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TO the MATTER of AZEOTROPIC LIQUID-ALLOYS of SELENIUM – TELLURIUM SYSTEM

Abstract: Partial pressure of elements was found by multiplication of resultant pressure to their share in condensate determined by chemical analysis, assuming the existence of ideal solutions. It avoids vapor molecular composition to be taken into account while partial pressure estimation. To determine boiling temperature of alloys in selenium-sulfur system boiling point method was used in order to determine values of partial pressures of elements with subsequent determination selenium and sulfur bulk quantities ratio in the vapor by means of vapor phase condensate analysis obtained by the static method at the boiling temperatures of solutions. Vapor phase composition at the boiling point was defined as selenium or tellurium partial pressure ratio to the total pressure at the boiling point. On the basis of an author of the partial pressure of steam quantities of selenium and tellurium, presented in the form of temperature and concentration dependences of the calculated phase transition boundary melt - steam system selenium - tellurium, presented in tabular form, and inflicted on the existing phase diagram of condensed phases. Azeotropic mix with maximum temperature was discovered at the state diagram: composition of azeotropic liquid at 995 °C corresponds to 7.5 at. % Se and 92.5 at. % Te. That is, distillation separation of selenium and tellurium is possible in selenium and azeotropic mixture, or tellurium and an azeotropic mixture. Comparison of the results of research with the calculated data obtained on the basis of the research results of other authors, in the presence of differences in the composition and the boiling temperature of the boiling liquid indivisible, essentially confirmed its existence. The latter is the cause of system separation difficulties using distillation methods, because alloy composition becomes identical to vapor phase composition if azeotropic liquid presents there.

Key words: selenium, tellurium, binary system, liquid-alloy, vapor pressure, state diagram, azeotropic liquid, azeotropic mixture.

Introduction. Difficulties of selenium and tellurium separation with distillation attracted researchers' attention to the liquid-vapor equilibria in the system indicated.

Researches of liquid-vapor equilibria in selenium – tellurium system were made by the authors of paper [1] to check out possibility of separation by rectification at atmospheric and low pressures. Trials were performed at the concentration range of 2-99 wt. % of tellurium at pressures of 6.7, 12, 20, 33.3, 60 and 101.3 kPa. Sampling to determine vapor phase composition was carried out at the boiling point in the form of solid condensate, assuming that liquid phase composition does not change. Selenium and tellurium content in condensate was determined by weighing. Finally, liquid – vapor aggregative transition was made for each pressure built and absence of azeotropic mix was established.

Selenium relative volatility coefficients were determined as ratio of concentrations in vapor and liquid states, in respect of tellurium – as ratio of concentration in liquid state to concentration in vapor state. Low values of relative volatility ratios were explained by the chemical compounds formation between selenium and tellurium in liquid and vapor states.

Sato T. & Kaneko H. [2] in course of thermodynamic study of selenium - tellurium system established presence of azeotropic liquid-alloy melt with minimum boiling point and Te concentration of 2 % in alloy that contradicts to current practice of elements separation by distillation including tellurium accumulation in distillation residue.

The author of the paper [3] determined selenium vapor pressure in hard alloys with Se content % of 22.0, 49.0, 69.7, and 85.2 94.5 at the specially designed equipment enabling to get continuous dependence of vapor pressure and temperature using radioactive isotope ⁷⁵Se as well as estimated data of selenium vapor composition were obtained using mass-spectrometric method with radioactive indication. Se, Se₂, Se₄, Se₆ and Se₈ ions were detected in the vapor state. Mean molecular composition of vaporous selenium was determined based on the ratio of different molecules ions number and it was equal to 443 that corresponds to molecular mass of six atoms. Strong abnormal negative deviation from the perfect solutions law was established. Formation of molecules of selenium with tellurium was assumed and purification of tellurium from selenium with vacuum distillation was proved as impossible.

Outcomes of liquid-vapor equilibria study for selenium- impurity liquid alloys were presented in

the paper [4], where selenium – tellurium, selenium – sulfur, selenium – mercury and selenium – arsenic systems were studied using circulation method and relative volatility ratios of impurity element were determined. In selenium liquid alloys containing $(1,1-2,0) \cdot 10^{-2}$ mass % of tellurium, average value of the ratio was equal to 2.62, and based on that distillation process was recognized as most promising. The latest is confirmed by the authors of [5, 6] while extra-pure elements production.

The author of [7] studied liquid - vapor phase equilibria in tellurium - selenium system in the area of selenium small concentrations with ebulliometric method and it was found that separation factor decreases while pressure reduction. The system is characterized by negative deviation from Raoult's law and that occurs due to mixed selenium and tellurium molecules formation under researcher assumption.

In the later study [8] thermodynamic properties of selenium – tellurium alloys were determined by measuring electromotive force of concentration chains in the liquid alloys with Te content up to 15 – 78 at. % at the temperature range of 723 – 880 K. Authors estimated partial and integral thermodynamic constant values of individual elements and system as a whole. Thus positive deviation from ideality was established at the concentration dependences of tellurium activity in the alloys, and in respect of selenium – change of deviation sign from ideality in the area of tellurium 60 at. %.

It is quite difficult to determine thermodynamic constant terms of selenium – tellurium system based on vapor pressure values because it is necessary to take into account molecular weight, distinguished by diversity of associates composition and assembly. Vapor might contain molecules of Se_2 , Se_4 , Se_6 , Se_8 , Te , Te_2 , Te_4 , $TeSe$, assembly of them varies depending on temperature variations and alloy composition [9, 10]. In this regard, the papers were made aimed to develop thermodynamic activity calculation method in alloys, equilibrium of complex composition [11] to vapor state as well as thermodynamic evaluation of the system based on the optimized data set about Se – Te system [12] enabling to align thermodynamic functions and a state diagram to the experimental evidence.

Later authors of paper [13] in the form of their contribution to liquid selenium – tellurium solutions thermodynamic properties simulation presented derivation of the Gibbs free energy equation during two isomorphic pure elements mixing, forming disordered substitution solution adjusted to excess volume account record to the system considered. It has

proven that recording of excess volumes contributions significantly improves alignment between estimated thermodynamic functions of mixture and experimental values of selenium – tellurium alloys.

Based on assessment of studies performed and outcomes established thereof, conclusion can be made about some inconsistencies and interpretation of data concerning vapor pressure, thermodynamic activity, complex molecular composition of the condensed and vapor phases, complexity of evaporative system separation into components, presence of azeotropic mixture or lack of it.

The purpose of this study was to determine liquid - vapor phase transition boundaries based on selenium and tellurium vapor pressure data, whereas vapor molecular composition was not taken into account during determination thereof.

Experimental Part and Discussion of Results. To determine boiling temperature of alloys in selenium-sulfur system boiling point method was used in order to determine values of partial pressures of elements with subsequent determination selenium and sulfur bulk quantities ratio in the vapor by means of vapor phase condensate analysis obtained by the static method at the boiling temperatures of solutions.

Partial pressure of elements was found by multiplication of resultant pressure to its share in condensate found upon its chemical analysis, assuming the existence of ideal solutions. It avoids vapor molecular composition to be taken into account while partial pressure estimation.

Vapor phase composition at the boiling point was defined as selenium or tellurium partial pressure ratio to the total pressure at the boiling point.

To conduct the trials alloys were prepared of selenium content of 10, 30, 45, 50, 55 and 70 at. %. In course of study CP grade tellurium and high-purity selenium of UHP -1 grade were used containing 99,992 % wt of the main component.

Alloys of these compositions were prepared in withdrawn quartz ampoules by heating above the melting temperature to 50 °C, aging for 12 hours at this temperature with stirring by shaking and subsequent quenching in water.

The partial pressure of the alloy components vapor is presented in the form of temperature-concentration dependencies, [14] for selenium:

$$\ln p_{Se} [Pa] = (-10775x_{Se}^3 + 16384x_{Se}^2 - 228x_{Se} - 17921) \cdot T^{-1} - 20,013x_{Se}^4 + 60,172x_{Se}^3 - 60,185x_{Se}^2 + 20,424x_{Se} + 24,399 + \ln x_{Se}$$

for tellurium:

$$\ln p_{Te} [Pa] = (10775x_{Te}^3 - 32104x_{Te}^2 + 31667x_{Te} - 24646 + 215 \ln x_{Te}) \cdot T^{-1} - 20,013x_{Te}^4 + 46,564x_{Te}^3 - 29,567x_{Te}^2 - 1,024x_{Te} + 26,901 + 1,518 \ln x_{Te}$$

Liquid – vapor phase transition boundaries were defined based on partial values of selenium and tellurium vapor pressure: boiling temperature adopted when sum of partial pressures is equal to atmospheric pressure (101325 Pa), vapor composition at the boiling point, as well as ratio of partial pressure to the total one are presented in table.

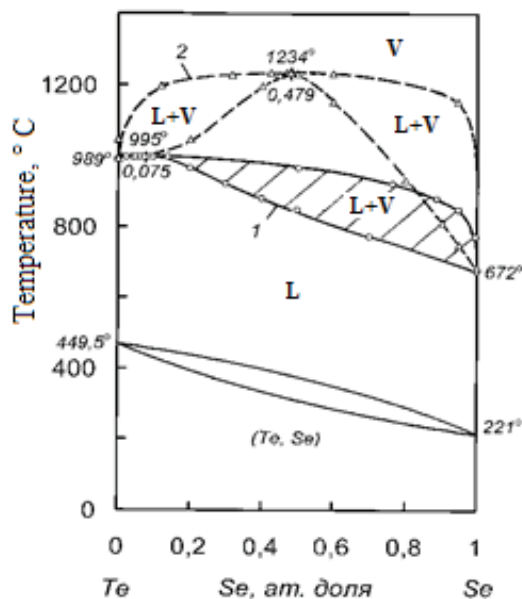
Table – Boiling point of alloys and vapor phase composition at the boiling point

The content of selenium in the alloy * atomic fraction	Alloy boiling point, ° C	The selenium content in a couple of * atomic fraction
1	672	1
0,70	772	0,9961
0,50	845	0,9500
0,40	879	0,8889
0,30	918	0,7662
0,20	963	0,5049
0,10	993	0,1380
0,08	994 (994,4)	0,0863
0,075	995 (994,5)	0,0750
0,06	994 (994,2)	0,0484
0,04	993	0,0232
0	989	0
* - the rest of tellurium		

In addition, boundaries of alloys and vapor phase coexistence were identified based on data of paper [1] under following conditions and assumptions;

- mass percent is converted into atomic percent;
- pressure in the system is equal to overall vapor pressure at the boiling point;
- condensate composition is identical to vapor composition;
- partial pressure of vapor components is pro rata with condensate composition;
- selenium vapor pressure values were used in calculations consisting of Se_8 molecules;
- thermodynamic functions of tellurium were estimated by Gibbs-Duhem equation integration in order to avoid any mismatch;
- tellurium is present in vapor in the form of Te_2 dimers;
- Se_8 and Te_2 pressure was borrowed from [15].

Liquid and vapor coexistence boundaries were marked at the state diagram [16, 17] figure.



1 – our data; 2 – by [1] data
Figure – the phase chart selenium-tellurium

In both cases azeotropes were presented at the state diagram at the maximum temperature: based on estimation with our data composition of azeotropic liquid at 995 °C corresponds to 7.5 at. % Se (the rest is tellurium), according to [1] – 47.9 at. % Se at 1234 °C. Therefore distillation separation of selenium and tellurium is possible into selenium and azeotropic mixture, or tellurium and azeotropic mixture.

Irrespective of differences in extreme values of composition and boiling temperature existence of azeotropic mixtures in selenium - tellurium system was confirmed in principle. Boundaries of liquid and vapor coexistence each side of azeotropic composition obtained based on study evidence [1], in our opinion, are not accurate due to the large number of assumptions. In addition, shape of boundaries of areas indicated (adjacent to Se – state diagram edge), supposes much better quality of distillation refining of selenium from tellurium, comparing to existing practice.

Conclusions. Phase transition boundaries for alloy– vapor in selenium – tellurium system were estimated based on values of selenium and tellurium vapor partial pressure determined by the authors and presented in characteristic curves of temperature and concentration.

Azeotropic mix with maximum temperature was discovered at the state diagram: composition of azeotropic liquid at 995 °C corresponds to 7.5 at. % Se and 92.5 at. % Te. That is, distillation separation of selenium and tellurium is possible in selenium and azeotropic mixture, or tellurium and an azeotropic

mixture. The latter is the cause of system separation difficulties using distillation methods, because alloy composition becomes identical to vapor phase composition if azeotropic liquid presents there.

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ТҮЙІНДЕМЕ

Элементтердің парциалды қысымы жалпы қысым мөлшерінің оның конденсаттағы химиялық талдаумен анықталған мөлшеріне көбейтіндісі арқылы табылды. Бұл будың молекулалық құрамын анықтамай-ақ парциалды қысымның мөлшерін анықтауға мүмкіндік береді. Селен-теллур жүйесінің балқымаларының қайнау температурасын анықтау үшін қайнау нүктелері әдісі қолданылды, балқымалардың қайнау температурасында элементтердің парциалды қысымдары анықталды, одан кейін селен және теллурдың массалық қатынастары бу фазасының талдау арқылы анықталды. Қайнау температурасы кезінде бу фазасының құрамы селен мен теллурдың парциалды қысымының жалпы қысымға қатынасы ретінде анықталды. Авторлардың анықтаған селен және теллурдың бу қысымының температуралы-концентрационды тәуелділіктер түрінде көрсетілген парциалды мөлшерлері негізінде селен – теллур жүйесіндегі балқыма – бу фазалық өтуінің шекаралары есептелген, олар кесте түрінде көрсетілген және конденсацияланған фазалардың фазалық диаграммасына салынған. Күй диаграммасында температуралық максимуммен азеотропты қоспа байқалды: 995 °С бірге балқитын қоспаның құрамы келесі 7,5 ат. % Se и 92,5 ат. % Te. Демек, селен мен теллурдың бөлінуі, селен және азеотропты қоспа немесе теллур және азеотропты қоспа жолымен жүруі мүмкін. Басқа авторлардың зерттеулері нәтижесінде алынған есептік мәліметтер мен осы зерттеу нәтижелерін салыстыру нәтижесінде принципиалды түрде әр түрлі құрамда, бірге балқитын сұйықтықтың қайнау температурасында мүмкін болуын дәлелдеді. Соңғысы жүйені элементтерге дистилляциялы әдіспен бөлуді қиындатады, себебі бірге қайнайтын сұйықтық бар кезде балқыманың құрамы бу фазасының құрамына сәйкес келеді.

Түйінді сөздер: селен, теллур, екілік жүйе, балқыма, бу қысымы, күй диаграммасы, бірге қайнайтын сұйықтық, азеотропты қоспа.

РЕЗЮМЕ

Парциальное давление элементов найдено произведением величины суммарного давления на его долю в конденсате, определенную химическим анализом, в предположении существования идеальных растворов. Это устраняет необходимость учета молекулярного состава пара при расчете величины парциального давления. Для определения температуры кипения сплавов системы селен-теллур использован метод точек кипения для определения суммы парциальных давлений элементов с последующим определением соотношения массовых количеств селена и теллура в паре анализом конденсата паровой фазы, полученного статическим методом, при температурах кипения растворов. Состав паровой фазы при температуре кипения определен как отношение парциального давления селена или теллура к суммарному давлению при температуре кипения. На основании определенных авторами парциальных величин давления пара селена и теллура, представленных в виде температурно-концентрационных зависимостей, рассчитаны границы фазового перехода расплав – пар в системе селен – теллур, представленные в виде табличных данных, и нанесенные на существующую фазовую диаграмму конденсированных фаз. На диаграмме состояния обнаружена азеотропная смесь с максимумом температуры: состав нераздельно кипящей при 995 °С жидкости соответствует 7,5 ат. % Se и 92,5 ат. % Te. То есть дистилляционное разделение селена и теллура возможно на селен и азеотропную смесь, или теллур и азеотропную смесь. Сопоставление результатов исследования с расчетными данными, полученными на основании результатов исследования других авторов, при наличии различий состава и температуры кипения нераздельно кипящей жидкости, принципиально подтвердило ее существование. Последнее является причиной трудностей разделения системы на элементы дистилляционными способами, так как при наличии нераздельно кипящей жидкости состав расплава идентичен составу паровой фазы.

Ключевые слова: селен, теллур, двойная система, расплав, давление пара, диаграмма состояния, нераздельно кипящая жидкость, азеотропная смесь.

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