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ORIGINAL PAPER

Thermodynamic study of the Ag-Tl-Se system using the EMF method with AG_4RbI_5 as a solid electrolyte

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Abstract

The Ag-Tl-Se ternary system in the composition region Ag_2Se-Tl_2Se-Se was studied in the temperature range 300–450 K by measuring the electromotive force (EMF) in a concentration cell containing a silver electrode and Ag_4RbI_5 as a solid electrolyte. A previously constructed solid-phase equilibria diagram of this system that included the ternary compounds AgTlSe, Ag_3TlSe_2, and Ag_7TlSe_4 was confirmed. The EMF measurements allowed the partial molar functions $\left(\Delta\overline{G}, \Delta\overline{H}, \Delta\overline{S}\right)$ of silver in some phase regions of the Ag_2Se-Tl_2Se-Se subsystem to be calculated. Using the solid-phase equilibria diagram, the potential-forming reactions were defined and the standard thermodynamic functions of formation and the standard entropy values of the ternary compounds mentioned above were calculated. Besides experimental results, data reported in the literature for thermodynamic functions of TlSe as well as the standard entropy values of silver and selenium were used in the calculations. The results of the calculations were compared with relevant data in the literature. The results confirmed that it is possible to study the thermodynamics of silver-containing complex systems using this modified EMF method, even if the system contains a more electropositive component than silver.

Keywords Silver-thallium selenides · EMF method · Thermodynamic functions · Solid electrolyte · Ag_4RbI_5

Introduction

Solid superionic conductors have been studied extensively in recent years due to their useful functional properties. These materials possess conductance arising from their ionic nature, so they are used in electrochemical sensors and as electrodes or electrolyte materials in devices for the electrochemical conversion of energy, including solid-state batteries, displays, high-temperature fuel cells, and so on [1–4].

The discovery of solid electrolytes with purely ionic conductivity has encouraged the use of the electromotive force (EMF) method in thermodynamic studies [4–8]. However, when used with a liquid electrolyte, the EMF method has limitations relating to the occurrence of side processes. In contrast to this, the conductivity of a solid electrolyte originates from the presence of ions of a single element with a strictly defined charge, which means that the charge on the potential-forming ions in equilibrium with the electrodes of the concentration cell is consistent and stable. Moreover, the solid electrolyte selectively transfers ions of a single type and thus essentially plays the role of a membrane that separates the two electrodes, preventing the occurrence of many side processes arising from interactions between the electrolyte and electrodes and between the electrodes via the electrolyte [7].

The study of superionic conductors started in the late nineteenth century. In 1914, Carl Tubandt and Erich Lorenz reported on the extraordinary properties of α-AgI [5, 9]. They proved that almost all of the mobile charge carriers in silver iodide are Ag^+ ions, whereas the I^- anions are practically immobile. α-AgI is the prototypical representative of conducting solid Ag^+ electrolytes, and is considered to be the fastest known ion conductor. This phase possesses high purely ionic conductivity (~1 Ω^{-1} cm^{-1}) in the temperature range 420–828 K. Attempts to obtain highly conductive AgI at lower temperatures led to the discovery of the compound

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Ag_4RbI_5 [10]. Ag_4RbI_5 melts at 505 K in a peritectic reaction, but below 300 K it decomposes in a solid-phase reaction [10]. Below its melting temperature, Ag_4RbI_5 presents high Ag^+ ion conductivity (according to various studies, σ = 0.2–0.3 Ω^{-1} cm^{-1}) and negligible electronic conductivity (about 10^{-9} Ω^{-1} cm^{-1}) [1–3]. This permits the use of Ag_4RbI_5 in thermodynamic studies of silver-based phases from room temperature to 505 K [7, 8, 11–16].

Complex silver chalcogenides are promising functional materials that possess photoelectric, thermoelectric, optical, and other properties [17–21]. In particular, some of these compounds show mixed ion–electron conductivity, leading to fundamentally new effects that significantly expand the range of possible applications of complex silver chalcogenides in comparison with materials with purely ionic or electronic conductivity [22, 23].

Experimental phase diagrams and reliable thermodynamic data are crucial to the development of modern preparative methods and the controlled synthesis of novel complex silver chalcogenides and phases based on them.

Phase equilibria in the Ag-Tl-Se system were studied in [24, 25]. In [24], a *T-x* diagram of the Ag_2Se-Tl_2Se quasi-binary system was constructed, while in [25] a complete *T-x-y* phase diagram of the Ag-Tl-Se system is presented. This system is characterized by the formation of three ternary compounds: AgTlSe, Ag_3TlSe_2, and Ag_7TlSe_4. The first compound melts congruently at 688 K, whereas the other two melt through decomposition in peritectic reactions at 663 and 699 K, respectively. Another ternary compound, $AgTlSe_2$, was found in this system in [26], but its presence was not confirmed in [25].

The results of a study [27] of the quasi-binary system Ag_2Se-Tl_2Se using the EMF method in the temperature range 350–493 K showed that the ternary compounds present in this system have the compositions $8Ag_2Se\cdot9Tl_2Se$ (instead of AgTlSe), Ag_3TlSe_2, and $17Ag_2Se\cdot3Tl_2Se$ (instead of Ag_7TlSe_4), although no crystallographic data confirming those conclusions were presented in that work. Crystallographic data for thallium-silver selenides were, however, provided in [28, 29].

The authors of [25] also determined the partial molar thermodynamic functions of thallium as well as the standard integral thermodynamic functions of the compounds AgTlSe, Ag_3TlSe_2, and Ag_7TlSe_4 using the EMF method with a liquid electrolyte. In [30], the specific heat of AgTlSe was measured between 1 and 50 K, and the Debye temperature (140 K) was determined.

The present paper reports the results of a study of the solid-phase equilibria in the Ag_2Se-Tl_2Se-Se subsystem and the thermodynamic properties of silver-thallium selenides as determined by the EMF method using Ag_4RbI_5 as a solid electrolyte.

Experimental

The following concentration cell was assembled for the EMF measurements of the Ag_2Se-Tl_2Se-Se subsystem:

$$(-)\ Ag(s)/Ag_4RbI_5(s)/(Ag\ \textit{in alloy})(s)(+) \qquad (1)$$

The superionic conductor Ag_4RbI_5 that was used as the solid electrolyte was synthesized from chemically pure RbI and AgI according to the technique described in [7, 8]. Briefly, a stoichiometric mixture of the iodides was heated to 600 K in a vacuum-sealed (~10^{-2} Pa) silica ampoule and then rapidly cooled to room temperature. The melt crystallized upon cooling into a fine-grained texture. Subsequent annealing at 400 K within 200 h resulted in complete homogenization of the Ag_4RbI_5. Pellets with thicknesses of 4–6 mm were then cut from the resulting cylindrical ingot (diameter ~8 mm), and those pellets were polished on a rotating lap. The pellets prepared in this way were used as the solid electrolyte in type (1) cells.

Metallic silver was used for the left (negative) electrode, while pre-synthesized and annealed alloys of the investigated system served as the right (positive) electrode.

In the present work, we used high-purity elements (not less than 99.999% pure). The synthesis of Ag_2Se and Tl_2Se was carried out in evacuated quartz ampoules at a temperature 20–30 K higher than the melting point of the synthesized compound. Taking into account the high vapor pressure of elemental selenium at the temperature applied during the synthesis of Ag_2Se, this synthesis was performed in an inclined two-zone furnace, with the hot zone kept at 1200 K and the cold zone at about 900 K (lower than the boiling point of selenium, i.e., 958 K [31]). After most of the selenium had reacted, the ampoule was relocated to the hot zone and then slowly cooled to 1100 K. Finally, homogeneous stoichiometric Ag_2Se was obtained by quenching the ampoule from this temperature in cold water [25].

Ag_2Se and Tl_2Se as well as elemental selenium were used to prepare the alloys of the Ag_2Se-Tl_2Se-Se subsystem (1 g each). The melting temperatures were chosen based on the phase diagram [25].

Considering that the electrode alloys should be as close as possible to the equilibrium state, the as-cast alloys were carefully powdered in an agate mortar, pressed into a pellet, and annealed at 500 K (1000 h) and 400 K (300 h).

The purity of the synthesized compounds Ag_2Se and Tl_2Se was monitored by DTA (using a 404 F1 Pegasus differential scanning calorimeter from NETZSCH, Selb, Germany) and XRD (using a D8 ADVANCE powder diffractometer from Bruker, Karlsruhe, Germany; CuK_α radiation was employed with $2\theta = 10$–$70°$). According to the DTA data, Tl_2Se melted congruently at 663 K while Ag_2Se underwent a polymorphic transition at 400 K and melted congruently at 1170 K; these values are in accordance with corresponding values reported in the literature [32]. The formation of single-phase Tl_2Se and Ag_2Se was verified from the XRD powder patterns. The calculated lattice parameters of Tl_2Se and Ag_2Se were $a = 8.5231(5)$, $c = 12.683(2)$, $z = 10$ (tetragonal, $P4/ncc$) and $a = 4.3327(3)$, $b = 7.0624(5)$, $c = 7.7644(5)$, $z = 4$ (orthorhombic, $P212121$), which are consistent with relevant data in the literature [33]. The phase compositions of the alloys of the Ag_2Se-Tl_2Se-Se subsystem were also found to correlate well with the solid-phase equilibria diagram [25].

In order to prepare the appropriate electrodes, the annealed alloys were ground into fine powder and pressed into cylindrical pellets (diameter ~8 mm, thickness ~4mm) under a pressure of ~0.1 GPa.

The electrochemical cell (described in detail elsewhere [7, 14]) was assembled, vacuumized, filled with argon, and placed in a tubular furnace. The cell was kept at ~380 K for 40–50 h. The initial equilibrium EMF was then measured, and the EMF was re-measured 4–5 h after reaching the desired temperature. Equilibrium was assumed to have been attained when the EMF values were constant or varied nonsignificantly (<0.2 mV), regardless of the direction of temperature change for repeated measurements at a given temperature. In order to eliminate the thermopower contribution, all contacts and leads were kept at the same temperature.

The EMF was measured using a high-impedance (10 GΩ) digital voltmeter (B7-34A). Most measurements were performed when heating and cooling the cell in steps ranging from 1 to 10 K. Chromel-alumel thermocouples and mercury thermometers with an accuracy of about ±0.5 K were used to measure the temperature of the electrochemical cell. The chromel-alumel thermocouples were calibrated in the temperature interval 300–510 K using elemental Ga, S, In, and Sn as reference materials.

The EMF measurements were performed in the temperature range 300–450 K. The upper limit of the temperature interval for the EMF measurements was selected so as to ensure that the phase composition remained constant during the experiment. The reversibility of the assembled concentration cells and the reproducibility of the results were monitored by checking the masses of and the XRD data for the electrodes before and after the measurements. The compositions and masses of the electrodes were found to remain constant during the experiment.

Results and discussion

The results from the EMF measurements of type (1) cells were in accordance with the solid-phase equilibria diagram of the Ag-Tl-Se system [25]; see Fig. 1. At a particular temperature, different three-phase regions show different EMFs, but the EMF remains constant in each three-phase region regardless of the alloy composition. For example, the EMF changes by 15 mV at the boundary between the $TlSe$-Ag_3TlSe_2-Ag_7TlSe_4 and the $TlSe$-Ag_7TlSe_4-Se three-phase regions at 400 K (Fig. 1). The measured EMF satisfies the known thermodynamic requirements, i.e., that the EMF does not decrease in the direction radiating away from the Ag corner of the concentration triangle [6–8].

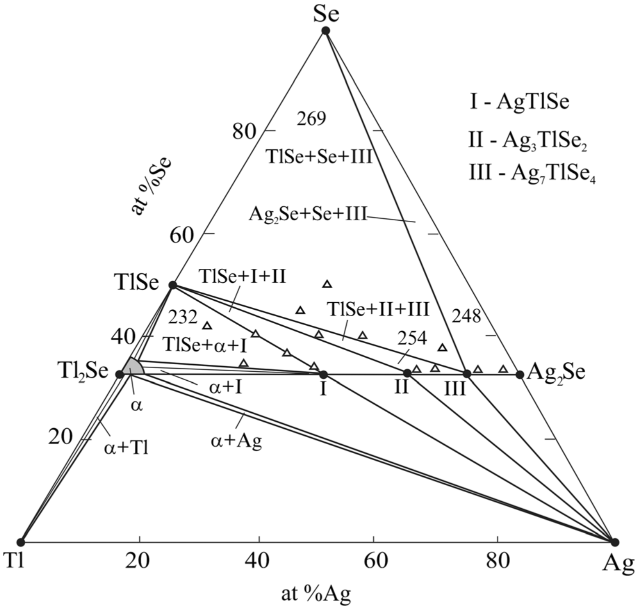

Fig. 1 Solid-phase equilibria diagram for the Ag-Tl-Se system [25]. *Triangles* mark the investigated alloy compositions for electrodes of type (1) cells. The EMF (mV) values at 400 K are shown in some three-phase regions

The EMF measurements for alloys from the TlSe-AgTlSe, $TlSe$-Ag_3TlSe_2-Ag_7TlSe_4, and $TlSe$-Ag_7TlSe_4-Se phase regions were used for thermodynamic calculations. The analysis showed that the EMF is linearly dependent on the temperature for various alloys of the Ag_2Se-Tl_2Se-Se subsystem. Experimentally obtained $E(T)$ data for the investigated alloys are shown in Fig. 2. This confirms the constancy of the phase compositions of the electrode alloys in the temperature range used for EMF measurements [6–8]. The experimental data $E(T)$ were analyzed using the least squares method assuming a linear dependence of the EMF on the temperature, and the results were expressed as recommended in the literature [6] as

$$E = a + bT \pm t\left[\frac{S_E^2}{n} + \frac{S_E^2\left(T - \overline{T}\right)^2}{\sum\left(T_i - \overline{T}\right)^2}\right]^{\frac{1}{2}}, \qquad (2)$$

where n is the number of pairs of E and T values, S_E is the error variance of the EMF readings, T is the mean absolute temperature, and t is the result of Student's test. At a confidence level of 95% and with $n \geq 20$, $t \leq 2$. The experimental data for T_i and E_i and data associated with the steps involved in this calculation for the phase region TlSe-AgTlSe are presented in

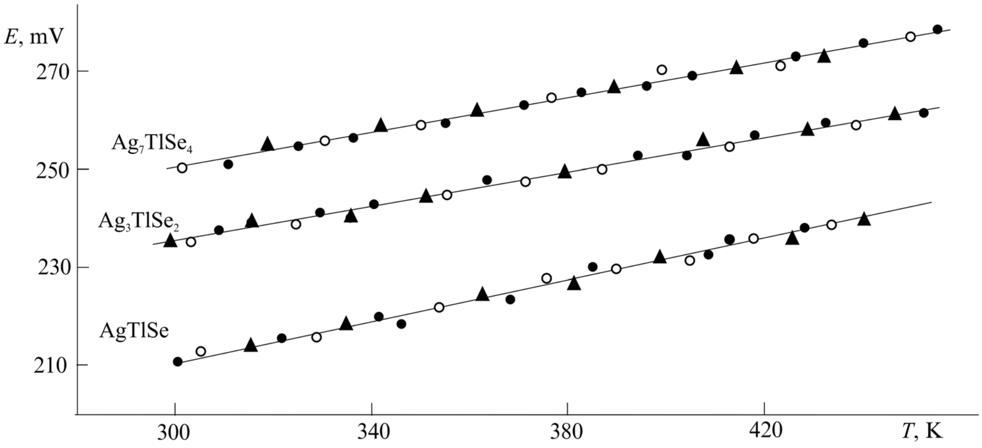

Fig. 2 Linear relationships between the EMF and the temperature for various alloys of the Ag-Tl-Se system

Table 1. The values of a, b, S_E^2, and $\overline{T}$ in the linear equation for this phase region (see Table 2) were calculated via Table 1. Other equations were obtained in a similar way.

Using the type (2) equations shown in Table 2 and the following thermodynamic expressions:

$$\Delta\overline{G}_{\mathrm{Ag}} = -zFE \tag{3}$$

$$\Delta\overline{S}_{\mathrm{Ag}} = zF\left(\frac{\partial E}{\partial T}\right)_P = zFb \tag{4}$$

$$\Delta\overline{H}_{\mathrm{Ag}} = -zF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] = -zFa, \tag{5}$$

the partial molar functions of silver in the alloys at 298 K were calculated (in the equations, z is the charge on the potential-forming cation Ag$^+$, F is Faraday's number, and a and b are constants). The results are displayed in Table 3.

According to the solid-phase equilibria diagram (Fig. 2), the values of the partial molar functions of silver in the three-phase regions are the thermodynamic characteristics of the

Table 1 Experimentally obtained data for T_i and E_i and data associated with the calculation steps for the phase region TlSe-AgTlSe of the Ag-Tl-Se system

T_i, K	E_i, mV	$T_i - \overline{T}$	$E_i(T_i - \overline{T})$	$(T_i - \overline{T})^2$	$\tilde{E}$	$E_i - \tilde{E}$	$(E_i - \tilde{E})^2$
301	211.4	−73.43	−15,522.05	5391.23	211.27	0.13	0.02
306.2	213.1	−68.23	−14,538.75	4654.65	212.33	0.77	0.59
315	213.9	−59.43	−12,711.01	3531.33	214.13	−0.23	0.05
322.2	216.2	−52.23	−11,291.05	2727.45	215.59	0.61	0.37
328.9	215.8	−45.53	−9824.30	2072.53	216.96	−1.16	1.34
334.3	218	−40.13	−8747.25	1610.02	218.06	−0.06	0.00
342.5	220.2	−31.93	−7029.89	1019.21	219.73	0.47	0.22
345.3	218.5	−29.13	−6363.81	848.27	220.30	−1.80	3.23
354.1	222.1	−20.33	−4514.18	413.11	222.09	0.01	0.00
362.6	224.5	−11.83	−2654.71	139.83	223.82	0.68	0.46
367.8	223.6	−6.63	−1481.35	43.89	224.88	−1.28	1.64
375.7	227.4	1.27	289.93	1.63	226.49	0.91	0.83
381.4	226.6	6.97	1580.53	48.65	227.65	−1.05	1.10
385.1	230	10.68	2455.25	113.96	228.40	1.60	2.55
390.3	229.9	15.88	3649.66	252.02	229.46	0.44	0.19
399.4	232.3	24.98	5801.69	623.75	231.32	0.98	0.97
404.6	231.5	30.18	6985.51	910.53	232.38	−0.88	0.77
408.3	232.7	33.88	7882.71	1147.52	233.13	−0.43	0.18
413.5	235.5	39.08	9202.16	1526.86	234.19	1.31	1.72
417.8	235.3	43.38	10,206.14	1881.39	235.06	0.24	0.06
425.7	235.5	51.28	12,075.26	2629.13	236.67	−1.17	1.38
428.6	237.8	54.18	12,882.82	2934.93	237.26	0.54	0.29
434.5	238.7	60.08	14,339.90	3609.01	238.47	0.23	0.06
441.4	239	66.98	16,007.03	4485.65	239.87	−0.87	0.76
$\overline{T} =$ 374.43	$\overline{E} =$ 226.23		$\sum E(T_i - \overline{T})$ = 8680.27	$\sum(T_i - \overline{T})^2$ =42,616.51			$\sum(E_i - \tilde{E})^2$ =18.76

Table 2 Relationships between the EMF and the temperature for type (1) cells with electrodes containing alloys of the Ag-Tl-Se system in the temperature range 300–450 K

Phase region	E (in mV) = $a + bT \pm 2S_E(T)$
AgTlSe + TlSe	$149.97 + 0.204T \pm 2\left[\frac{0.78}{24} + 1.83 \times 10^{-5}(T{-}374.4)^2\right]^{1/2}$
$Ag_7TlSe_4 + Ag_3TlSe_2$ + TlSe	$181.46 + 0.182T \pm 2\left[\frac{0.92}{24} + 1.85 \times 10^{-5}(T{-}375.5)^2\right]^{1/2}$
Ag_7TlSe_4 + TlSe + Se	$197.73 + 0.177T \pm 2\left[\frac{0.8}{24} + 1.71 \times 10^{-5}(T{-}374.6)^2\right]^{1/2}$

Table 3 Relative partial thermodynamic functions of silver in the alloys of the Ag-Tl-Se system at 298 K

Phase area	$-\Delta\overline{G}_{Ag}$ (kJ mol^{-1})	$-\Delta\overline{H}_{Ag}$	$\Delta\overline{S}_{Ag}$ J (K^{-1} mol^{-1})
AgTlSe + TlSe	20.33 ± 0.07	14.47 ± 0.31	19.65 ± 0.83
$Ag_7TlSe_4 + Ag_3TlSe_2$ + TlSe	22.74 ± 0.07	17.51 ± 0.31	17.57 ± 0.83
Ag_7TlSe_4 + TlSe + Se	24.18 ± 0.07	19.08 ± 0.30	17.12 ± 0.80

following potential-forming reactions (all substances considered here are crystalline):

$$Ag + TlSe = AgTlSe \quad (6)$$

$$Ag + \frac{1}{7}TlSe + \frac{3}{7}\ Se = \frac{1}{7}Ag_7TlSe_4 \quad (7)$$

$$Ag + 0.5Ag_7TlSe_4 + TlSe = 1.5Ag_3TlSe_2 \quad (8)$$

Reactions 6–8 allowed us to calculate the standard thermodynamic functions of formation and the standard entropy values of the ternary phases. For example, the calculations for AgTlSe (reaction 6) were based on the following relations:

$$\Delta G^{\circ}_{AgTlSe} = \Delta\overline{G}_{Ag} + \Delta G^{\circ}_{TlSe}$$
$$\Delta H^{\circ}_{AgTlSe} = \Delta\overline{H}_{Ag} + \Delta H^{\circ}_{TlSe}$$
$$S^{\circ}_{AgTlSe} = \Delta\overline{S}_{Ag} + S^{\circ}_{Ag} + S^{\circ}_{TlSe}$$

The standard integral thermodynamic functions for other ternary compounds (Table 4) were calculated in a similar way.

For the calculations, as well as our own experimental data (Table 4), we used thermodynamic data for TlSe (Table 4) [34] and standard entropy values for silver (42.55 ± 0.13 J mol^{-1} K^{-1}) and selenium (42.13 ± 2.09 J mol^{-1} K^{-1}) [35, 36] obtained from the literature. In all cases, the estimated standard deviations were calculated as the accumulation of errors.

Table 4 Standard integral thermodynamic functions of silver-thallium selenides

Compound	$-\Delta_f G^{\circ}(298K)$ kJ mol^{-1}	$-\Delta_f H^{\circ}(298K)$	$S^{\circ}(298K)$ J K^{-1} mol^{-1}	Ref.
TlSe	60.1 ± 0.1	61.0 ± 0.5	103.4 ± 1.8	[34]
AgTlSe	83.4 ± 0.2	75.5 ± 0.8	165 ± 2.8	This work
	82.4 ± 0.5	75.8 ± 1.8	176.9 ± 7.7	[25]
Ag_3TlSe_2	131.7 ± 0.3	117.2 ± 1.4	282.7 ± 4.6	This work
	133.3 ± 0.9	116.8 ± 3.2	292.2 ± 14.1	[25]
Ag_7TlSe_4	229.4 ± 0.6	194.6 ± 2.6	647.5 ± 14.6	This work
	234.8 ± 1.9	198.3 ± 6.7	652.9 ± 27.9	[25]

Table 4 also summarizes the thermodynamic functions and standard entropies for AgTlSe, Ag_3TlSe_2, and Ag_7TlSe_4 obtained from EMF measurements of concentration cells with a liquid electrolyte and a thallium electrode [25].

Our data are in good accord with the results of [25] (within error limits). It should be noted that the two sets of thermodynamic data recorded in that work were obtained by experimentally determining the partial thermodynamic functions of various components (Ag and Tl) of the Ag-Tl-Se system from potential-forming reactions in which silver selenide Ag_2Se participated, while thallium monoselenide participated in potential-forming reactions 6–8 in the present work.

The good agreement between the results reported in [25] and our data as well as the accuracy of the experimental data for the partial thermodynamic functions of silver and thallium imply that the literature data for thallium [34] and silver selenides [37] used in our calculations are also relatively accurate.

Conclusion

In this experimental study, the new complex of the thermodynamic data for ternary compounds AgTlSe, Ag_3TlSe_2, and Ag_7TlSe_4 was obtained using the EMF method with a solid Ag^+ electrolyte. These data are in good agreement with each other and with a diagram of solid-phase equilibria of the Ag-Tl-Se system. The resulting data also are in good agreement with previously attained data generated using the classical EMF method (i.e., measurements of concentration cells utilizing a thallium electrode, the most active component of the system). Our results indicate that it should be possible to apply the EMF method with a solid Ag^+ electrolyte to systems containing a component that is less noble than silver (in our case, thallium).

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