Saturated Vapor Pressure of Tellurium and Sulfur over Their Melts

**Abstract**: Saturated sulfur vapor pressure over its melts with tellurium was determined using the boiling point method and represented by temperature-concentration dependences for alloys containing 0 – 45 at. % S (100 – 55 at. % Te) and 45 – 100 at. % S (55 – 0 at. % Te). Due to a large difference in saturated vapor pressure values of sulfur and tellurium, the total pressure over melts was taken equal to the partial pressure of sulfur. The partial vapor pressure of tellurium was determined for the specified concentration ranges by numerical integration of the Gibbs-Duhem equation with the mean error of 9.69 %. Based on the total vapor pressure, the boiling points for tellurium-sulfur system were determined, and the boundaries for liquid melts on the temperature-dependent phase diagram were identified: the liquidus curve is below, and the boiling temperature curve is above. The system demonstrates an alternating-sign deviation of activities from the ideal solutions rule, where the negative deviation is in the area of alloys rich in tellurium and the positive is in the area of solutions rich in sulfur (> 50 at. %). The dependence of the total vapor pressure of selenium and tellurium on the composition shows no extrema in the area of liquid solutions, indicating that there is no constant boiling mixture, i.e. an azeotrope. Taking this fact and the large difference in the vapor pressure of the components into account, we see no technological difficulties in the system separation into elements by distillation.

**Keywords**: sulfur, tellurium, vapor pressure, concentration, melt, state diagram, liquidus, boiling point, activity, distillation

**Introduction**: Distillation technologies of chalcogen (sulfur, selenium and tellurium) purification face the problem of isolating one of the elements in pure form in the presence of the other two. When obtaining high-purity elements, the elements are distributed by derivative products. Prior to the present studies, there was no explanation for the technological difficulties in the distillation refining of one of the chalcogenes. Previously, we found that this is due to the narrow temperature range of coexistence of the melt and the vapor in the binary selenium-sulfur system [1, 2] and due to the existence of an azeotrope in the case of tellurium-selenium system [3, 4]. In spite of our attempts, no similar study of the tellurium-sulfur system was found in the literature.

In the theory of the distillatory refining of element, it is important to determine the melt-vapor phase transition boundaries on the basis of experimental vapor pressure of elements, which is the reason for the present study of the tellurium-sulfur system.

**Experimental part. Results and discussion**: The tellurium-sulfur system is represented by an eutectic-type diagram having a limited region of solid solutions [5]. Eutectic temperature is 109 °C with a sulfur content of 98.6 at. %. The change of the temperature of the liquidus curve from tellurium to sulfur is about 100 °C in the concentration range 0 - 80 at. % S with a sharp decrease to the eutectic point for melts containing more than 80 at. % S, indicating that the state of melts is close to aliquation.

Taking into account tellurium melting (449.57 °C [5]) and sulfur boiling temperatures (429 °C [2]) at atmospheric pressure, a narrow temperature range of the existence of liquid alloys is expected, that was taken into consideration when choosing the range (of temperatures) in experiments on saturated vapor pressure determination.

When considering the sulfur vapor pressure at temperatures above the liquidus curve, the application of the boiling point method is viable [6]. In view of the fact that the saturated sulfur vapor pressure at its boiling point (429 °C) is 8.5·10¹⁰ times higher than the tellurium vapor pressure, it is taken that the vapor phase is represented only by sulfur.

The vapor composition over sulfur is represented by molecules, where the number of atoms varies from 2 to 8 [1, 2, 6, 7]. Moreover, the ratio of polymers in the vapor phase depends on temperature. Taking this into account we used the boiling point method [8] to determine directly the total contribution of the partial pressure values of different molecules. This method allows to exclude from consideration a molecular weight of the vapor introducing an error when calculating the values of the partial pressure of the sulfur vapor.
The sulfur vapor pressure was determined by the boiling point method (isothermal method) for alloys, whose composition is given in Table 1.

### Table 1 – Composition of tellurium-sulfur alloys.

<table>
<thead>
<tr>
<th>Alloy Number</th>
<th>Alloy composition, atom %:</th>
<th>Alloy composition, wt. %:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sulfur</td>
<td>tellurium</td>
</tr>
<tr>
<td>Alloy No. 1</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>Alloy No. 2</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>Alloy No. 3</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>Alloy No. 4</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Alloy No. 5</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

A high-purity tellurium and sulfur with a content of the main element of not less than 99.99 wt. % were used to prepare alloys. A certain amount of sulfur and tellurium were placed into a quartz vessel, the air was evacuated to 13 Pa and sealed. Vessel with ingredients were kept at 500 °C for 24 hours, followed by tempering in water.

Since the vapor pressure in coordinates \( \ln p - T^{-1} \) represents a linear dependence, the measurements are also performed for the boundary temperatures. Data on the sulfur vapor pressure are approximated by a formal temperature-concentration polynomial dependence. Saturated tellurium vapor partial pressure \( p_{Te} \) over its melts with sulfur was determined by the numerical integration of the Gibbs-Duhem equation using the auxiliary function proposed by Darken [8] as:

\[
\ln \gamma_{Te} = -\ln \gamma_S \cdot x_S \cdot x_{Te} + \int_{y=0}^{x_S} \ln \gamma_S \cdot (1 - x_{Te}) \cdot dx_S.
\]

Here and elsewhere: \( p_{Te} \) – saturated tellurium vapor pressure; \( \gamma_{Te} \) – tellurium activity coefficient; \( x_S \) and \( x_{Te} \) – a content of sulfur and tellurium in the alloy, atomic fraction.

Due to the complexity of the entire data array approximation, the dependences of sulfur and tellurium vapor partial pressures for concentration ranges of 0 - 45 at. % S and 45 – 100 at. % Te were determined.

The value of the partial pressure of saturated sulfur vapor \( p_S \) for alloys containing 0 - 45 at. % S and 100 - 55 at. % Te is given by the dependence:

\[
\ln p_S = (34715x_S^3 - 134155x_S^2 + 200983x_S - 115851 - 36818 \ln x_S) \cdot T^{-1}.
\]

Here and elsewhere: \( T \) – temperature, K.

Pressure dependences of the saturated vapor of elements above alloys with the concentration of 45 - 100 at. % S and 55 - 0 at. % Te, have the form:

\[
\ln p_S = (4668x_S^3 - 7336x_S^2 + 748x_S - 6886) \cdot T^{-1} - 7818x_S + 21375x_S^2 - 27349x_S^3 + 20767x_S + 17098 + \ln x_S
\]

and

\[
\ln p_{Te} = (4668x_{Te}^3 + 13670x_{Te}^2 - 13416x_{Te} - 9894 + 800x_{Te}) \cdot T^{-1} - 7818x_{Te} + 20321x_{Te}^2 - 24978x_{Te}^3 + 21342x_{Te} + 13994 - 0.078 \ln x_{Te}.
\]

Experimental and calculated values of saturated sulfur vapor pressure with the accuracy of measurements are given in Table 2.

### Table 2 – Sulfur vapor pressure over melts of the tellurium-sulfur system

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Alloy composition, at. %:</th>
<th>Temperature, K</th>
<th>Sulfur vapor pressure experimental, KPa</th>
<th>Sulfur vapor pressure calculated, KPa</th>
<th>Error, %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>S 100 Te 0</td>
<td>473</td>
<td>0.23</td>
<td>0.23</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>S 100 Te 0</td>
<td>623</td>
<td>23.83</td>
<td>20.71</td>
<td>+15.06</td>
</tr>
<tr>
<td>3</td>
<td>S 100 Te 0</td>
<td>623</td>
<td>19.52</td>
<td>20.71</td>
<td>-5.74</td>
</tr>
<tr>
<td>4</td>
<td>S 100 Te 0</td>
<td>623</td>
<td>20.62</td>
<td>20.63</td>
<td>-0.05</td>
</tr>
<tr>
<td>5</td>
<td>S 100 Te 0</td>
<td>623</td>
<td>21.45</td>
<td>20.63</td>
<td>+3.97</td>
</tr>
<tr>
<td>6</td>
<td>S 100 Te 0</td>
<td>623</td>
<td>19.79</td>
<td>20.63</td>
<td>-4.07</td>
</tr>
<tr>
<td>7</td>
<td>S 100 Te 0</td>
<td>623</td>
<td>75.99</td>
<td>83.09</td>
<td>-8.54</td>
</tr>
<tr>
<td>8</td>
<td>S 100 Te 0</td>
<td>623</td>
<td>30.66</td>
<td>28.43</td>
<td>+7.84</td>
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<tr>
<td>9</td>
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<td>28.43</td>
<td>+0.81</td>
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<td>28.43</td>
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<tr>
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<td>70.31</td>
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<td>89.33</td>
<td>70.31</td>
<td>-1.39</td>
</tr>
<tr>
<td>13</td>
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<td>623</td>
<td>70.66</td>
<td>70.31</td>
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<td>73.77</td>
<td>+13.85</td>
</tr>
</tbody>
</table>

The sulfur vapor pressure was determined by the boiling point method (isothermal method) for alloys, whose composition is given in Table 1.
<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tr>
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<td>70</td>
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<tr>
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<td></td>
<td></td>
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<td>16.87</td>
<td>+16.18</td>
</tr>
</tbody>
</table>

A total error, as a sum of the independent-measurement errors, is equal to 9.69 % with contributions from: temperature – 1 %, weighing – 0.1 %, pressure – 0.5 % and experimental data approximation – 8.09 %.

A relatively large variation of the experimental data observed is typical of all chalcogenes and chalcogenides, as noted by the authors [9].

The values of sulfur and tellurium vapor partial pressures were used to determine the melting point of melts. At this temperature the sum of partial pressures of the elements is equal to the atmospheric pressure. For sulfur concentration in the alloy in the range of 5-100 at. % the boiling point corresponds to the dependence:

\[
l_{\text{boiling}}[\degree C] = 261x_S^4 - 451x_S^3 + 342x_S^2 - 277x_S + 554.5
\]

The area corresponding to the liquid solutions and limited by the liquidus curve from below and by the boiling point of the alloys from above, is plotted on the tellurium-sulfur state diagram [5] as shown in Figure 1 (shaded).

The change in the partial and total vapor pressures over tellurium and sulfur in the area of liquid solutions and a change in the concentration of the elements at temperatures 698 and 723 K (425 and 450 °C) are shown in Figure 2. The total saturated vapor pressure above melts practically coincides with saturated sulfur vapor partial pressure, and the vapor pressure of tellurium is not significant.

The absence of extrema in the fragmentary curves (cf. Figure 2) of the dependence of total vapor pressure on the composition of melts indicates no constant boiling liquid in the system and a possibility of system separation into elements by distillation.

![Figure 2 - Dependence of partial (1, 3) and total (2, 4) vapor pressures on composition](image)

Thermodynamic activity for the area of liquid solutions was determined as the ratio of the partial pressure of the tellurium or sulfur vapor to the saturated vapor pressure over a pure element. Since the melt area is limited by temperature the activities are determined fragmentarily (Figure 3) for isothermal sections of the liquid region.

![Figure 3 – Change in the activity of sulfur (1-3) and tellurium (4-6) in the Te-S system](image)
The system demonstrates an alternating-sign deviation from the Raoult’s law: a slightly negative for alloys with a content of less than ~ 40 at. % of sulfur, and a significantly positive – above the specified concentration. The latter indicates a tendency of the system for separation in liquid state. Upon increase in temperature the system regardless of the sign of deviation tends to an ideal state, but the activity (activity coefficient) dependence on temperature is weak.

Conclusions. Saturated sulfur vapor pressure over its melts with tellurium was determined using the boiling point method and represented by temperature-concentration dependences. Since the saturated sulfur vapor pressure at its boiling point (429 °C) is 8.5·10⁴ times higher than the tellurium vapor pressure, the total pressure was taken equal to sulfur partial pressure. The partial vapor pressure of tellurium was determined by the numerical integration of the Gibbs-Duhem equation with the mean error of 9.69 %.

Based on the total vapor pressure, the boiling points for tellurium-sulfur system were determined, and the boundaries for liquid melts were identified on the temperature-dependent phase diagram: the liquidus curve is below, and the boiling temperature curve is above. The system demonstrates an alternating-sign deviation of activities from the ideal solutions rule, where the negative deviation is in the area of solutions rich in sulfur (> 50 at. %). The dependence of the total vapor pressure of selenium and tellurium on the composition shows no extrema in the area of liquid solutions, indicating that there is no an azeotrope. Taking this fact and the large difference in the vapor pressure of the components into account, we see no technological difficulties in the system separation into elements by distillation.

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ТҮЙІНДЕМЕ

Қайнау нүктелері әдісі арқылы құрамы 0 – 45 ат. % S (100 – 55 ат. % Те) және 45 – 100 ат. % S (55 – 0 ат. % Те) құрамынан булынған құсымының қысымы анықталды. Температура мен құрылған құсымға бу құсымдарының еш келістірінің жарықты төмendezей упін тұрмайтады. Құрылылған балқымалардың құрылысы температура-концентрациялық тәуелділік түрінде ұсынған температурасы графикалық түрде әдіс-әрекетге арналған. Құсымының қысымы графикалық түрде құрылысы температура-концентрациялық тәуелділік түрінде ұсынған. Құрылысы температура-концентрациялық тәуелділік түрде ұсынған. Температура-концентрациялық тәуелділік түрінде ұсынған. Температура-концентрациялық тәуелділік түрінде ұсынған. Температура-концентрациялық тәуелділік түрінде ұсынған. Температура-концентрациялық тәуелділік түрінде ұсынған. Температура-концентрациялық тәуелділік түрінде ұсынған.

Түйін сөздер: күкірт, теллур, бу қысымы, концентрация, балқыма, күй диаграммасы, ликвидус, қайнау температура, белсенділік, дистилляция.

РЕЗЮМЕ

Методом точек кипения определено давление насыщенного пара серы над расплавами ее с теллуром, представленное температурно-концентрационными зависимостями для сплавов, содержащих 0 – 45 ат. % S (100 – 55 ат. % Те) и 45 – 100 ат. % S (55 – 0 ат. % Те). В исследовании вследствие весьма большой разницы в величинах давлений насыщенного пара серы и теллура принято допущение о том, что суммарное давление над расплавами соответствует парциальному давлению серы. Парциальное давление пара температура найдено для указанных концентрационных интервалов численным интегрированием уравнения Гиббса-Дюгема. Средняя погрешность измерений составила 9,69 %. На основании суммарного давления пара определены температуры кипения сплавов системы температура – сера и определены границы поля жидкных расплавов на диаграмме состояния по температуре: снизу линия ликвидуса, сверху – кривая температуры кипения. Систему отличает знакопеременное отклонение активностей от закона идеальных растворов: отрицательное в области сплавов богатых теллуром и положительное для растворов с содержанием более 50 ат. % серы. На зависимости суммарного давления пара серы и температура от состава в поле существования жидкных растворов не отмечено экстремумов, что свидетельствует об отсутствии нераздельно кипящих жидкости – азеотропной смеси, и, с учетом большой разницы в величинах давления пара компонентов, технологических затруднений дистилляционного разделения системы на элементы.

Ключевые слова: сера, теллур, давление насыщенного пара, концентрация, расплав, диаграмма состояния, ликвидус, температура кипения, активность, дистилляция.

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