

# Thermodynamics of Formation and Evaporation of Aluminum and Aluminum Telluride Melts

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**Abstract** - Based on the values of aluminum telluride vapor pressure determined by the boiling point method and aluminum found by integration, the partial and integral thermodynamic functions of formation and evaporation of the aluminum-telluride system melts have been calculated. The vapor pressure of aluminum telluride ( $\ln p_{Al_2Te_3}^0 [Pa] = 18,828 - 11865 \cdot T^{-1}$ ) above the melting point has been determined for the first time. Integral functions of alloys mixing have a maximum (entropy -  $5.23 \pm 0.31$  J/(mol·K), enthalpy -  $4.17 \pm 0.24$  kJ/mol) at monotectic corresponding to 42 - 44 at. % Te in the melt. The formation of alloys is accompanied by an increase in disorder in the system and goes with heat absorption. Integral functions of evaporation monotonically decrease from aluminum to telluride, and the entropy of evaporation  $Al_2Te_3$  ( $60.71 \pm 3.37$  J/(mol·K)) indirectly confirms the congruent nature of aluminum telluride evaporation. The state diagram is supplemented with the fields of melt and vapor co-consistency at atmospheric pressure and in a vacuum of 6.67 kPa, which testify to the possibility of distillation separation of the Al -  $Al_2Te_3$  system.

**Keywords:** aluminum, aluminum telluride, alloy, vapor pressure, distillation.

## 1. Introduction

If the number of studies of semiconductor tellurides of metals carried out in recent years is very significant [1-4], the work on the physicochemical study of aluminum chalcogenides, in retrospect of seventy years, almost none, and most of the few associated with the aluminum - telluride system.

The authors [5] found the heat of formation of aluminum sesquichalcogenides, for the compound with tellurium -  $326.3 \pm 21$  kJ/mol by direct determination of the heat of interaction of the metal with chalcogens in the Bertleau-Roth microbomb. A close value of enthalpy of formation of aluminum telluride ( $-318.8 \pm 4$  kJ/mol) based on calorimetric measurements were obtained in [6]. As a result of a tentative calculation, the heat of formation of gaseous  $Al_2Te_3$  was  $-364$  kJ/mol.

Mass spectrometric studies [7] of the vapor phase composition over aluminum telluride established the presence of  $AlTe^+$ ,  $Al_2Te^+$ ,  $Al_2Te_2^+$ , and  $AlTe_2^+$  ions with low relative intensity and found the enthalpies and entropies of formation of compounds of this composition at 1,292K (1,019°C). The dissociation energy of AlS was determined to be  $359.8 \pm 12.6$  kJ/mol.

The group of authors first determined the enthalpies of formation and melting of alloys with concentrations up to 70 at. % Te by calorimetric method [8], where the congruent nature of melting of  $Al_2Te_3$  was established and then using the differential thermal analysis the presence of the region of the partitioning of liquid solutions was established. Mass-spectrometric studies and values of enthalpies of formation obtained in the same study confirmed the presence of two liquid phases.

In the study of the vapor pressure and composition by mass spectroscopic, static, and torsion diffusion methods [9] in the temperature range of 538-760 K, it was found that the only component of the gas phase above the crystal  $Al_2Te_3$  is a  $Te_2$  dimer, and the temperature dependence of the dissociation pressure was equal to, where T is temperature, K.

The partial and integral thermodynamic functions of metals were determined in the study [10] using the method of measuring the electromotive forces of concentration chains at 700 - 820 K (427 - 547 °C) in the composition range of aluminum-tellurium alloys up to 20 at. % Te.

The authors [11] in the study of phase equilibria and intermediate phases in the Al - Te system discovered the presence of superstructure in the compound  $\alpha - Al_2Te_3$ .

Excess thermodynamic functions in the concentration range of 0-60 at. % tellurium for 1,190 K (917°C) are given in [12], indicating very small values of its thermodynamic activity.

The study [13] is devoted to thermodynamic modeling and optimization of the Al - Te system based on and using previously performed experiments, including [8,9].

More recent publications on the thermodynamics of the aluminum-tellurium system have not been found. From the analysis of the results of the studies outlined above, it follows that there is a clear lack of information about the aluminum-tellurium system concerning technologies of tellurium purification by physical and physical-chemical methods.

When considering the Al - Te system as a whole, congruent nature of the melting and existence of aluminum telluride in solution [8], a very small value of the Te activity in the liquid phase at concentrations of 0-60 at. %, which refers to the element obtained by dissociation  $\text{Al}_2\text{Te}_3$ , as well as its small value of dissociation pressure at melting temperature 1,168 K (895°C) –  $9.97 \cdot 10^{-3}$  kPa (we calculated from data [14]). This, as well as a significant value of the free energy of aluminum telluride formation, gives reason to assume the congruent nature of the compound evaporation. In this connection, the Al - Te system can be considered as two partial Al -  $\text{Al}_2\text{Te}_3$  and  $\text{Al}_2\text{Te}_3$  - Te.

The purpose of the present study was to determine the thermodynamic functions of mixing and evaporation of the alloys of the private Al -  $\text{Al}_2\text{Te}_3$  system, as well as to determine the boundaries of the melt and vapor coexistence fields at atmospheric and low pressures.

## Experimental procedure

The thermodynamic functions of mixing and evaporation of nickel-calcium system alloys are based on the values of the partial pressure of saturated vapor of the system components. The partial entropies and enthalpies of melt formation have been calculated according to known dependences on the values of thermodynamic activity defined as the ratio of the vapor pressure above the solution to the vapor pressure above the pure element or compound; the vaporization functions have been calculated as functions of the partial vapor pressure. The integral functions are found as the sum of the fractions of the partial functions.

When determining the boundaries of liquid phase-melt and vapor coexistence, the melt boiling temperature was the temperature at which the sum of the partial pressures of aluminum and telluride vapor was equal to atmospheric or another corresponding to the conditions of vacuum technologies. The composition of the gas phase at the boiling temperature above the binary solution was determined as the part of the partial pressure of the component in the total pressure above the alloy.

To determine the value of calcium saturated vapor pressure, we used the boiling point method (isothermal variant), which is based on a sharp increase in the evaporation rate at equal external pressure and saturated vapor pressure of the component under study at decreasing pressure above the melt, described in detail by one of the authors earlier [15]. The advantage of the method is that there is no need to establish the composition of the vapor. Since the vapor pressure of aluminum telluride (as it will be shown below) at the same temperature is several orders of magnitude higher than that of aluminum, we assumed that the vapor phase is represented only by  $\text{Al}_2\text{Te}_3$ . The magnitude of the partial pressure of saturated aluminum vapor over the solution was calculated by numerical integration of the Gibbs-Duhem equation [16] using the substitution proposed by Darken [17]. The value of saturated vapor pressure over elemental liquid aluminum was taken from the monograph [18]. The temperature dependence of the partial vapor pressure of aluminum telluride for each of the compositions was described by the Arrhenius equation. Further, by approximating the dependence of the coefficients in the equation on the  $\text{Al}_2\text{Te}_3$  concentration (at  $0 \leq x_{\text{Al}_2\text{Te}_3} \leq 1$ , where  $x_{\text{Al}_2\text{Te}_3}$ , mole fraction), obtained the temperature-concentration dependence of the partial vapor pressure of telluride ( $\bar{p}_{\text{Al}_2\text{Te}_3}$ ):  $\ln \bar{p}_{\text{Al}_2\text{Te}_3} [Pa] = f(x_{\text{Al}_2\text{Te}_3}, T)$ . A similar equation for the dependence of the partial vapor pressure of aluminum ( $\bar{p}_{\text{Al}}$ ) on composition and temperature [ $\ln \bar{p}_{\text{Al}} [Pa] = f(x_{\text{Al}}, T)$ ] is derived by integrating the Gibbs-Duhem equation, where  $x_{\text{Al}}$  - aluminum content, mole fraction, and, a  $x_{\text{Al}} = 1 - x_{\text{Al}_2\text{Te}_3}$ .

The values of the vapor pressure of the elements presented in this way made it possible to calculate the thermodynamic functions of mixing and vaporization of the alloys, as well as the boundaries of the liquid-vapor phase transition: the boiling point and the corresponding vapor composition in the Al –  $\text{Al}_2\text{Te}_3$  system.

Alloys were prepared as an object of study, the tellurium content in which (the rest aluminum) was, wt. %: 40.21, 59.54, 72.52, 80.47 and 87.65 (12.45, 23.73, 35.82, 46.56 and 60.00 at. %, respectively).

The alloys were prepared by slow heating of corresponding amounts of tellurium (99.99 wt. %) and aluminum (99.99 wt. %) in sealed quartz ampoules, from which the air was evacuated beforehand. Heating was performed at a rate of 100 °C per hour to a temperature of 50-100 °C above achieving a homogeneous state in liquid form - above the area of

stratification, the melt was kept at this temperature for 12 hours with subsequent quenching in water. The boundaries of melt and vapor coexistence fields for atmospheric and low pressures were plotted on the known aluminum-tellurium state diagram [18], represented by a fragment (up to 60 at. % Te).

## Results and their discussion

The values of the partial vapor pressure of aluminum telluride ( $\bar{p}_{Al_2Te_3}$ ) over the alloys with aluminum are given in Table 1 and approximated by the dependence:

$$\ln \bar{p}_{Al_2Te_3} [Pa] = (-3921x_{Al_2Te_3}^4 + 9231x_{Al_2Te_3}^3 - 9322x_{Al_2Te_3}^2 + 3632x_{Al_2Te_3} - 11485) \cdot T^{-1} + 2,334x_{Al_2Te_3}^4 - 5,97x_{Al_2Te_3}^3 + 7,788x_{Al_2Te_3}^2 - 6,756x_{Al_2Te_3} + 20,432 + \ln x_{Al_2Te_3},$$

где:  $0 \leq x_{Al_2Te_3} \leq 1$ .

Table 1. Vapor pressure of aluminum and aluminum telluride in the Al – Al<sub>2</sub>Te<sub>3</sub> system.

[Te], at. %	T, K	$\bar{p}_{Al_2Te_3}$ , Experiment, kPa	$\bar{p}_{Al_2Te_3}$ , Estimated, kPa	$\bar{p}_{Al}$ , Estimated, kPa	$\Delta$ , %
12.45	1,273	7.96	8.96	$2.42 \cdot 10^{-5}$	-11.16
		9.26			+3.35
		9.62			+7.37
	1,473	28.26	29.15	$1.05 \cdot 10^{-3}$	-3.05
		29.83			+2.33
		28.26			-3.05
23.73	1,273	9.27	10.19	$2.30 \cdot 10^{-5}$	-9.03
		10.26			+0.69
		11.62			+14.03
	1,473	32.39	33.04	$1.00 \cdot 10^{-3}$	-1.97
		33.76			+2.18
		35.57			+7.66
35.82	1,173	4.73	4.99	$2.10 \cdot 10^{-6}$	-5.21
		4.83			-3.21
		5.36			+7.41
	1,473	33.13	34.75	$9.50 \cdot 10^{-4}$	-4.66
		35.00			+0.72
		36.01			+3.63
46.56	1,173	5.51	5.30	$1.82 \cdot 10^{-6}$	+3.96
		5.51			+3.96
		4.96			-6.42
	1,373	21.43	21.80	$1.35 \cdot 10^{-4}$	-1.70
		21.74			-0.28
		22.42			+2.84
60.00	1,173	5.73	6.08	-	-5.76
		6.11			+0.49
		6.42			+5.59
	1,373	27.52	26.54	-	+3.70
		26.73			+0.72
		25.43			-4.18

	1,473	46.40	47.72	-	-2.77
		49.06			+2.81
Notes: [Te] - tellurium content in the alloy; $\Delta$ - relative error, $\Delta _{\text{mean}}=4.25$					

In this case, the dependence for the first time of a certain vapor pressure over liquid  $\text{Al}_2\text{Te}_3$  corresponds to the dependence:  $\ln p_{\text{Al}_2\text{Te}_3}^0 [\text{Pa}] = 18,828 - 11865 \cdot T^{-1}$

Total error of measurements is defined as a sum of errors of independent measurements: temperature - 1 %, weighing - 0,1 %, pressure - 0,5 %, approximation of the experimental data - 4,25 %, equal to 5,85 %.

The partial pressure of saturated aluminum vapor corresponds to the dependence:

$$\ln \bar{p}_{\text{Al}} [\text{Pa}] = (-3921x_{\text{Al}}^4 + 11681x_{\text{Al}}^3 - 14834x_{\text{Al}}^2 + 13313x_{\text{Al}} - 41563 - 3003 \ln x_{\text{Al}}) \cdot T^{-1} + 2,334x_{\text{Al}}^4 - 6,478x_{\text{Al}}^3 + 9,931x_{\text{Al}}^2 - 12,01x_{\text{Al}} + 30,396 + 3,246 \ln x_{\text{Al}}$$

with the dependence of the saturated vapor pressure of elemental aluminum on temperature is borrowed from [17].

The changes in the partial and integral entropies and enthalpies of formation depending on the alloy composition are shown in Fig. 1.

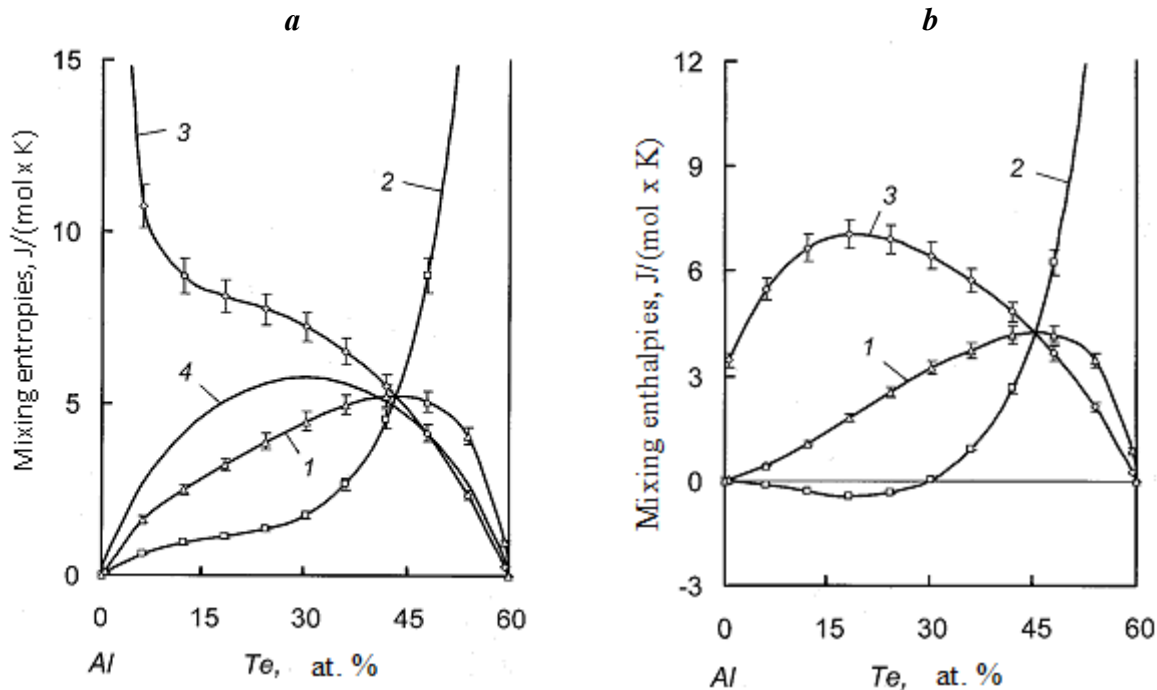


Fig. 1. Dependence of integral (1,4) and partial (2,3) entropies (a) and enthalpies (b) of mixing on the alloy composition: 2 - aluminum; 3 - aluminum telluride; 4 - ideal system.

Analyzing the dependencies, it can be seen that the integral mixing functions of the alloys have a maximum at the monotectic corresponding to the composition of 42 - 44 at. % Te in the melt. The formation of alloys is accompanied by an increase in disorder in the system and goes with heat absorption. The extremum of the integral entropy of mixing reaches a value of  $5.23 \pm 0.31 \text{ J/(mol} \cdot \text{K)}$ , the enthalpy of mixing is  $-4.17 \pm 0.24 \text{ kJ/mol}$ . Moreover, the excess entropy of mixing is negative until it reaches an extremum and positive for the compositions adjacent to aluminum telluride. The partial enthalpy of aluminum mixing has an insignificant negative value for melts containing up to 30 at. % Al, indicating weak interaction of the particles in the liquid bath.

Partial enthalpy and entropy functions of aluminum and aluminum telluride evaporation ( $\Delta\bar{H}_{Al(Al_2Te_3)}^{evap.}$ ,  $\Delta\bar{S}_{Al(Al_2Te_3)}^{evap.}$ ) were found by differentiating the partial Gibbs energy of evaporation ( $\Delta\bar{G}_{Al(Al_2Te_3)} = -RT \ln p_{Al(Al_2Te_3)}$ ) by temperature; integral functions were found by summing the shares of partial functions:  $\Delta H_{Al-Al_2Te_3}^{evap.}(\Delta S_{Al-Al_2Te_3}^{evap.}) = x_{Al} \cdot \Delta\bar{H}_{Al}^{evap.}(\Delta\bar{S}_{Al}^{evap.}) + x_{Al_2Te_3} \cdot \Delta\bar{H}_{Al_2Te_3}^{evap.}(\Delta\bar{S}_{Al_2Te_3}^{evap.})$ .

Thermodynamic functions of evaporation of aluminum-telluride system alloys are given in Tables 2 and 3.

Table 2. Changes in partial and integral entropy of evaporation of Al – Al<sub>2</sub>Te<sub>3</sub> system

Alloy composition, at. %		$\Delta\bar{S}_{Al_2Te_3}^{evap.}$ , J/(mol×K)	$\Delta\bar{S}_{Al}^{evap.}$ , J/(mol×K)	$\Delta S_{Al-Al_2Te_3}^{evap.}$ , J/(mol×K)
Te	Al			
0	100	-	105.15±5.84	105.15±5.84
10	90	44.41±2.46	100.91±5.60	91.49±5.08
20	80	62.08±3.44	95.46±5.30	84.31±4.68
30	70	64.80±3.60	93.87±5.21	79.36±4.40
40	60	62.44±3.47	97.27±5.40	74.09±4.11
50	50	60.60±3.36	102.82±5.71	67.61±3.75
60	40	60.71±3.37	-	60.71±3.37

Table 3. Changes in partial and integral enthalpy of evaporation of the Al – Al<sub>2</sub>Te<sub>3</sub> system

Alloy composition, at. %		$\Delta\bar{H}_{Al_2Te_3}^{evap.}$ , kJ/mol	$\Delta\bar{H}_{Al}^{evap.}$ , kJ/mol	$\Delta H_{Al-Al_2Te_3}^{evap.}$ , kJ/mol
Te	Al			
0	100	-	293.72±16.30	293.72±16.30
10	90	121.55±6.75	291.73±16.19	263.40±14.62
20	80	125.12±6.94	290.98±16.15	235.64±13.08
30	70	117.93±6.55	296.39±16.45	207.15±11.50
40	60	108.29±6.01	310.11±17.21	175.61±9.75
50	50	101.25±5.62	331.52±18.40	139.60±7.75
60	40	98.65±5.48	-	98.65±5.48

The integral function of the entropy of vaporization within the error of the experiment, and the enthalpy depend almost exactly linearly on the alloy composition and decrease from aluminum to telluride. The entropy of evaporation of Al<sub>2</sub>Te<sub>3</sub> is equal to 60.71±3.37 J/(mol×K), which, per Trouton's rule, indicates the presence of associates in the vapor phase and indirectly confirms the congruent nature of telluride evaporation.

Based on the temperature-concentration dependences of the values of the partial pressure of saturated aluminum and its telluride vapor, we calculated the boundaries of the fields of coexistence of liquid and vapor of the Al - Al<sub>2</sub>Te<sub>3</sub> system, supplementing the state diagram by liquid-vapor phase transitions at atmospheric (101.325 kPa) and low pressure of 6.67 kPa (Fig. 2.).

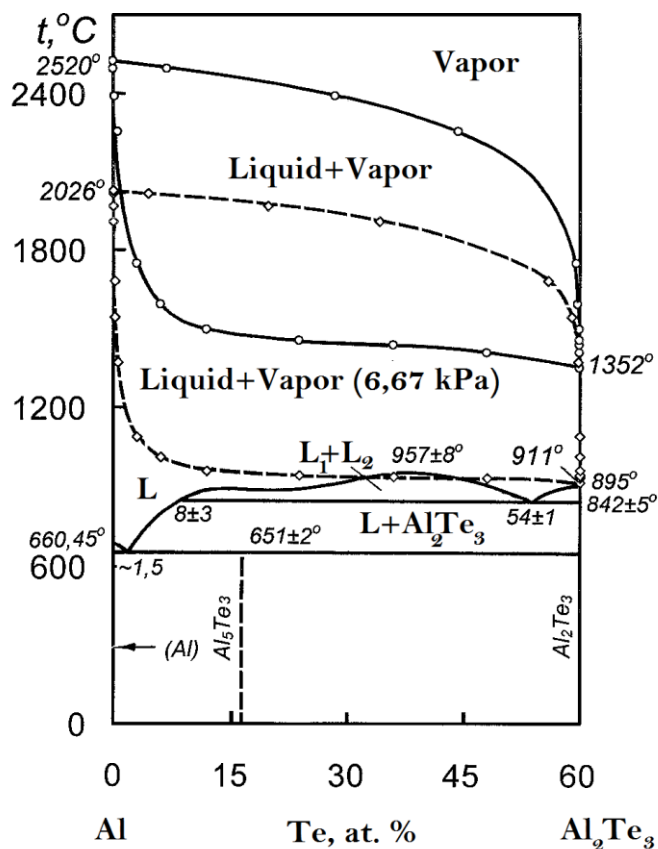


Fig. 2. Fragment of the aluminum-tellurium system state diagram.

At low pressure, the field boundaries (L+V) are highlighted by a dotted line. The choice of the latter value of pressure is due to the fact that at this pressure the melt boiling curve is superimposed on the region of stratification, and increasing rarefaction to 3.70 kPa is accompanied by a decrease in the boiling temperature, which, in this case, falls on the field of existence of liquid and crystal phase  $\text{Al}_2\text{Te}_3$ . The latter makes it difficult to remove tellurium from aluminum by distillation in a vacuum.

Obviously, the process of removal of tellurium from aluminum by evaporation in the form of compound  $\text{Al}_2\text{Te}_3$  does not represent technological difficulties. The composition of the vapor phase in a vacuum is almost completely represented by telluride. So, at distillation of  $\text{Al}_2\text{Te}_3$  from an alloy containing 0.5 at. % Te (the rest is aluminum) at a pressure of 6.67 kPa in the vapor phase, and hence in the condensate will be present only  $1,32 \cdot 10^{-3}$  at. % ( $2,79 \cdot 10^{-4}$  wt. %) Al.

When the pressure drops below 3.70 kPa, the (L+V) field partially overlaps with the field of existence of condensed heterogeneous phases, which can cause technological difficulties in the distillation separation of the melt into components.

## Conclusion

The vapor pressures of aluminum telluride determined by the boiling point method (isothermal version) at 900-1,200°C (1,173-1,473 K) and aluminum found by numerical integration of the Gibbs-Duhem equation have been used to calculate the partial and integral thermodynamic functions of the aluminum-telluride melts. For the first time the determined saturated vapor pressure of molten aluminum telluride corresponds to the dependence:  $\ln p_{\text{Al}_2\text{Te}_3}^0 [\text{Pa}] = 18,828 - 11865 \cdot T^{-1}$

Based on the values of the saturated vapor pressure of the components, the thermodynamic activities of the alloy components have been determined, based on which the thermodynamic functions of the formation of melts of the Al -  $\text{Al}_2\text{Te}_3$  system have been calculated. Integral functions of alloys mixing have a maximum (entropy -  $5.23 \pm 0.31$  J/(mol·K),

enthalpy -  $4.17 \pm 0.24$  kJ/mol) at the monotectic composition corresponding to 42 - 44 at. % Te in the melt. The formation of alloys is accompanied by an increase in disorder in the system and goes with heat absorption.

The integral functions of the entropy of evaporation monotonically decrease from aluminum to telluride. Evaporation entropy of  $\text{Al}_2\text{Te}_3$  ( $60.71 \pm 3.37$  J/(mol $\times$ K)) indirectly confirms the congruent nature of aluminum telluride evaporation.

Based on the data on the value of the saturated vapor pressure of aluminum and its telluride, the diagram of the state is supplemented by the fields of co-precipitation of melts and vapor at atmospheric pressure and in a vacuum of 6.67 kPa.

The location of the boundaries of the vapor-liquid equilibrium fields indicates the possibility of distillation separation of the Al -  $\text{Al}_2\text{Te}_3$  system into aluminum and telluride by distillation of the latter in a vacuum, with the vapor phase represented practically by the compound  $\text{Al}_2\text{Te}_3$ .

This work was financially supported by the Ministry of Education and Science of the Republic of Kazakhstan (grant AP09058077).

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