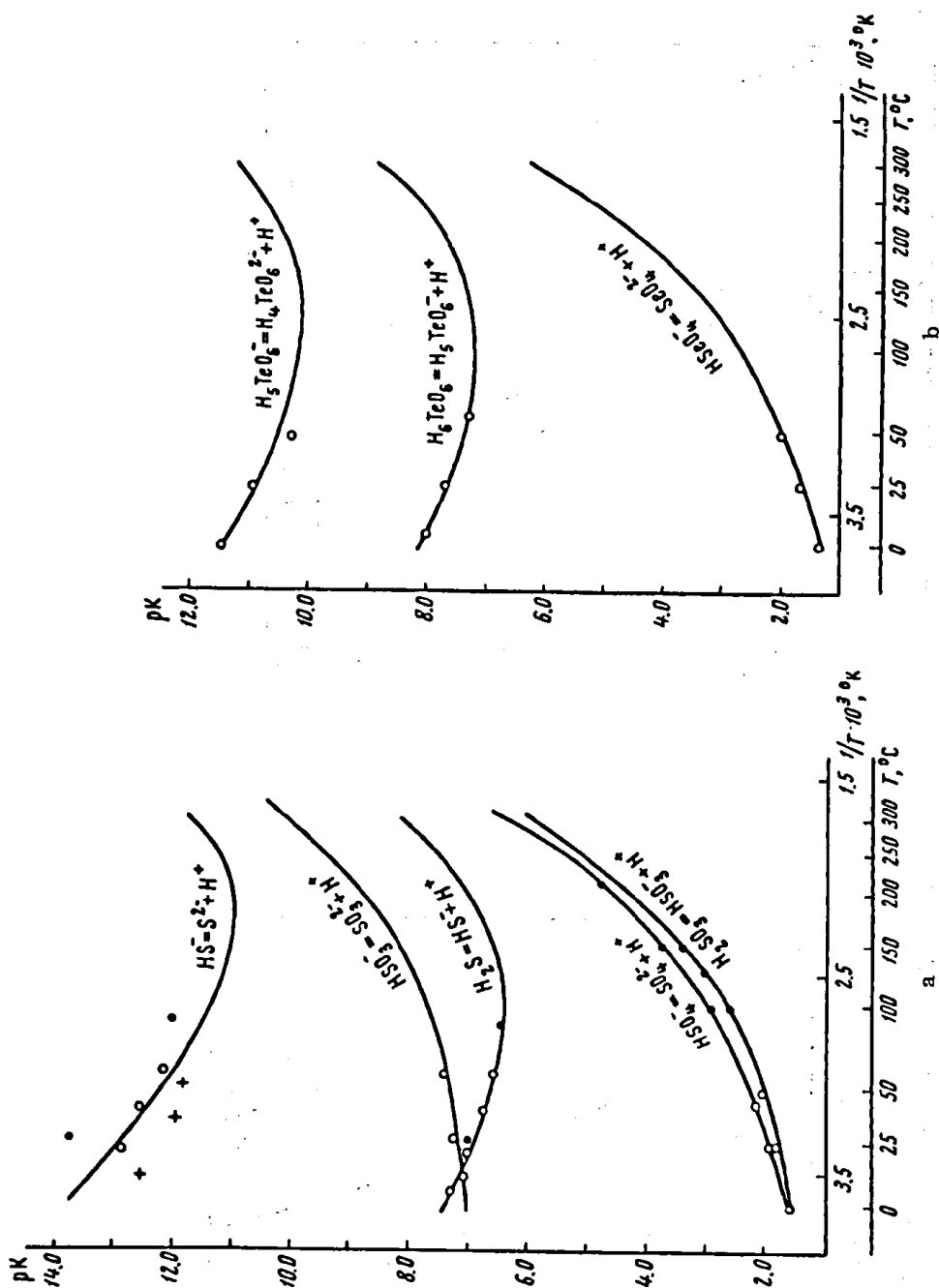
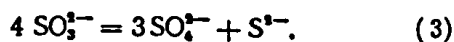
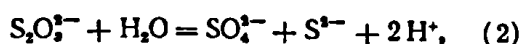


Fig. 1. Theoretical and experimentally determined temperature dependences of reaction constants.
 a) $HS^- = S^{2-} + H^+$ ●—experimental data of Ellis and Milestone [15]. O—experimental data of Zavodnov and Kryukov [16]. +—experimental data of Tumanova et al. [7]; $HSO_3^- = SO_3^{2-} + H^+$ O—experimental data of Arkhipova et al. [18]; $H_2S = HS^- + H^+$ O—experimental data of Wright and Maase [19]; ●—experimental data of Ellis and Milestone [15]; $HSO_4^- = SO_4^{2-} + H^+$ O—experimental data of Nair and Nancollas [20]; ●—experimental data of Ryzhenko [21]; $H_2SO_3 = HSO_3^- + H^+$ O—experimental data of Johnston and Leppla [22]; ●—experimental data of Ingruber [23]; b) $H_5TeO_6^- = H_4TeO_6^{2-} + H^+$ experimental data of Ellison et al. [24]; $H_6TeO_6 = H_5TeO_6^- + H^+$ experimental data of Ellison et al.; $HSeO_4^- = SeO_4^{2-} + H^+$ experimental data of Nair [25].

sulfur in solutions, we calculated the equilibrium constants of the disproportionation reactions of these forms of sulfur:



Calculation of the equilibrium concentrations $\Sigma S_{\text{sulfite}}$ and $\Sigma S_{\text{thiosulfate}}$ (taking into account the hydrolysis of SO_3^{2-} and $S_2O_3^{2-}$ ions), using the values of equilibrium constants of reactions (2) and (3) (Table 3),

has shown that the concentrations of these forms of sulfur in the range of temperatures, pH and Eh under consideration, are substantially lower than the concentration of its sulfide and sulfate forms; this causes the absence of stability fields of these forms of sulfur on the Eh - pH diagrams.

Experimental data show that at high temperatures, even the kinetic effect cannot introduce any substantial corrections into the expected theoretical concentrations. Thus, in experiments carried out by A. Pryor [33]

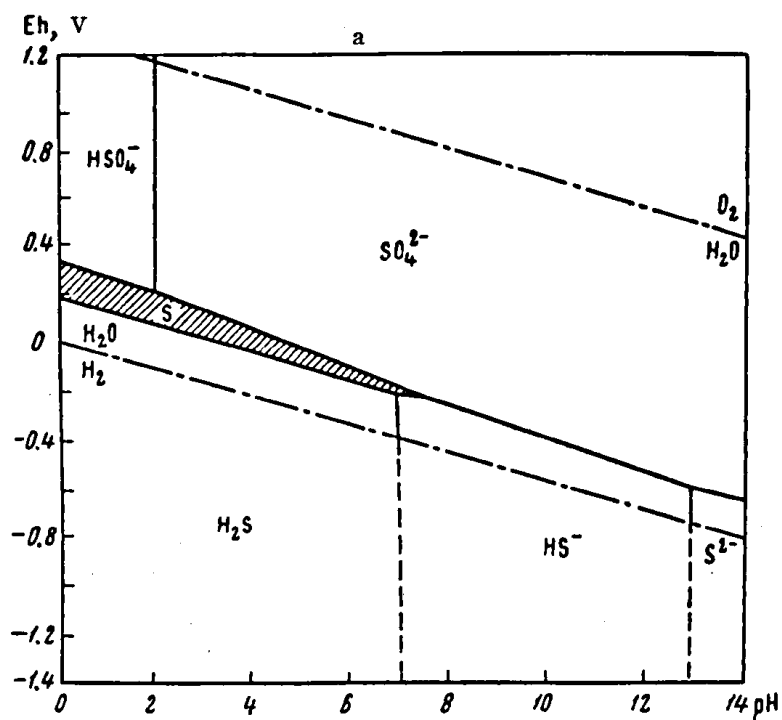


Fig. 2

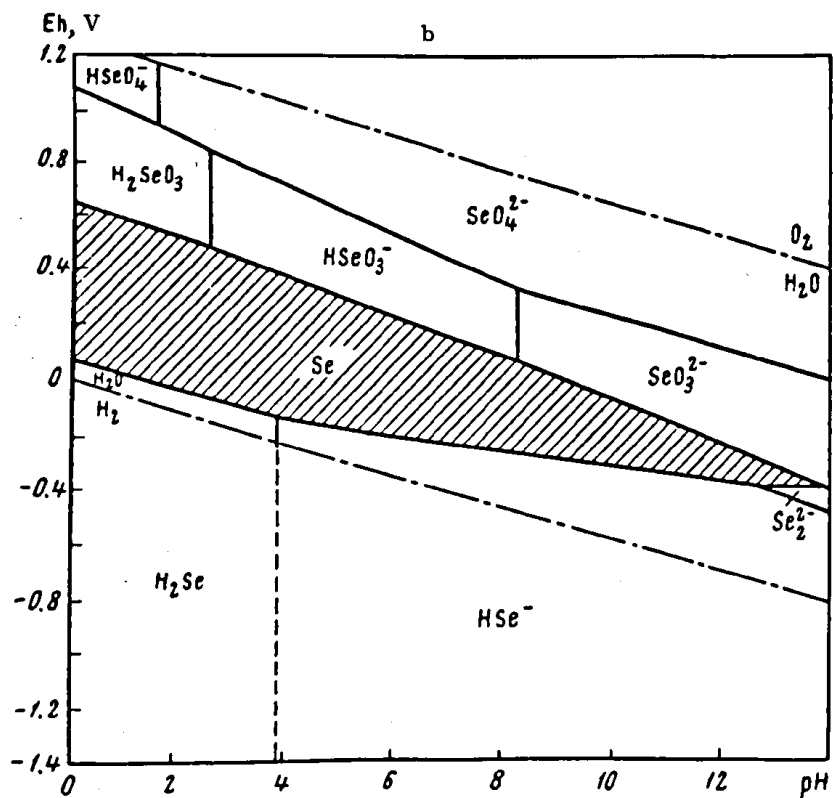


Fig. 2b

THERMODYNAMIC EQUILIBRIA IN THE SYSTEMS S - H₂O, Se - H₂O, AND Te - H₂O

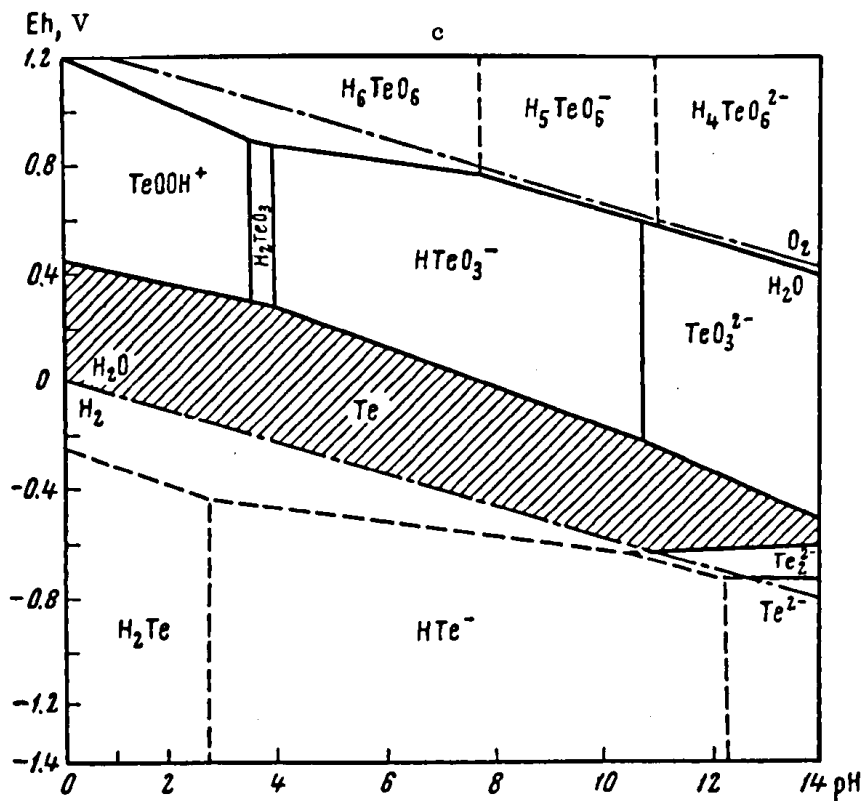


Fig. 2c

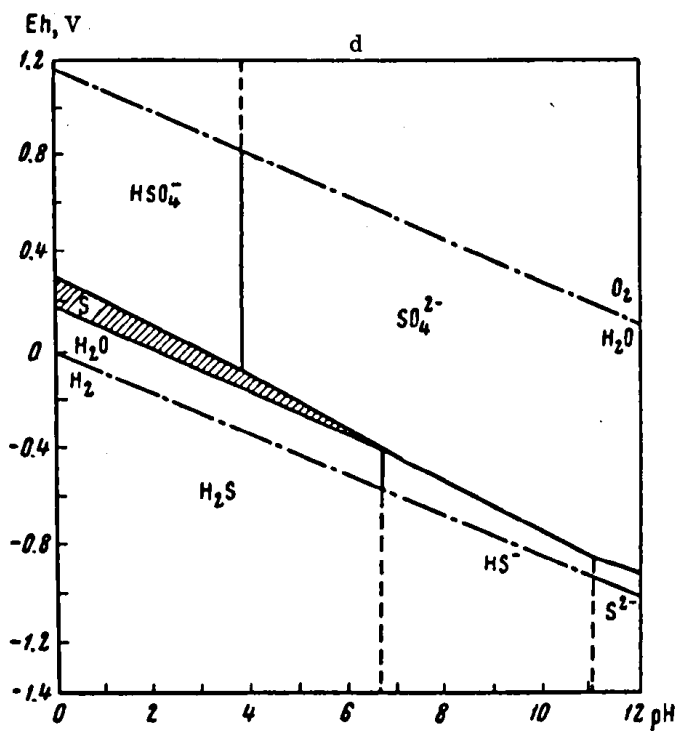


Fig. 2d

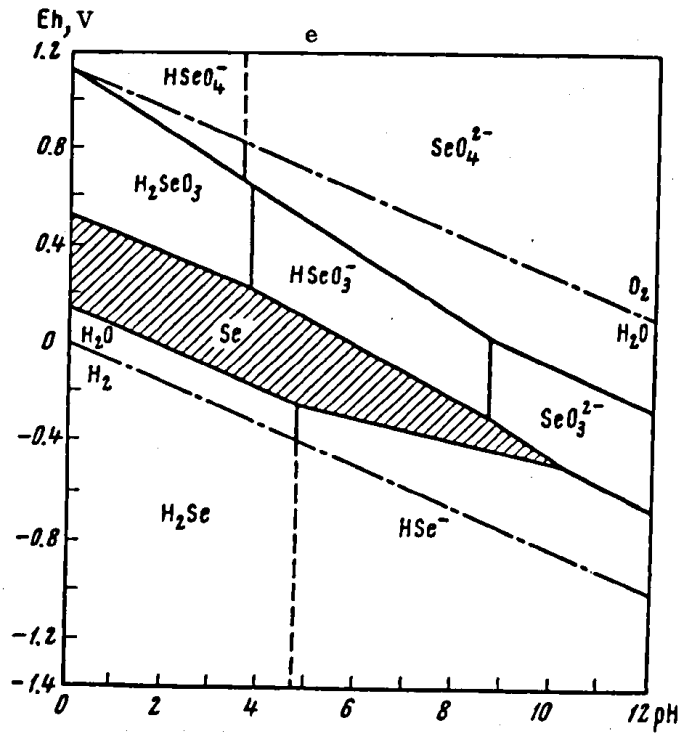


Fig. 2e

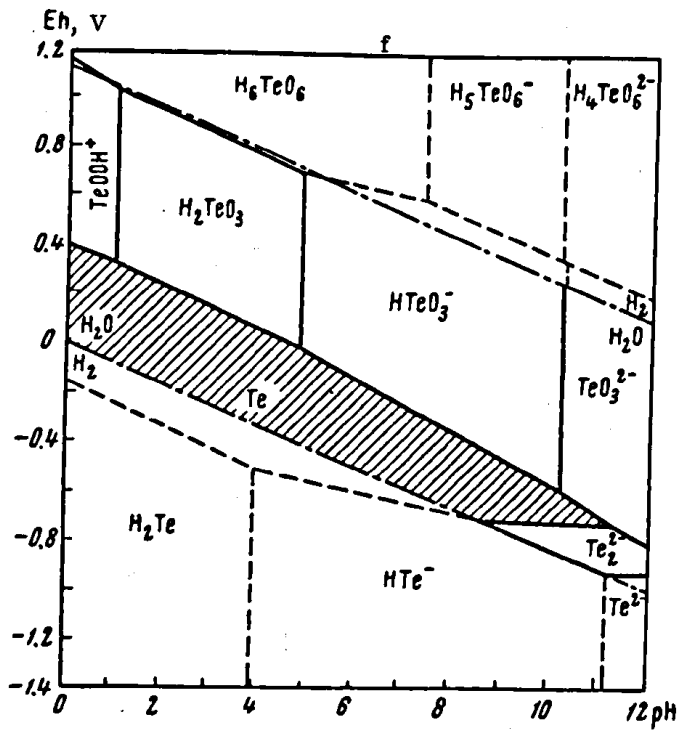


Fig. 2f

THERMODYNAMIC EQUILIBRIA IN THE SYSTEMS S - H₂O, Se - H₂O, AND Te - H₂O

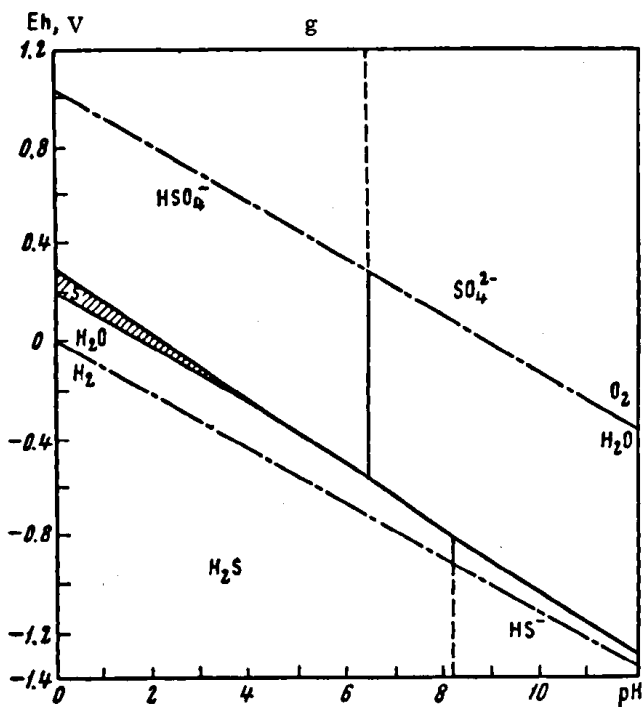


Fig. 2g

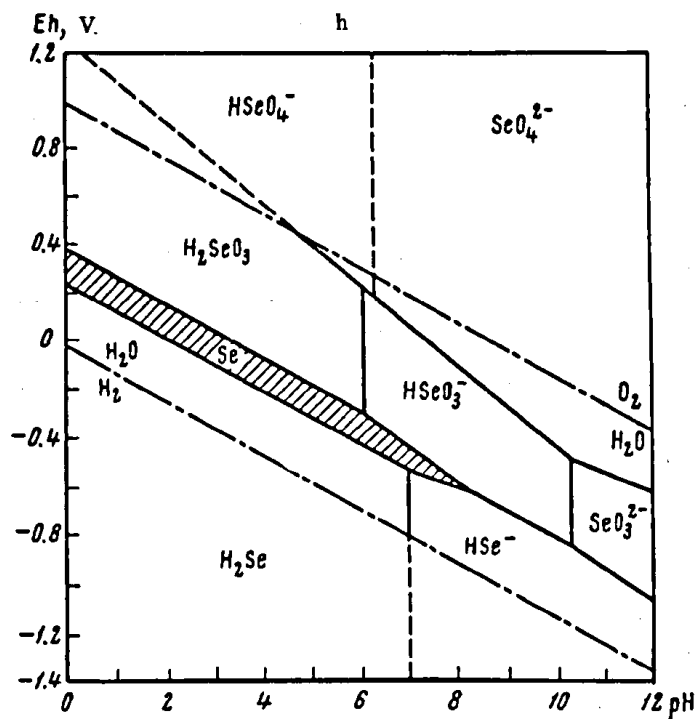


Fig. 2h

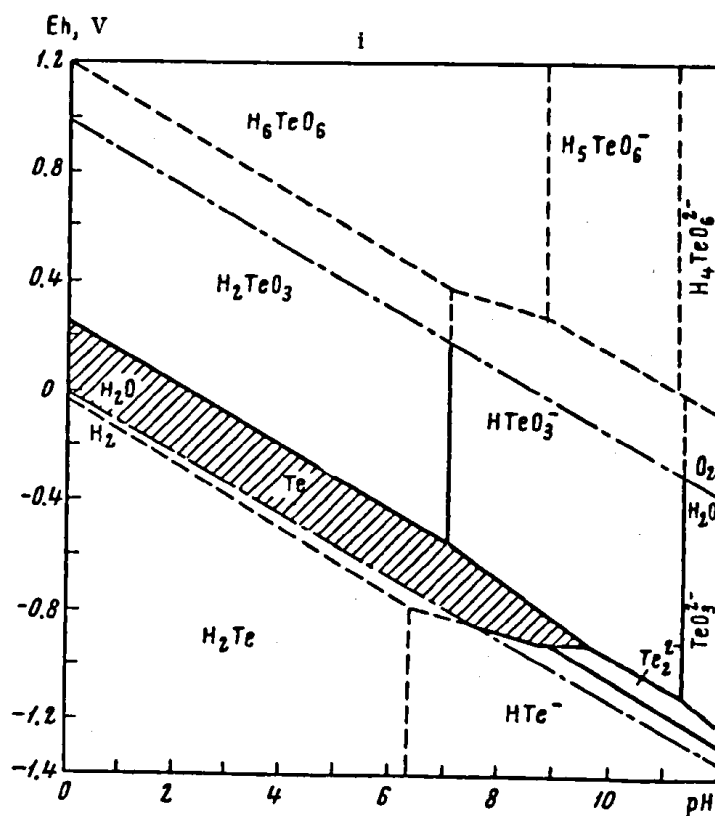


Fig. 2i

Fig. 2. Stability fields of various forms of sulfur (a, d, g), selenium (b, e, h) and tellurium (c, f, i) in the coordinates Eh - pH at $\Sigma S = 10^{-1}$, $\Sigma Se = 10^{-6}$ and $\Sigma Te = 10^{-7}$.

a, b, c) temperature 25°C, P = 1 atm; d, e, f) temperature 150°C, P = 5 atm; g, h, i) temperature 300°C, P = 85 atm.

Table 3

Equilibrium Constants (pK) of Reactions (2) and (3)

T, °C	25	50	100	150	200	250	300
$S_2O_3^{2-} + H_2O = SO_4^{2-} + S^{2-} + 2H^+$ pK	16.13	15.40	14.61	14.47	14.8	15.4	16.3
$4SO_3^{2-} = 3SO_4^{2-} + S^{2-}$ pK	-35.23	-33.12	-29.55	-26.6	-24.1	-21.8	-19.8

after heating a solution with 0.83 M $Na_2S_2O_3$ to 270°C (pH 6.00) for 8 hrs, 0.62 M sulfide, 0.76 M sulfate, 0.00 M sulfite, 0.01 M polysulfide-sulfur and 0.07 M thiosulfate were detected in this solution. Thus it was shown that at a higher temperature thiosulfate and sulfite are practically completely decomposed in a short period of time, producing sulfides and sulfates. It should be noted that extrapolation of the rate constant of thiosulfate decomposition

to lower temperatures for the purpose of showing the possibility of finding this form of sulfur in hydrothermal solutions from A. Pryor's data, as was done by N.G. Tyurin [34], is unreliable, since it is based on an experiment carried out in a very narrow temperature range.

On the Eh - pH diagrams of the stability fields of sulfur, as the temperature rises,

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the sulfide-sulfate boundary gradually approaches the limit of stability of water. This indicates a shift of the equilibrium toward oxidation of sulfide sulfur to sulfate sulfur as the temperature rises. Earlier, this effect was observed by B.N. Ryzhenko [35]. To better illustrate the influence of temperature on the sulfide-sulfate equilibrium, Fig. 3 shows a graph of the dependence of the hydrogen concentration necessary for maintaining this equilibrium at 25, 150 and 300°C. As is evident from the figure, with rising temperature at constant ratio $[\Sigma S_{\text{sulfates}}]/[\Sigma S_{\text{sulfides}}] = 1$, the hydrogen concentration increases by approximately 5 orders of magnitude at all the pH values taken.

As the temperature rises, the fields of the elemental forms of sulfur, selenium and tellurium decrease in size. At 300°C, only the field of elemental tellurium still retains a fairly impressive size. This is in agreement with the facts of the observation of native tellurium in hypergenic ores. Native tellurium was found in many deposits of the world: Kawatsu (Japan) [36], Colorado (USA) [37], Kadzharan [38], Bukuka [39], Zavodinskoye [40], Tyrny-Auz [41] in the USSR. The absence of native sulfur in hypergenic ores may restrict the expected acidity limits of hydrothermal solutions to some extent. Thus, on the Eh - pH diagram

of the stability fields of sulfur at 300°C, the field of elemental sulfur tapers off in the range of pH 5. As far as native selenium is concerned, the possibility of its occurrence in hypogenic ores is not excluded.

Since the deposition of sulfides, selenides and tellurides depends on the active concentration of the ions $[S^{2-}]$, $[Se^{2-}]$ and $[Te^{2-}]$ in the solutions and on their ratios, it was of interest to calculate the equilibrium reactions of these ions with other substances in the systems S - H₂O, Se - H₂O and Te - H₂O, and then to examine the ratios $[Se^{2-}]/[S^{2-}]$ and $[Te^{2-}]/[S^{2-}]$. The calculations showed that at high Eh values, independently of temperature, the highest activities in solution are retained by the Se^{2-} ion, lower ones by Te^{2-} , and still lower ones by S^{2-} . Since the solubility products of selenides and tellurides are similar, and that of sulfides is much greater (Table 4), the following order of deposition of minerals can be established with decreasing oxidation-reduction potential of the medium: selenides-tellurides-sulfides.

As shown by observations of the natural pyrogeneses of minerals, in contrast to selenides, tellurides do not display any particular confinement to oxidized associations, but are found under relatively varied conditions. In the formation of tellurides, of

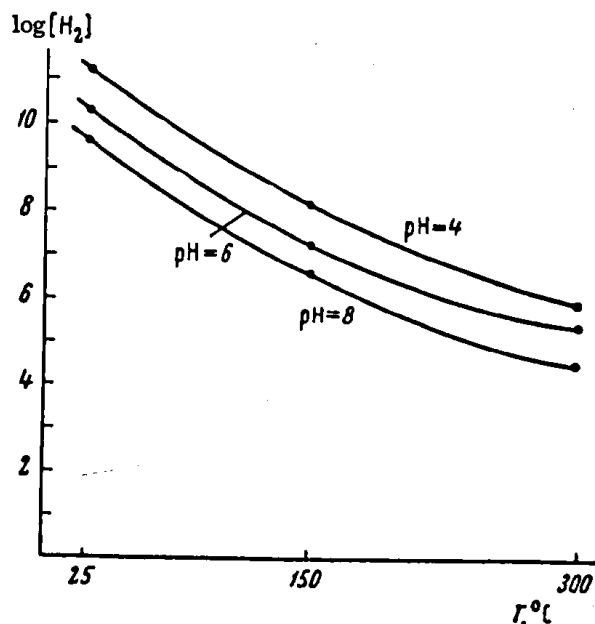


Fig. 3. Dependence of hydrogen concentration in solution on the temperature and pH with $\Sigma S_{\text{sulfates}} = \Sigma S_{\text{sulfides}}$.

Table 4

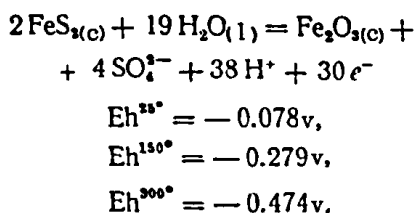
Solubility Products of Certain Sulfides, Selenides and Tellurides at 25, 150 and 300°C

Compounds	SP values			Compounds	SP values		
	25° C	150° C	300° C		25° C	150° C	300° C
PbS (galena)	28.07	22.6	22.2	ZnS (sphalerite)	24.50	21.3	21.9
PbSe (clausthalite)	38.30	30.5	28.7	ZnSe (stilleite)	27.74	24.5	25.0
PbTe (altaite)	38.60	31.1	29.2	ZnTe	25.87	22.9	23.4
Ag ₂ S	49.20	36.3	30.8	CdS (greenockite)	21.70	22.8	22.9
Ag ₂ Se	60.70	45.0	37.7	CdSe (cadmoselite)	35.10	23.9	28.4
Ag ₂ Te	64.00	47.2	39.2	CdTe	34.40	28.9	28.1

*The solubility products were calculated by the authors by the method mentioned earlier [13, 14].

great significance is the limited extent of the isomorphism of tellurium and sulfur, and for this reason the influence of the oxidation-reduction factor manifests itself much less.

The illustrated graphs (Fig. 4a and b) show the dependence of the ratios $[Se^{2-}]/[S^{2-}]$ and $[Te^{2-}]/[S^{2-}]$ on the temperature at various Eh values, with pH = 6. The ratios $[Se^{2-}]/[S^{2-}]$ and $[Te^{2-}]/[S^{2-}]$ used to plot curve I were calculated at Eh values corresponding to the oxidation-reduction potential of the equilibrium reaction hematite-pyrite of 25, 150 and 300°C



The Eh values at which curves II and III were plotted were taken 0.1 V higher and 0.1 V lower respectively, and thus characterize the ratios $[Se^{2-}]/[S^{2-}]$ and $[Te^{2-}]/[S^{2-}]$ under oxidation and reduction conditions relative to the hematite-pyrite equilibrium.

As is evident from these graphs, the ratios $[Se^{2-}]/[S^{2-}]$ and $[Te^{2-}]/[S^{2-}]$ under oxidation conditions substantially exceed those for reduction conditions. The influence of temperature on the ratios $[Se^{2-}]/[S^{2-}]$ and $[Te^{2-}]/[S^{2-}]$ is manifested in the fact that under oxidation conditions these ratios decrease with rising temperature, while they

increase under reduction conditions. Thus, in the deposition of selenides and tellurides under oxidation conditions, other parameters being equal, low temperature conditions should be more favorable. In the formation of sulfides under reduction conditions, the higher temperature sulfides should contain larger amounts of selenium and tellurium. The frequently observed accumulation of selenium and tellurium relative to sulfur toward the end of the hydrothermal process should be attributed to an increase in the oxidation-reduction potential rather than to a decrease of the solution temperature. A study of the behavior of selenium in the process of ore formation in pyrite-polymetallic deposits of alkali type [42] has shown that, indeed, the highest concentrations of selenium in sulfides correspond to the crystallization interval characterized by a rise of the oxidation potential of the medium and manifested in a change of the sphalerite-chalcopyrite association to the galena-sphalerite and barite-galena associations with hematite, barite and sulfo salts.

The effect of pH on the magnitude of the ratios $[Se^{2-}]/[S^{2-}]$ and $[Te^{2-}]/[S^{2-}]$ at 25°C is shown on the graphs of Fig. 5, a and b. At 150 and 300°, the peaks on curves I, II and III are slightly displaced toward higher pH values under oxidation conditions and toward lower pH values under reduction conditions. On the whole, however, the dependence of the ratios of the selenide and telluride ions to the sulfide ion on pH is manifested to a much lesser extent than the dependence on the oxidation-reduction potential.

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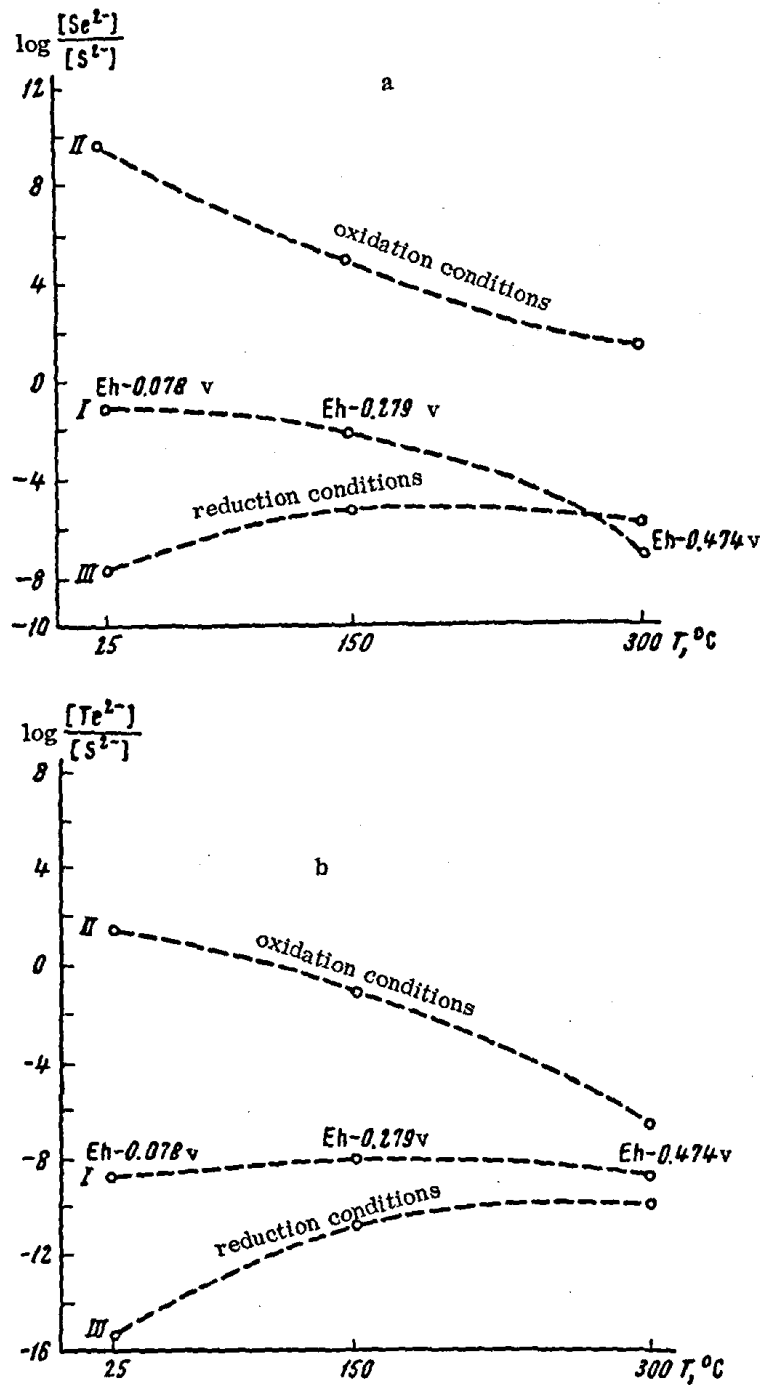


Fig. 4. Graphs of the temperature dependence of the ratio of the concentration of selenium (a) and tellurium (b) to the concentration of sulfur in the solution.

pH 6, $\Sigma S = 10^{-1}$, $\Sigma Se = 10^{-6}$, $\Sigma Te = 10^{-7}$.

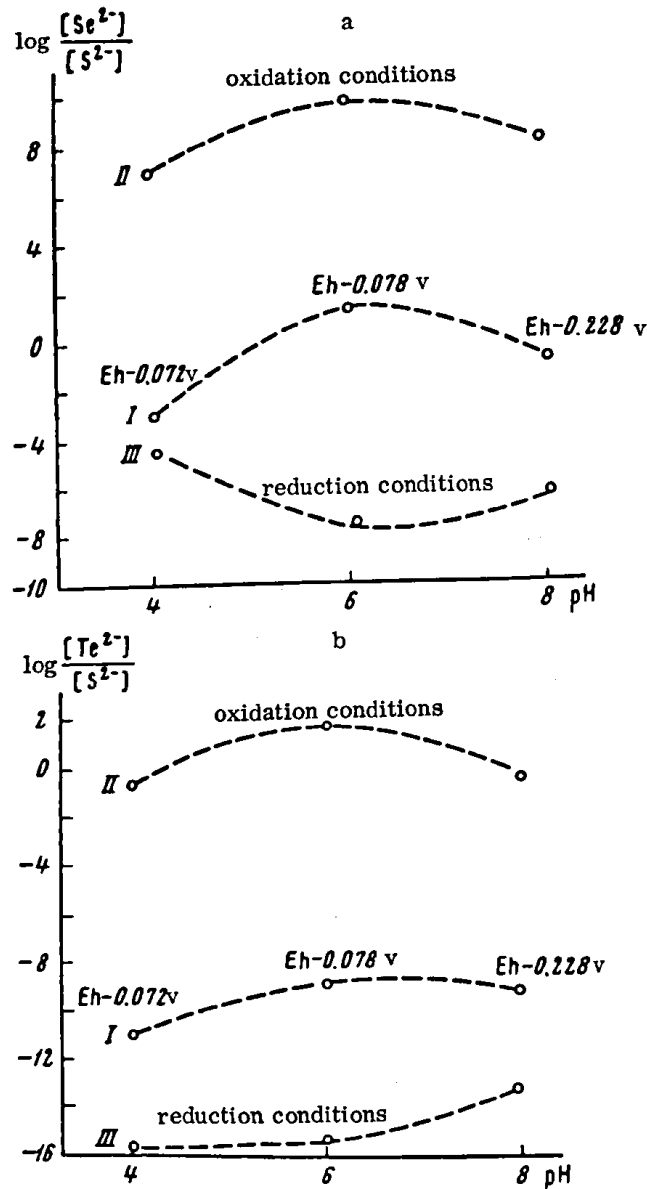


Fig. 5. Graphs of the pH dependence of the ratios of concentrations of selenium (a) and tellurium (b) to the concentration of sulfur at various Eh values.

$t = 25^{\circ}C$, $\Sigma S = 10^{-1}$, $\Sigma Se = 10^{-6}$, $\Sigma Te = 10^{-7}$.

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