Original articles

High-temperature spectrophotometry of indium chloride vapours as a method of study of the In – Se system

N. Yu. Brezhnev, A. V. Kosyakov, A. V. Steich, A. Yu. Zavrazhnov✉

Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

The goals of this work are as follows: (a) searching for a method of study of the In – Se system taking into account the specified problems and difficulties, (*b*) choosing a way for the instrumental implementation of this method, and (*c*) obtaining experimental evidence that this method and its implementation are promising.

The choice of the In – Se system is related to the fact that indium selenides, layered structures and semiconductor phases with stoichiometric vacancies, are promising from the point of view of materials science. This choice is also related to the use of binary precursors for the synthesis of heterostructures based on CIS compounds.

We studied the possibility of applying the auxiliary component method using the equilibrium with the participation of indium chloride vapours which were made to contact the condensed phases of the In – Se system. Equilibrium was achieved using high-temperature spectrophotometry of the vapour phase. The experiment had two stages. During the first stage we determined the absorption characteristics of the $InCl_3$ vapour. During the second stage we studied the heterogeneous equilibrium of the unsaturated indium chloride vapour with several phases of the In – Se system. Over the course of the study, we determined the molar attenuation coefficients of the $InCl_3$ vapour and plotted the temperature dependences of the value $K_P^{\#}$.

It was found that the phase composition of the alloys significantly influences the position of the corresponding lines on the $K_P^{\#}-T$ diagram, which proves the possibility of using the suggested auxiliary component method in its specific instrumental (spectrophotometric) implementation in order to study the In – Se system. We also showed the additional possibilities of using this method for plotting *T-x* diagrams of binary systems in such high-temperature areas where the binary solid phase is in equilibrium with the melt. This application of the method is related to the solubility of a vapour of an auxiliary component (chlorine in the form of indium chlorides) in the melts of binary phases (indium selenides).

Keywords: High-temperature spectrophotometry, In – Se system, Phase diagram, Heterogeneous equilibria, Indium chlorides

✉ Alexander Yu. Zavrazhnov, e-mail: alzavr08@rambler.ru

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1. Introduction

The systems where non-equilibrium and/or metastable states easily emerge but are hard to eliminate cause most difficulties in the studies of phase diagrams. Among the examples of them are A(III) – B(VI) systems. For instance, metastable states (and a corresponding metastable *T-x* diagram) were observed at heating rates over ~10 K/min during the study of the In – S system using differential thermal analysis (DTA). The elimination of non-equilibrium states in this system required thorough dispersion and extensive annealing of the samples. This problem is even more serious for a similar chalcogenide In – Se system studied in this article. This was also proved by the results of our preliminary DTA experiments. The data on the system are incomplete and controversial, which indirectly indicates the same problem. The existence of In_4Se_3, InSe, In_6Se_7, and $In_{2.66}Se_4$ (or β-In_2Se_3) and various polymorphic forms of In_2Se_3 of almost stoichiometric composition is obvious [1–7]. Several contemporary studies also justify the existence of two more selenides on the phase diagram, In_9Se_{11} and In_5Se_7 [3–6] (Fig. 1). At the same time, we found no data on the assignment of these phases to certain structures (in [5, p. 459] they only mention the In_5Se_7 phase as a cubic one but without any argumention or details). In calculations performed in 2020 [7] the *T-x*

diagram of the In – Se system was presented without these two phases. The situation with the extent of the homogeneity ranges and, particularly, with the limits of the temperature stability of indium selenides seems even more confusing [5, 6].

Such disagreement in the published data is not unexpected if we take into account the fact that non-equilibrium and metastable states emerge easily. The reasonable approach for this system is the following: the study of phase equilibria must be preceded by the development of appropriate methods and methodologies. The goals of this work are the following:

(a) searching for a method of study of the In – Se system taking into account the specified problems and difficulties, (b) choosing a way for the instrumental implementation of this method, and (c) obtaining experimental evidence that this method and its implementation are promising. The goals were considered to be achieved only in case the reproducibility was proved and the results were internally consistent.

The In – Se system was not chosen randomly but due to the expected high materials science prospects of:

– Layered phases (InSe and some modifications of In_2Se_3) as 2D materials.

– Semiconductor compounds with the so-called stoichiometric vacancies.

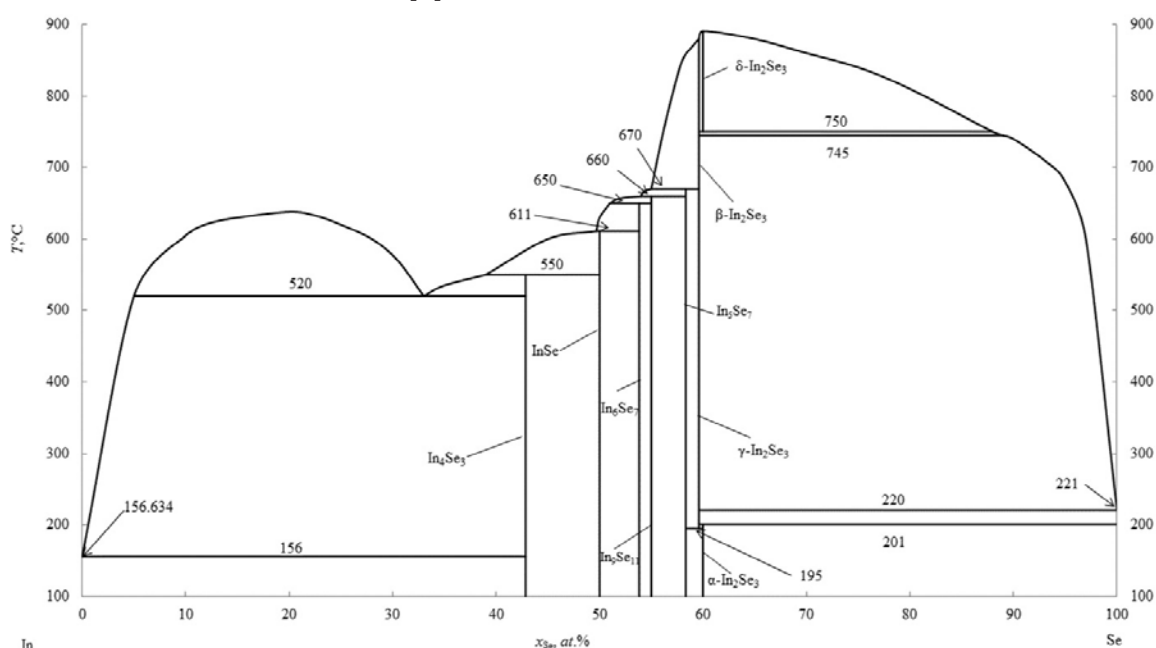**Fig. 1.** *T-x* diagram of the In –Se system according to the review article [1]

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– Binary precursors for the synthesis of heterostructures based on CIS compounds.

1.1. The applied method

The auxiliary component method and the choice of the component. As for the systems where it is difficult to eliminate non-equilibrium states, we can use the *auxiliary component method* [8, 9], the idea of which is to bypass the equilibrium that is hard to achieve with the participation of the components of the initial system (in this case In – Se) and replace it with an equilibrium with the participation of an auxiliary component introduced to the system. Chlorine in the form of indium chlorides was chosen as this component.

Such an experiment, where indium chlorides in the state of unsaturated vapour would interact with the studied indium selenides, can be organised in a closed isothermal system. Based on the data from [9, 10], it was assumed and then confirmed that such an interaction leads to a heterogeneous equilibrium

$$2\text{In}'' + \text{InCl}_3' \rightleftarrows 3\text{InCl}', \tag{1}$$

$$K_P^{\#} = \frac{(p_{\text{InCl}})^3}{p_{\text{InCl}_3}}. \tag{2}$$

In (1) the "″" symbol stands for the condensed state of the substance, while "′" stands for the vapour; so In″ corresponds to indium in the composition of condensed phases of the In – Se system. Selenium (Se″) chemically bound by indium must be inert with respect to the vapour of indium chlorides. Such inertness was expected due to the fact that the vapours of indium chlorides dissociate considerably at high temperatures [11] so we did not record them on the spectra, while ternary phases in the In – Se – C system were formed only in an oxidising environment (the interaction of In$_2$Se$_3$ + InCl$_3$ with an excess of selenium [12]).

The exchange of substance between various condensed phases of the In – Se system can be achieved if the reaction (1) proceeds mainly in the forward or backward direction. The state of equilibrium is achieved as a result of the transfer of chemical substances. This allows obtaining a sample of the studied binary system (in this case In – Se) that is internally in equilibrium, while the correct determination of temperature dependences of the $K_P^{\#}$ values for the series of various compositions in the state of equilibrium

allows extracting the information on the phase diagram of this system. The $K_P^{\#}$ value links the partial pressures of vapours in equilibrium (1) according to the expression (2), that is similar to the "classic" equilibrium constant K_P. However, unlike the latter, the "pseudoconstant" $K_P^{\#}$ depends not only on the temperature (T) but also on the composition (x) of the condensed phase that is in equilibrium with the vapour. (Also, $K_P^{\#}$ depends on pressure P, although this dependence is usually insignificant.) The thermodynamic meaning of the $K_P^{\#}$ value and its connection with the chemical potential of indium participating in reaction (1) were analysed in more detail in [8, 10, 13]. In these works it was also stated that $K_P^{\#}$–T diagrams look very similar to classic P–T diagrams obtained without the introduction of an auxiliary component. The analysis of $K_P^{\#}$–T diagrams, in particular, can help to identify phase relations in the studied binary system.

The experiments were performed at temperatures of 400–700 °C for the compositions with the selenium content not extending 60 mol%. Under these conditions, the selected method is also convenient due to the fact that the pressure of their "own" vapours (In$_2$Se, Se$_2$) on indium selenides is low (P <1 Pa) [5] and does not hinder the registration of partial pressures of molecular forms created by the auxiliary component. Chlorine was chosen as the auxiliary component due to the following:

a) Low solubility of chlorine in indium selenides, according to indirect data [14], which makes it unlikely that there is a significant distortion of information on the phase diagram due to the solution with a foreign impurity (chlorine atoms) in the binary phase.

b) Possibility of obtaining vapours of indium chlorides with a concentration appropriate for correct spectrophotometric measurement [15, 16].

c) Various ratios of the components in the molecules of indium chloride present in the vapour (In$_2$Cl$_6$, InCl$_3$, In$_2$Cl$_4$, and InCl [15, 17]). Due to the differences in these ratios, in other words, in the oxidation states of indium, reaction (1) and similar independent reactions become possible.

d) Expectation, similar to the Ga – Se – Cl and In – S – Cl systems, of a *selective* interaction between indium chloride vapours and the condensed selenides, where only indium participates in a reversible reaction [10, 13].

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As this work is focused on the determination of the $K_P^{\#}$ value at different temperatures and the compositions of the In – Se system, high-temperature spectrophotometry was chosen for the instrumental implementation of the auxiliary component method. High-temperature spectrophotometry allowed obtaining absorption UV spectra of indium chloride vapours that were in equilibrium with the condensed sample of the In – Se system of the set composition. Processing these spectra, we found the values of concentrations and partial pressures of the InCl and $InCl_3$ vapours, and then we substituted them in expression (2) and calculated the $K_P^{\#}$ values.

2. Experimental

Taking into account the aforementioned, we decided that the main goal of the work to be achieved should consist in the determination of the temperature dependences of the $K_P^{\#}$ value for various compositions of indium selenides that are in equilibrium with the unsaturated vapour of indium chlorides (see formula 1). This problem was solved in two stages: During the **first stage** we determined the molar attenuation coefficients of indium trichloride $\varepsilon_\lambda(InCl_3)$ where λ is the wavelength for the typical absorption band. As for indium monochloride, similar values $\varepsilon_\lambda(InCl)$ were determined for several typical peaks in the previous work [16]. After that, we moved to the **second stage** and studied the equilibria of indium selenides with indium chloride vapours. During this stage, we obtained the absorption spectra of the equilibrium vapour of indium chloride at various temperatures. Based on these spectra and taking into account the molar attenuation coefficients, we calculated the values of partial pressures of the p_{InCl3} and p_{InCl} vapours and then the value of $K_P^{\#}$. Finally, we analysed the temperature dependences of the $K_P^{\#}$ values obtained for the In – Se alloys of various compositions.

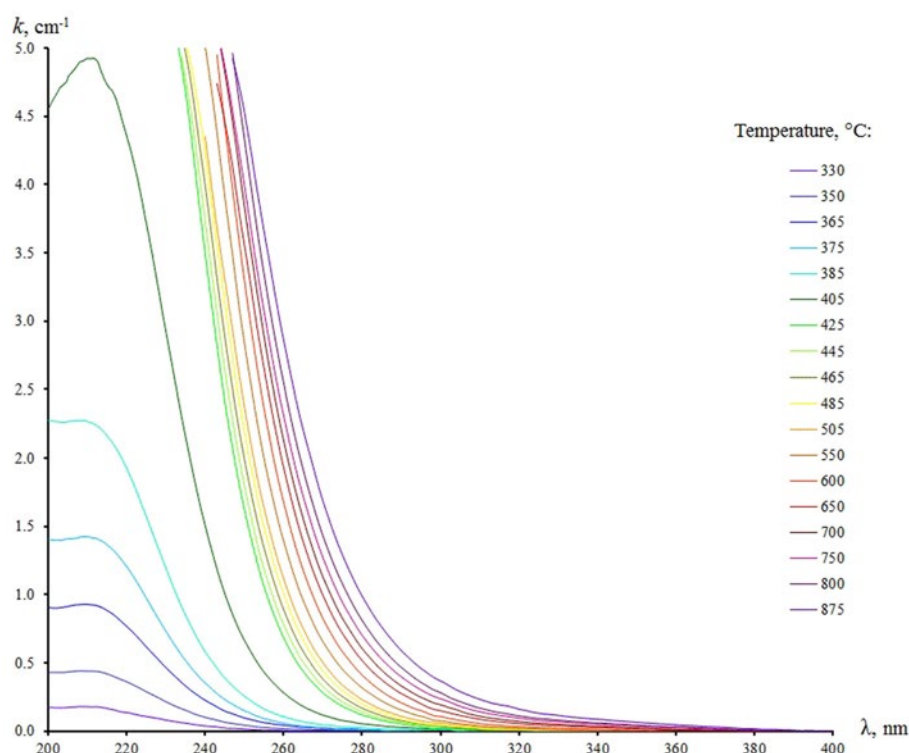### 2.1. Stage 1. Spectrophotometric study of $InCl_3$ vapours

For this study we used a methodology similar to the one described in our previous works [16, 18]. Indium trichloride was synthesised from simple substances [15]. The studied equilibrium was implemented in a sealed optical quartz cuvette (~25×10×10 mm^3) with the optical path of 10.0 mm inside the cuvette. Very small quantities

of indium trichloride were introduced to the cuvette in such a way so that at temperatures of 400–450 °C solid $InCl_3$ would completely sublime and form an unsaturated vapour. During one of the two experiments, a small amount of chlorine gas was also introduced to the system in order to suppress the thermal dissociation of $InCl_3$. The methods of the synthesis and introduction of small amounts of indium trichloride and chlorine into the cuvette are described in [15].

The sealed-off cuvette was placed in a resistance heating furnace. The furnace had small openings (windows) for the transmission of light through it. Absorption spectra were obtained in the range of 200–400 nm using an array based on an MDR-41 monochromator. The furnace with the cuvette inside it was mounted in the array. Typical spectra obtained during the experiment with the excess of chlorine are presented in Fig. 2. As can be seen from Fig. 2, the only broad absorption band with the maximum absorption at 210–215 nm can be observed in the specified spectral range.

This band was also observed in [15] where it was associated with indium trichloride. Fig. 2 also shows that typical light absorption grows with increasing temperature (*t*): it grows sharply at $t \leqslant 425$ °C and gradually at higher temperatures. We associated this change in the temperature course of absorption with the "Saturated vapour ↔ Unsaturated vapour" transition as the amount of $InCl_3$ in the experiment and the cuvette volume were chosen so that such transition would be observed in the temperature range of 400–450 °C.

A similar change in this spectral band with the temperature was observed in a similar experiment where indium trichloride was used, but chlorine was not added. A series of sharp peaks (in the ranges of 260–290 and 337–363 nm) typical for indium *monochloride* InCl were also seen on the spectra. However, the content of InCl in the vapour calculated using the values of the molar attenuation coefficients did not exceed 2% of the content of $InCl_3$. Also, neither in this experiment, nor in any other experiments we saw any noticeable bands with a wavelength of about 320 nm, which is typical for indium (II) chloride In_2Cl_4. Taking this into account, the data of the experiment conducted without the addition of chlorine was also used to determine the absorption properties of indium trichloride, ignoring its insignificant degradation in this experiment.

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Fig. 2. UV absorption spectra of saturated and unsaturated (over 425 °C) vapours of InCl$_3$ at various temperatures specified in the legend

The *optical absorption coefficient* ($k_\lambda(i)$) was the basic value measured in our spectrophotometric experiments. Each specific value of $k_\lambda(i)$ was determined for the specific wavelength at which the light absorption of the *i*-th substance takes place*. To calculate the values of the *molar attenuation coefficients* ($\varepsilon_\lambda(InCl_3)$), we extracted $k_\lambda(InCl_3)$ from the registered spectra in those temperature ranges that corresponded to the *saturated* vapour of InCl$_3$. The measurements were performed for the wavelengths of 240, 245, and 250 nm. These values correspond to the InCl$_3$ absorption band but they are situated on its wavelength edge in relation to the <u>absorption maximum</u>. This choice is explained

* In these and other spectrophotometric experiments performed in this work, the measurement error for the intensity of radiation ($\Delta I°$) passing through an empty cuvette did not exceed 0.5% of the measured value ($I°$). The calculation by the error accumulation method showed that the error for the determination of the optical absorption coefficient was minimal for $k_\lambda = 1.3$ cm^{-1} and was about 1.8 % of the measured value. The error increased in case of the increase or decrease in the optical absorption coefficient. For the further calculations in this work we used the values of k_λ in the range from 0.1 to 4.5 cm^{-1} with the error not exceeding 10 %. When calculating the errors of other values ($C(i), p(i), K_P^\#$), it was assumed that only the discussed value made significant contribution to random errors.
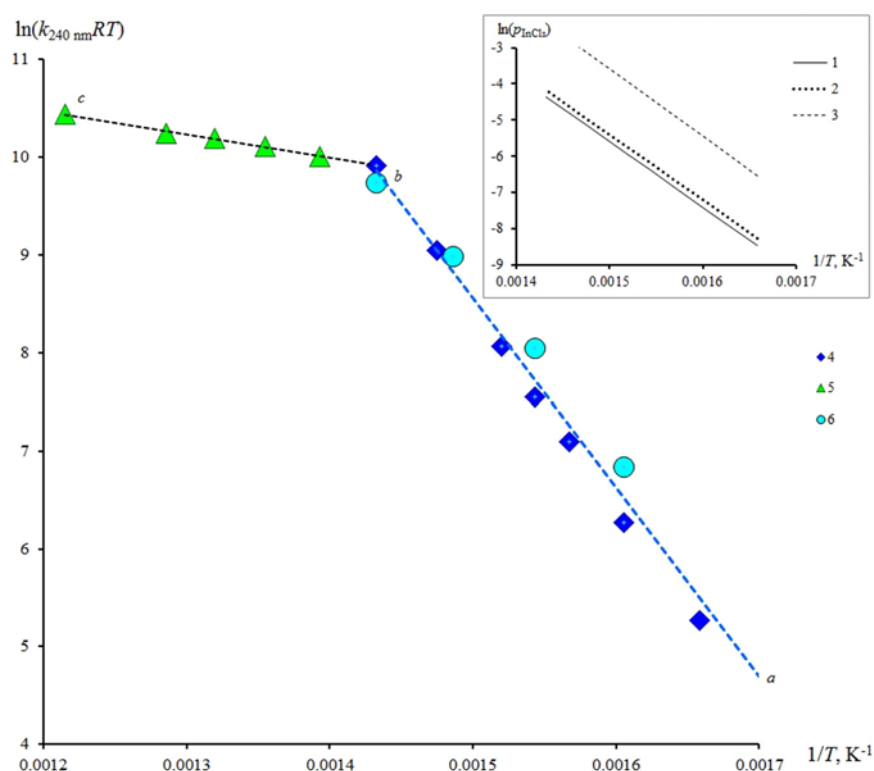
by the fact that the applied array provided a radiation intensity which was too low for the wavelengths of up to 240 nm, and the quantitative determination of absorption was performed with poor accuracy. Moreover, as many substances have great attenuation in the short-wave region of the UV spectrum (up to 240 nm), as a result, the quantitative determination of InCl$_3$ in this spectral region can be distorted even by the presence of impurity traces in vapour.

To obtain the required values ($\varepsilon_\lambda(InCl_3)$), we used the correlation (3) between the partial vapour pressure ($pInCl_3$) and the optical absorption coefficient $k_\lambda(InCl_3)$, which was obvious from Beer's law and the ideal gas law.

$$k_{\lambda\,(InCl_3)} \cdot R \cdot T = p_{(InCl_3)} \cdot \varepsilon_{\lambda\,(InCl_3)} \cdot \ln(10) \qquad (3)$$

This expression was primarily used to assess the validity of the obtained results. To do that, we compared the dependence of the $\ln(k_\lambda(InCl_3) \cdot R \cdot T)$ value on the reciprocal temperature obtained from the experimental data with a similar dependence of $\ln(pInCl_3)$ on T^{-1} according to the <u>data from [19]**</u> (Fig. 3).

** There are significant discrepancies in the published data on the temperature dependence of the saturated vapour pressure of InCl$_3$ over solid indium trichloride, which is

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Fig. 3. The data on the temperature dependences of the value $k_{240\,nm}$ (InCl$_3$)·R·T (our experiment) and pressures of the InCl$_3$ saturated vapour (inset in the right upper corner; published data) presented in Arrhenius coordinates. **Legend:** *1*, *2*, and *3* are published data of [19], [20], and [21] respectively. *4* and *5* are the experiment with an excess of chlorine and areas of saturated and unsaturated steam, respectively; *6* is the experiment without an excess of chlorine and saturated vapour. Errors in the determination of the ln(k_λ(InCl$_3$)·R·T) value do not exceed the sized of experimental dots

Taking into account the Clausius–Clapeyron relation for small temperature ranges and assuming that the temperature dependence of the attenuation coefficient is insignificant, both dependences must be almost linear for the *saturated vapour area*. In addition, both lines must have the same angular coefficient that corresponds to the enthalpy of sublimation of ($\Delta_S H(T$av.).) of indium trichloride with a precision of up to the *R* factor. It should be stressed that the $\Delta_S H(T$cp.) value calculated for the average temperature of the study area (325–425 °C) refers to the sublimation of solid indium trichloride with the formation of vapours of a certain molecular form, which is InCl$_3$.

Indeed, the dependence of ln(k_λ(InCl$_3$)·R·T) on the reciprocal temperature turned out to be

close to linear (line |*ab*| Fig. 3). Calculated for the temperature range of 325–425 °C, the value of enthalpy of sublimation of indium trichloride was 161±3.0 kJ/mol, which within the range of 4–6 % corresponds with the results in [15], [19], and [20] (156, 152, and 151 kJ/mol, respectively). Therefore, the obtained data are internally consistent and correlate with the published data.

This allowed us to assume that the values of the molar attenuation coefficients calculated from expression (3) were correct. To make calculations from (3), we evaluated ε$_\lambda$(InCl$_3$) and substituted the experimental values of k_λ(InCl$_3$), temperature *T*, and the values of p(InCl$_3$) from the published data on the saturated vapour of InCl$_3$ into the obtained expression. The values of p(InCl$_3$) were obtained for specific temperatures based on the temperature dependences [19]. The obtained averaged values of ε$_\lambda$(InCl$_3$) are presented in Table 1.

Therefore, we obtained all the required data in order to proceed to the second and final stage of

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selectively presented on the inset in Fig. 3. In our opinion, it is difficult to determine this dependence correctly because of the complex composition of the saturated vapour with a commensurable presence of InCl$_3$ and In$_2$Cl$_6$ molecules, and because of the possible thermal dissociation of InCl$_3$ into InCl and Cl$_2$. In this work, we used the data from a detailed work [19], which correlate well with the results of [20].

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Table 1. Values of the molar attenuation coefficients of the InCl and InCl$_3$ vapours

Molecular shape for which the calculation is performed	Wavelengths corresponding to the calculated values ε_λ λ, nm	Molar attenuation coefficient ε_λ, cm^2/mol	Source
InCl$_3$		$(6.1 \pm 0.6)\cdot10^6$	This work
InCl$_3$		$(4.1 \pm 0.5)\cdot10^6$	This work
InCl$_3$		$(2.7 \pm 0.4)\cdot10^6$	This work
InCl	267.0	$1.167\cdot10^8$	[16]
InCl	270.4	$3.822\cdot10^7$	[16]
InCl	342.4	$5.240\cdot10^5$	[16]
	Wavelength range $\lambda_1 - \lambda_2$ (nm), corresponding to the values $\varepsilon_{\lambda_1-\lambda_2}$ for the calculations by the peak area	$\varepsilon_{\lambda_1-\lambda_2}$, cm^3/mol	
InCl	337–365	$2.283\cdot10^6$	[16]

Notes to Table 2. 1 and 2 are the calculations of the the partial pressure of InCl vapours by the absorption with the wavelengths of 342.4 and 270.9 nm respectively; 3 is the calculation of the the partial pressure of InCl$_3$ vapours by the absorption with the wavelength of 240.0 nm, 4 is the mole fraction of indium monochloride in vapour calculated to the approximation of the presence of only two forms, InCl and InCl$_3$, in the vapour.

the work. Before we describe this stage, it should be added that the specific features of the changes in light absorption in the *unsaturated* vapour of InCl$_3$ are not directly related to the goal and purpose of the work, so they are analysed in the APPENDIX.

2.2. Stage 2. Spectrophotometric study of the equilibrium of vapours of indium chlorides with some condensed phases of the In – Se system

In this part of the study, we introduced crushed powder of an alloy of the In – Se system to the point of equilibrium with the vapour of indium chlorides. It was important to show that alloys with different phase compositions provide noticeably different quantitative characteristics of equilibrium with the vapour of the auxiliary component. We used two alloys to identify these differences: one with the selenium content of 49.9 mol% Se (alloy 1) and another with the selenium content of 58.5 mol% Se (alloy 2). The poorest phases were to be contained in the first one and the phases rich in selenium in the second one. However, polymorphic modifications of the most selenium-rich phases that almost corresponded to the stoichiometry of In$_2$Se$_3$ were not used in this work as these substances may have noticeable values of vapour pressures of their own components (In$_2$Se, Se$_x$) at temperatures of the planned experiments (400–800 °C). Molecular forms of selenium (Se$_x$; x =1, 2, 3, 4...8) and diindium selenide (In$_2$Se), in their turn, would be seen on the spectra and would make it difficult to analyse them.

Both alloys were synthesised during the interaction of stoichiometric amounts of simple substances (In-00, high purity Se, double distilled) in the evacuated quartz ampoules at 900 °C. The melts were stirred and the ampoules were occasionally shaken within two hours, then cooled down to 600 °C, and after that the samples were kept at this temperature for 24 hours. The annealing was finished by quenching the ampoules in iced water. The quartz ampoules were opened, and the ingots weighing 2–3 g were extracted from them.

The DTA and XRD data showed that both alloy 1 (49.9 mol% Se) and alloy 2 (58.5 mol% Se) are heterogeneous: the first one is almost exclusively presented by the hexagonal phase of InSe-2H with a negligible impurity of In$_4$Se$_3$, while alloy 2 contained β-In$_2$Se$_3$ and In$_6$Se$_7$ phases.

To conduct a spectrophotometric experiment, we placed a weighed portion of the alloy ground into powder on the bottom of the cuvette and then introduced a certain amount of an auxiliary component into the cuvette. As for the auxiliary component, at this stage of work it was more convenient to initially introduce indium *monochloride* into the cuvette since it is not important which initial phase of indium chloride is introduced into the system to achieve heterogeneous equilibrium. The amount of InCl was selected on the condition that *unsaturated* vapour must be formed in the system

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at temperatures over 400 °C. Taking into account the small volume of the cuvette and the high absorption of indium chlorides, we are referring to the introduction of a very small amount (~10^5 g), which cannot be measured directly using analytical scales. A special methodology described in [16] was developed for the synthesis and transfer of such small amounts into the cuvette. Once the defined microquantity of InCl was transferred into the cuvette, it was evacuated, sealed off, and placed as necessary in the furnace of the spectrophotometric unit. It should be noted that as the total amount of the In – Se alloy exceeds the amount of halides in vapour

by 4–5 orders of magnitude, the change of the composition of liquid (molten) indium selenides must be negligibly small in case of any deviations in the equilibrium (1) during the experiment.

3. Results and Discussion

Typical absorption spectra of indium chloride vapours that are in equilibrium with alloy 1 at temperatures from 410 to 610 °C are presented in Fig. 4. At a temperature of 400 °C, a typical series of sharp peaks are observed in the wavelength ranges of 260–290 and 337–362 nm on these spectra indicate the appearance of noticeable concentrations of indium *monochloride* in the
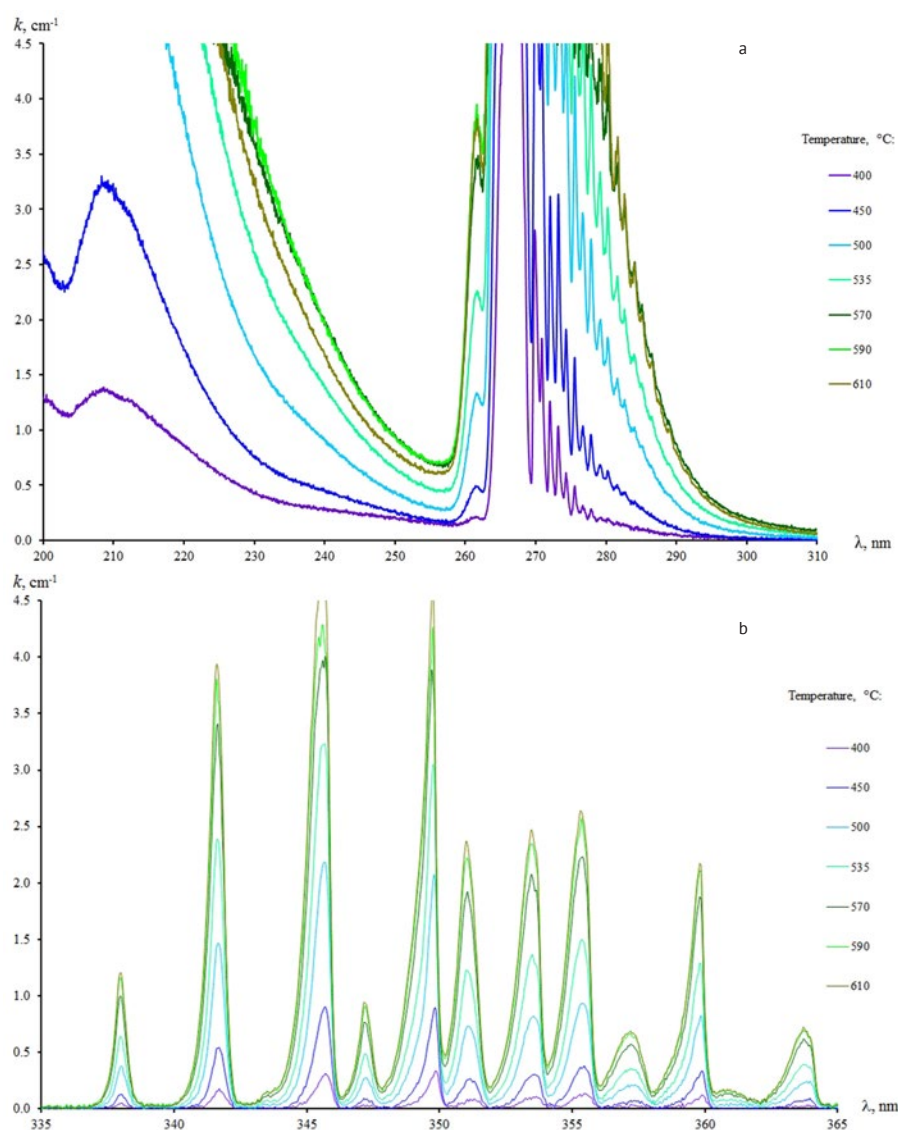
Fig. 4. UV absorption spectra of indium chloride vapours obtained at temperatures from 410 to 610 °C and being in equilibrium with alloy 1 (phase 2H-InSe and traces of In$_4$Se$_3$): *a*) spectral area of 200–310 nm where a wide absorption band of InCl$_3$ (shortwave part of the spectrum ~up to 250 nm) and a series of peaks of InCl (~260–300 nm) appear; *b*) spectral area of 335–365 nm where InCl absorption peaks appear

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vapour. As for the specified temperature range, the intensities of the characteristic peaks of InCl significantly increased together with the temperature, which is indicative of a strong deviation of equilibrium (1) to the right. Similarly, at temperatures from 400 to 650 °C, the shape of spectral curves for the experiment with alloy 2 also changed due to a higher content of selenium (58.5 mol%).

The known values of the molar attenuation coefficients of InCl and $InCl_3$ (Table 1) allowed determining the equilibrium concentrations of these molecular forms in the vapour and then determining the values of partial pressures $p(InCl)$ and $p(InCl_3)$ and, finally, the $K_P^{\#}$ value (2). Table 2 and Fig. 5 show these results referring to the temperatures at which alloys 1 and 2 remain crystalline (there are no melts or their fraction is negligibly small).

The data provided in this table indicate a clear deviation of equilibrium (1) to the right with an increase in the temperature (see the columns with the $K_P^{\#}$ values). As for alloy 2 with a relatively low content of indium (41.5 mol%), the $K_P^{\#}$ values were several orders of magnitude smaller than the ones for alloy 1 (50.1 mol % In) which contained indium-rich phases. This was indicative of a great increase in the affinity of indium to selenium in the transition from lower to higher selenides.

However, despite a significant difference between the $K_P^{\#}$ values for the equilibria with alloys of various compositions (including phase composition), noticeable concentrations of $InCl_3$ and InCl always remained in the vapour.
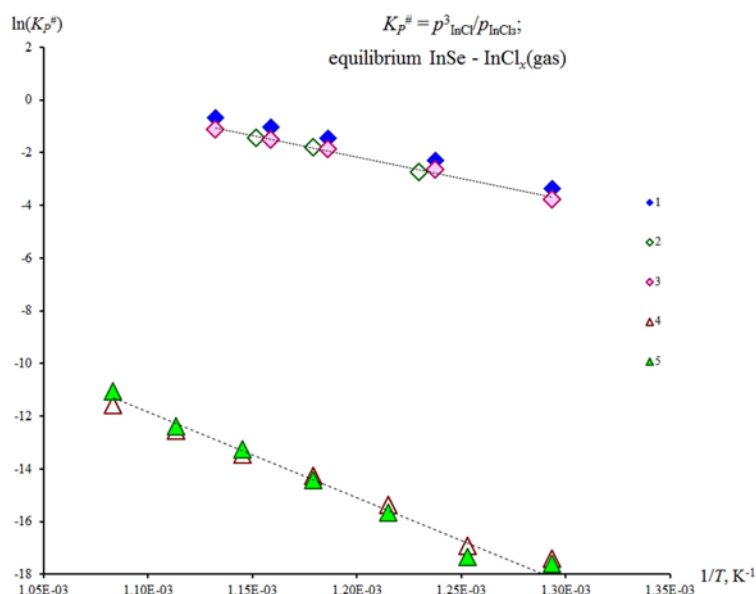
Their joint presence should accelerate the achievement of the equilibrium state and the obtaining of samples of indium selenides with internal equilibrium upon their contact with the vapour of these halides under the conditions of a spectrophotometric experiment. It should be noted that in a number of cases the contact of condensed phases with vapour contributes not only to the achievement of the equilibrium position but also to the elimination of metastable states. For instance, [22] showed that marcasite (α-FeS_2) is a metastable phase in relation to pyrite (β-FeS_2). It was proved by a monotropic transformation of marcasite to pyrite, which occurred only upon the contact with a liquid phase, specifically an iron carrier ($FeCl_2$). In [23], metastable inclusions of γ-GaSe in ε-GaSe were eliminated upon annealing of gallium monoselenide crystals with an excess of gallium in the presence of GaI and GaI_3 iodide vapours that ensured the transfer of gallium between the solid phases and the vapour.

Going back to Fig. 5, it should be noted that $K_P^{\#}$ temperature dependences in Arrhenius coordinates are a) similar to linear ones and b) are very different both in the absolute values of $K_P^{\#}$ and in the slope. Greater $K_P^{\#}$ values correspond to the equilibrium with the alloy with a greater indium content (alloy 1), while the temperature dependence of this value presented in Arrhenius coordinates has smaller slope.

The identified features on Fig. 5 corresponded to those expected and showed quality analogy between $K_P^{\#} - T$ and $p_i - T$ diagrams. For instance,

Table 2. Partial pressures of the $InCl_3$ and InCl vapours in equilibrium with the alloys of the In – Se system with a selenium content of 49.9 and 58.5 mol %

Equilibrium with the In – Se alloy; 49.9 mol% Se					Equilibrium with the In – Se alloy; 58.5 mol% Se				
t, °C	p_{InCl} (1)	p_{InCl3} (3)	$K_P^{\#}$	x_{InCl}, % (4)	t, °C	p_{InCl} (2)	p_{InCl3} (3)	$K_P^{\#}$	x_{InCl},% (4)
400	0.006	0.003	7E-05	68.9	400	1.1E-04	4.7E-02	5.6E-12	0.2
450	0.020	0.004	0.002	82.5	425	1.9E-04	4.6E-02	2.1E-11	0.4
500	0.060	0.009	0.023	86.5	450	2.6E-04	4.3E-02	3.0E-10	0.6
535	0.10	0.015	0.07	87.2	475	2.9E-04	3.6E-02	7.5E-10	0.8
570	0.15	0.022	0.15	87.2	500	4.6E-04	3.2E-02	3.6E-09	1.4
590	0.17	0.023	0.22	88.2	525	4.9E-04	2.8E-02	6.4E-09	1.7
610	0.19	0.020	0.32	90.3	550	7.8E-04	2.0E-02	3.2E-08	3.7
					575	1.1E-03	1.4E-02	1.0E-07	7.0
					600	1.5E-03	1.2E-02	2.4E-07	11.0
					625	1.7E-03	6.7E-03	6.2E-07	20.3
					650	2.3E-03	4.4E-03	1.7E-06	34.6

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Fig. 5. Temperature dependences of the $K_P^{\#}$ value for equilibrium (1): indium chlorides in the vapour phase, alloys of the In – Se system in the condensed phase. Line | *cd* | is an alloy of the 49.9 mol% Se composition, line | *ef* | is an alloy of the 58.5 mol% Se composition. **Legend:** *1 – 3* are data of two experiments with the In – Se alloy of the 50.0 mol% composition Se, *1*, and *2* are the calculation of p(InCl) by the absorption coefficient with the wavelength of 342.4 nm; *3* is the calculation by the peak area within the wavelength range of 337-362 nm. *4* and *5* are the experiment with an alloy of the 50.0 mol% composition % Se; calculations of p(InCl) by the absorption coefficient with the wavelengths of 267.5 and 270.9 nm respectively

if the temperature dependence of the partial pressure of indium vapors p_{In} over heterogeneous samples of alloy 1 and alloy 2 were studied directly in the In – Se system (without an auxiliary component), we should have observed the dependences of $\ln(p_{In})$ on T^{-1} similar to the ones shown in Fig. 5. Such behaviour stems from the connection (4), shown in [8], between the chemical potential of indium (μ_{In}) in the condensed phase of the In – Se system and the $K_P^{\#}$ value for equilibria of type (1).

$$\mu_{In} = 0.5 \cdot RT \cdot \ln(K_P^{\#}) + F(T), \qquad (4)$$

where $F(T)$ is the element depending only on the temperature.

3.1. Additional possibilities of spectrophotometry with the vapours of the auxiliary component when studying T – x diagrams of the In – Se system
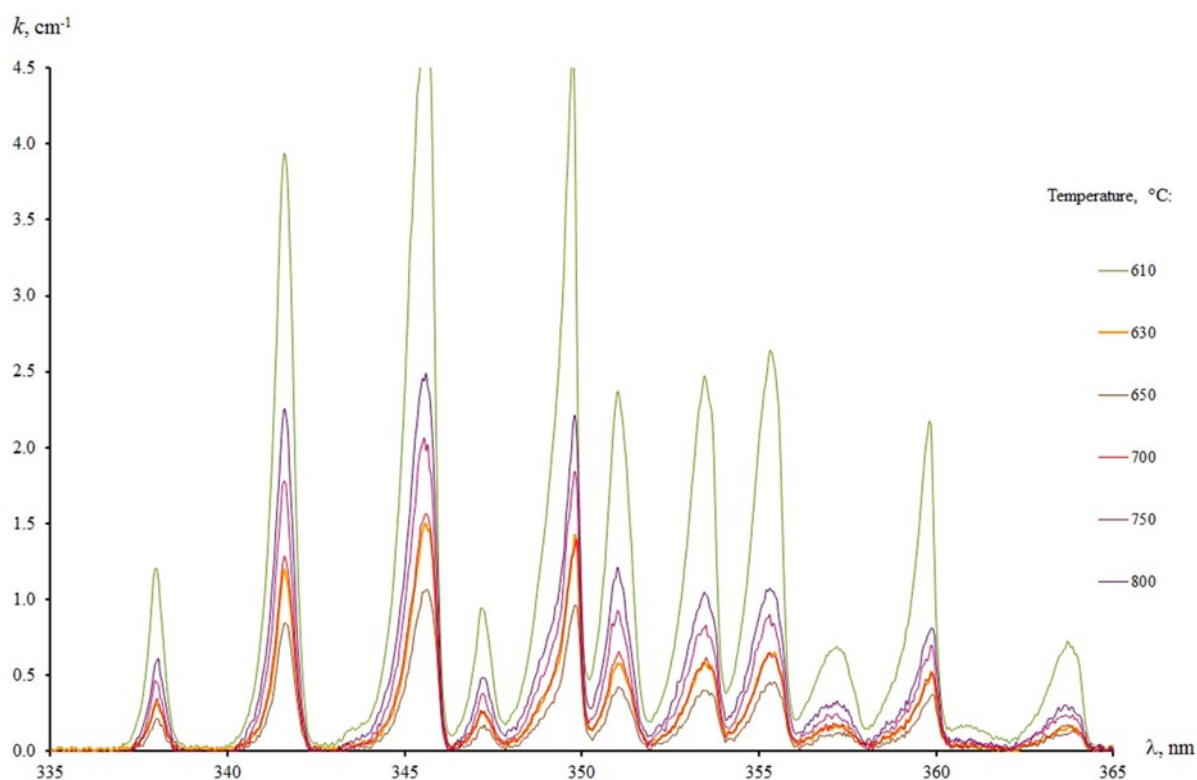
The analysis of the behaviour of absorption spectra at temperatures over 610 °C for alloy 1 and over 665 °C for alloy 2 allowed identifying unexpected features. Under these conditions, at first a sharp decrease and then a smooth increase of the intensities of InCl peaks was observed on the spectra upon the increase of temperature (Fig. 6 and Fig. 7). It is obvious that the *concentration* of indium monochloride in the vapour changed in the same way. Similar changes were observed also in the concentration of indium *trichloride* in the vapour.

We associated such an unusual course of the temperature dependence of the InCl and $InCl_3$ concentration in the vapour with a noticeable solubility of indium chlorides in the melt of indium selenides. Since alloy 1 consisted practically of the InSe phase (the fraction of the In_4Se_3 phase was very small), the appearance of the first noticeable amounts of the melt must correspond to the incongruent melting temperature of InSe.

Then, practically, the beginning of the reduction in the concentration of halides in the vapour must correspond to this temperature* on the corresponding temperature dependence.

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* It was already noted that the total amount of the In – Se alloy exceeds the amount of halides in vapour by 4 – 5 orders of magnitude. As a result, the cryoscopic effect, a reduction of the temperature of phase melting due to the solubility in the melt of halides, must be much smaller than the error in the determination of the temperature using a thermocouple (2 K).

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Fig. 6. UV absorption spectra of indium chloride vapours obtained at temperatures from 610 to 800 °C and being in equilibrium with alloy 1 (phase 2H-InSe and traces of In_4Se_3) Spectral area of 335 – 365 nm where InCl absorption peaks appear
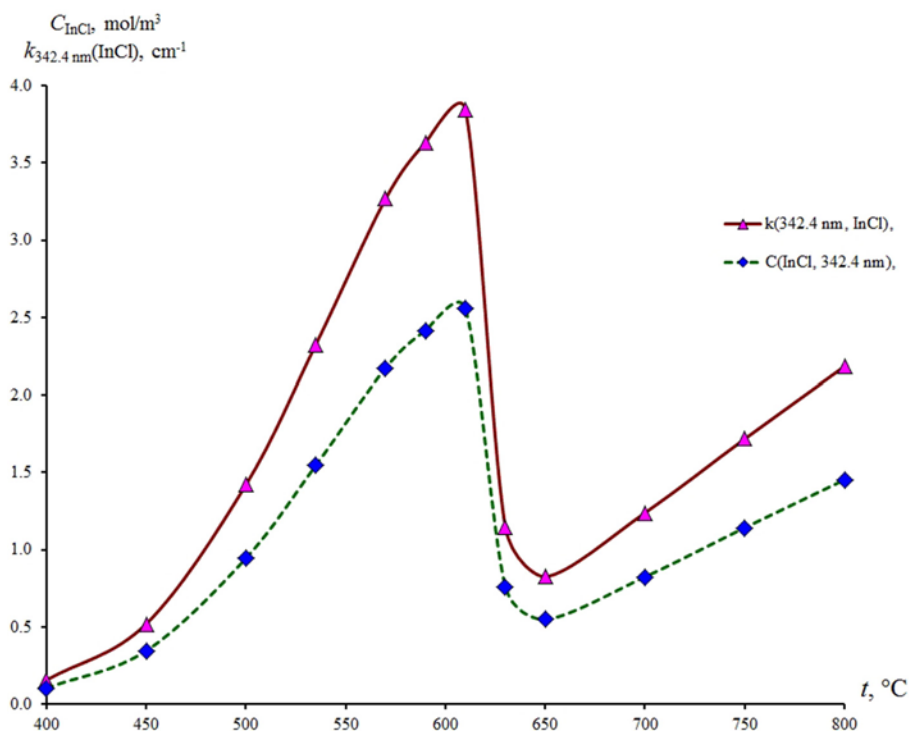
Fig. 7. Temperature dependences of the optical absorption coefficient of the InCl vapour for the wavelength of 342.4 nm (curve *1*) and concentrations of InCl in vapour (curve *2*) over the whole studied temperature range (400 – 800 °C). Equilibrium of the unsaturated indium chloride vapour with alloy 1 (49.9 mol% Se composition, phase 2H-InSe, and traces of In_4Se_3)

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Taking into account the incongruent melting of the studied sample, a further increase in temperature should obviously result in the increased amount of melt in the system. Then the amount of vapour absorbed by the melt may increase with the temperature, and the concentration of chlorides remaining in the vapour may decrease within the range from the temperature of incongruent melting to the temperature corresponding (for this alloy composition) to the liquidus line.

This reduction should stop at a temperature similar to liquidus as the selenide sample becomes a homogeneous alloy under these conditions, while the solubility of gas a homogeneous liquid should decrease when the temperature increases. Indeed, as for alloy 1, the reduction of light absorption characteristic for InCl with an increase of temperature coincided with the melting temperature of InSe (610 °C according to the data from [24]) and stopped at about 650 °C, which also corresponded well with the value of the temperature for the point on the liquidus line corresponding to the composition of this alloy.

The same reasoning can also be used for the equilibria of chloride vapour with any other samples of the In – Se system. Indeed, in the experiment with alloy 2 the temperature of the beginning of the reduction of absorption (and, correspondingly, concentration) of InCl in the vapour (665 °C) correlated well with the incongruent phase melting temperature of In_6Se_7 (663 °C according to the data from [24]).

Therefore, the obtained effect allows constructing a phase diagram of the In – Se system in the region of coexistence of the liquid and solid phases and identifying the solidus and liquidus lines using an independent static method (Fig. 8). It should be noted that a similar method has already been used by one of the authors of this work for the construction of the *T-x* diagram of the Ga – Se system [25].

3. Conclusions

It can be concluded that the spectrophotometric study of a set of alloys of the In – Se system with various compositions conducted using indium chlorides will allow clarifying the issue of phase relationships in the studied system. However, such a study goes beyond the goals and objectives of this work. Our experiments based on the example of a specific system showed that it is possible to use the promising auxiliary component method and high-temperature spectrophotometry as an instrumental basis for this method. We also showed additional possibilities of this method for plotting *T-x* diagrams of binary systems in such high-temperature areas where the binary solid phase is in equilibrium with the melt. This application of the method is related to the solubility of vapour of an auxiliary component (chlorine in the form of indium chlorides) in the melts of binary phases (indium selenides).

APPENDIX

Let us analyse the data on the **unsaturated** vapour of $InCl_3$. Fig. 2 shows the change in the nature of the temperature dependence related to the "saturated vapour – unsaturated vapour" transition, and this transition becomes even more evident in Fig. 3 in the form of a fracture in point b on the dependence of the $\ln(k_{240\,nm}(InCl_3)\cdot R\cdot T)$ value on reciprocal temperature. In the area
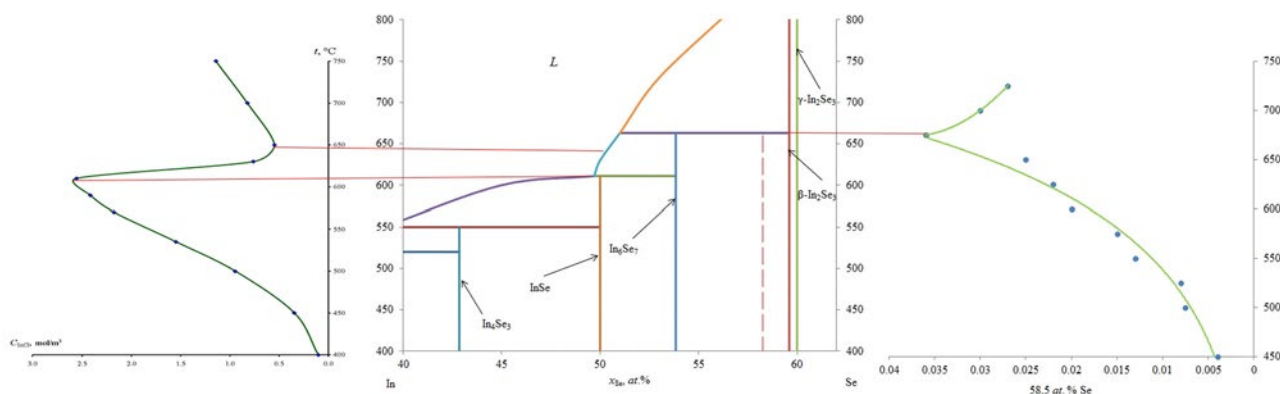
Fig. 8. Fragment of a *T – x* diagram of the In – Se system according to the data from [24] and temperature dependences of the concentration of InCl vapour that is in equilibrium with the alloys of the In – Se system with selenium content of 49.9 mol% (on the left) and 58.5 mol% (on the right)

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of **un**saturated vapour (line |*bc*| Fig. 3), we should pay attention to the ongoing increase of characteristic absorption of InCl$_3$ together with the temperature (Fig. 2, spectra at $t \geq 425$ °C). We associated this phenomenon with the increase of the concentration of InCl$_3$ molecules in the vapour, which is explained by the following. According to [15, 17], both monomer (InCl$_3$) and dimer molecules (In$_2$Cl$_6$) must be present in the indium trichloride vapours under the conditions similar to our experiment, while dimer molecules do not appear in the studied spectral area [15]. Increased temperature shifts the equilibrium in the unsaturated vapour towards the monomer [17]. In its turn, this should lead to an increase in the concentration of indium trichloride in unsaturated vapour when temperature increases.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about the authors

Nikolay Yu. Brezhnev, Junior Researcher in Chemistry, PhD student, Department of General and Inorganic Chemistry, Voronezh State University; Voronezh, Russian Federation; e-mail: brezhnevnick@gmail.com. ORCID iD: https://orcid.org/0000-0002-3287-8614.

Andrey V. Kosyakov, PhD in Chemistry, Assistant Professor, Department of General and Inorganic Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail: lavchukb@mail.ru. ORCID iD: https://orcid.org/0000-0001-9662-7091.

Anastasia V. Steich, Student, Department of General and Inorganic Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail: Nastya.steitch@yandex.ru. ORCID iD: https://orcid.org/ 0000-0003-3945-896X.

Alexander Yu. Zavrazhnov, DSc in Chemistry, Professor at the Department of General and Inorganic Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail: alzavr08@rambler.ru. ORCID iD: https://orcid.org/ 0000-0003-0241-834X.

Translated by Marina Strepetova
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