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PHASE EQUILIBRIUM LIQUID-VAPOR IN THREE-COMPONENT SYSTEM UF_6 - IF_5 - BrF_3 AT COMPLETE MUTUAL COMPONENTS SOLUBILITY

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The results of studying phase equilibrium liquid-vapor at 353,15 K in the system of uranium hexafluoride, iodine pentafluoride, bromine trifluoride have been presented. The dependences of saturated vapor pressure on condensed phase composition, the results of analysis of studied system deviation from error-free behavior, the data on equilibrium vapor phase are given.

Applying halogen-fluorides in processing materials of nuclear power engineering is of great importance. Use of halogen-fluoride mixture for fluoridation of uranium-containing compounds is rather actual. Applying gaseous mixture BrF_3 - IF_5 for these purposes allows fluoridating uranium compounds at low temperatures and pressures in contrast to elemental fluoride [1]. In this case multi-component systems are formed. They contain uranium hexafluoride and halogen-fluorides which should be separated for extracting pure UF_6 and regeneration of fluoridating agents. Besides, using halogen-fluorides and their mixtures at processing nuclear fuel improves significantly process variables and reduces production string and decreases considerably waste volumes.

Thermodynamics of phase equilibrium liquid-vapor of three-component system UF_6 - IF_5 - BrF_3 at temperature 353,15 K was studied. As the given system at the specified temperature has unlimited reciprocal components solubility [2, 3] heterogeneous equilibrium between liquid and vapor was studied.

For researching phase equilibria in three-component systems the selection of changing technique of three-component system composition is of great importance [4, 5]. We selected the technique of composition changing by secant planes passing through the top meeting uranium hexafluoride. The triangle of Gibbs-Rosebum compositions of three-component system UF_6 - IF_5 - BrF_3 indicating secants by which the compositions of condensed system were changed is presented in Fig. 1.

The composition was changed adding uranium hexafluoride to the mixture of iodine pentafluoride and bromine trifluoride the content of which in the mixture decreases at hexafluoride addition. However, the ratio of

concentrations x_{IF_5} to x_{BrF_3} remains constant along the whole secant and expressed by the coefficient a_i :

$$a_i = \frac{x_{IF_5}}{x_{BrF_3}} = \text{const},$$

where i is the number of the plane.

Thus, each secant may be presented in the form of pseudobinary system in which uranium hexafluoride is one of the components and another one is the mixture of iodine pentafluoride and bromine trifluoride at constant ratio of the components

According to the experimental data of the dependence of saturated vapor pressure on solution composition at constant temperature the dependence of saturated vapor pressure on liquid and vapor phases composition was calculated on the basis of Wilson equation [6]. The dependences of saturated vapor pressure on liquid phase composition for the system UF_6 - IF_5 - BrF_3 by the secants with corresponding values of the coefficient a_i are given in Fig. 2.

One of the peculiarities of the system UF_6 - IF_5 - BrF_3 is different character of deviations from Raoult law in binary system constituents. In three-component systems it should be taken into consideration that factors influencing the character of deviation from the ideal behavior act simultaneously in solution therefore the deviations observed in three-component systems are the result of overlapping deviations opposite in sign which are introduced by each component. As it was stated in the work [5] very often simultaneous action of opposite factors and deviation character are mainly defined by condensed system composition.

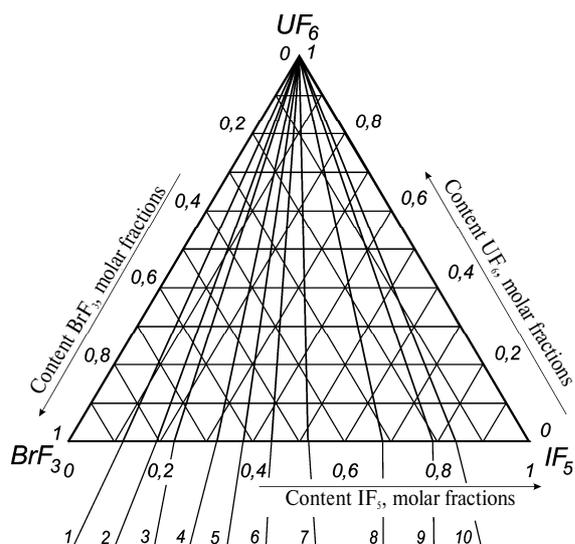


Fig. 1. Secants at the triangle of compositions of the system UF_6 - IF_5 - BrF_3 at a : 1) 0,13; 2) 0,23; 3) 0,29; 4) 0,47; 5) 0,61; 6) 0,78; 7) 1,08; 8) 2,12; 9) 3,76; 10) 5,25

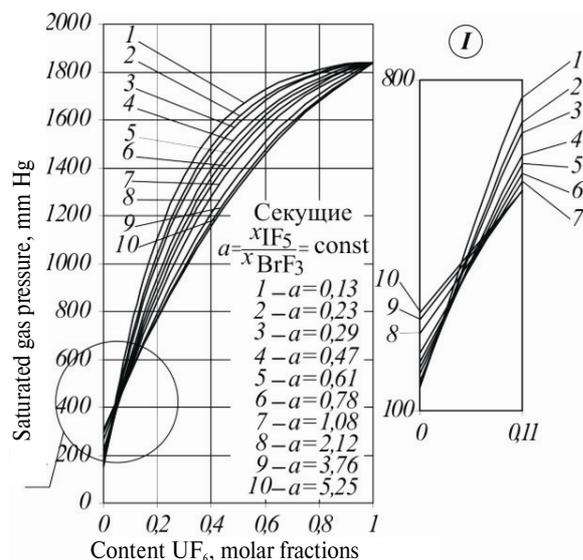


Fig. 2. Dependence of saturated vapor pressure on liquid composition in three-component system UF_6 - IF_5 - BrF_3 by secants

General deviation from Raoult law in the system UF_6 - IF_5 - BrF_3 was estimated in the following way. Deviation from the ideal behavior observed in any real systems when studying phase equilibria in isothermal conditions may be expressed as the ratio of saturated vapor pressure observed in the studied system to the pressure of ideal saturated vapor calculated by Raoult law and additive Dalton law [5, 7]. Thus, denoting system deviation in the whole from the ideal behavior by coefficient η it may be expressed by the equation:

$$\eta = \frac{P}{P'}$$

where P is the saturated vapor pressure observed in real system; P' is the saturated vapor pressure observed in ideal system, calculated by Raoult law. In this case it is obvious that if the deflection coefficient is greater than a unit

($\eta > 1$) then real pressure in the system exceeds the ideal one and deflection in the system is positive, at $\eta < 1$ the deflection from ideal behavior in the system is negative.

The deflection coefficient η for the system UF_6 - IF_5 - BrF_3 was calculated by the equation:

$$\eta = \frac{P_{UF_6}^0 \cdot x_{UF_6} \cdot \gamma_{UF_6} + P_{IF_5}^0 \cdot x_{IF_5} \cdot \gamma_{IF_5} + P_{BrF_3}^0 \cdot x_{BrF_3} \cdot \gamma_{BrF_3}}{P_{UF_6}^0 \cdot x_{UF_6} + P_{IF_5}^0 \cdot x_{IF_5} + P_{BrF_3}^0 \cdot x_{BrF_3}}, (*)$$

where $P_{UF_6}^0$, $P_{IF_5}^0$, $P_{BrF_3}^0$ are elasticity of pure UF_6 , IF_5 and BrF_3 vapors; x_{UF_6} , x_{IF_5} , x_{BrF_3} is the content of UF_6 , IF_5 and BrF_3 in liquid phase, molar fractions; γ_{UF_6} , γ_{IF_5} , γ_{BrF_3} are the activity factors of UF_6 , IF_5 and BrF_3 .

It is necessary to keep in mind that the deflection coefficient η is the characteristic of one of the set of points in the field of compositions of the system UF_6 - IF_5 - BrF_3 , therefore for the equation (*) it is necessary to fulfill the condition:

$$x_{UF_6} + x_{IF_5} + x_{BrF_3} = 1.$$

Dependence of deflection coefficient η logarithms from three component mixture composition at 353,15 K for all ten secants is presented in Fig. 3. The existence domain of negative deflection in the system UF_6 - IF_5 - BrF_3 , Fig. 3 (I), and existence domain of positive deflection from Raoult law are seen from Fig. 3. In this case at uranium hexafluoride dominance in condensed phase in the system UF_6 - IF_5 - BrF_3 the positive deflection is observed. Transition from positive deflection to the negative one is stipulated by halogen fluorides dominance in the system UF_6 - IF_5 - BrF_3 therefore properties of three component system in this region are close to the properties of the system IF_5 - BrF_3 .

The regularity is well seen from Fig. 3: changing the composition of the system UF_6 - IF_5 - BrF_3 from binary system UF_6 - BrF_3 to the system UF_6 - IF_5 (increasing a), deflection coefficient η decreases. In this case the peak typical for the system UF_6 - BrF_3 ($x_{UF_6}=0,11$ molar fractions, Fig. 3) adding iodine pentafluoride to the system UF_6 - IF_5 - BrF_3 shifts to the peak in the system UF_6 - IF_5 ($x_{UF_6}=0,32$ molar fractions, Fig. 3). This phenomenon may be explained in the following way. Molecules of bromine trifluoride and iodine pentafluoride interact differently with molecules of uranium hexafluoride. So increasing iodine pentafluoride content in liquid phase of the system UF_6 - IF_5 - BrF_3 forces of intermolecular interactions in solution increase that results in decrease of positive deflection of the system from the ideal behavior.

As it was stated before factors influencing the character of deflections from the ideal behavior act simultaneously in solution therefore, deflections observed in real systems are the result of overlapping the deflection of opposite signs which are introduced by each component.

The numerator of the equation (*), which describes total deflection of the system UF_6 - IF_5 - BrF_3 from the ideal behavior consists of three members. Each of them includes elasticity of pure component vapor – the constant, component concentration in solution and activity coefficient of the same component. The latter depend on solution composition and their changes are given in Fig. 4.

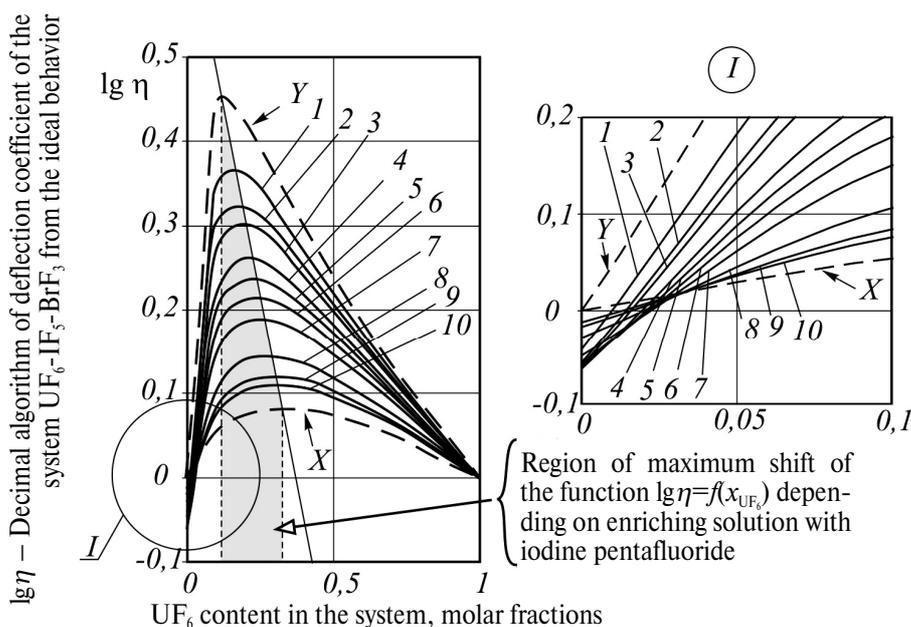


Fig. 3. Dependence of $\lg \eta$ on content of UF_6 in condensed system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$ at secants a : 1) 0,13; 2) 0,23; 3) 0,29; 4) 0,47; 5) 0,61; 6) 0,78; 7) 1,08; 8) 2,12; 9) 3,76; 10) 5,25. X, Y – dependence of $\lg \eta$ for content of UF_6 in systems $\text{UF}_6\text{-IF}_5$ and $\text{UF}_6\text{-BrF}_3$

It is seen from Fig. 4 that logarithm values of activity coefficients of uranium hexafluoride are greater than zero in the whole region of compositions of three component system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$.

For iodine pentafluoride (Fig. 4, б) there is a number of concentrations in the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$, at which logarithm of its activity coefficients has negative values and they appear to the greatest degree when increasing bromine trifluoride concentration that is shifting concentration in the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$ to the binary system $\text{UF}_6\text{-BrF}_3$.

For bromine trifluoride (Fig. 4, в) there is also a range of concentrations in the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$, at

which activity coefficient logarithm of this component has the highest negative values and the region of negative values $\lg \gamma \text{BrF}_3$ is close to the system $\text{UF}_6\text{-IF}_5$.

It is also seen from Fig. 4 that it is in the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$ when opposite factors act simultaneously. Deflection which is observed in the system in whole is the result of imposition of deflections opposite in sign.

To analyze the distillation system separation the data on system component content in vapor phase are necessary. For this purpose the graphical interpolation of the obtained experimental and calculated data by phase

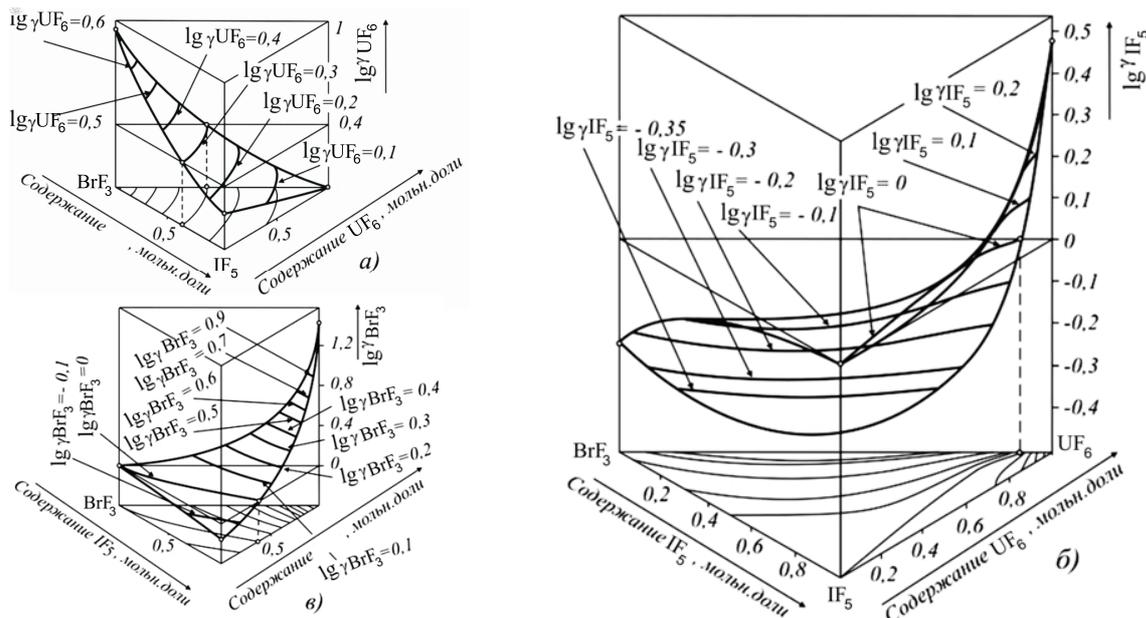


Fig. 4. Dependences of activity coefficient logarithms of UF_6 (Fig. 4, а), IF_5 (Fig. 4, б) and BrF_3 (Fig. 4, в) on composition of the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$

equilibrium liquid-vapor in the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$, given above was carried out.

The technique of graphical interpolation of the experimental data consists in the following. To plot the lines of constant content of uranium hexafluoride in vapor phase the diagram of dependence of uranium hexafluoride in vapor on its content in liquid is plotted for all secants stated above (Fig. 5).

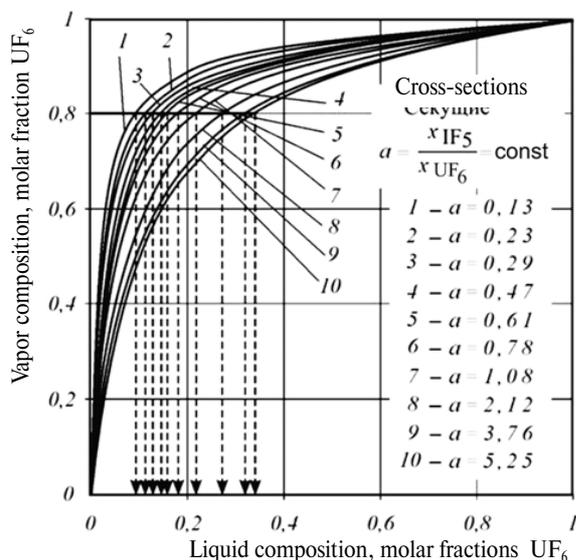


Fig. 5. Dependence of UF_6 content in vapor on its content in liquid in the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$

Then by these magnitudes the UF_6 content in liquid phase at its constant content in vapor phase for all secants is determined and these data are plotted to the triangle of concentrations. The lines of constant content of uranium hexafluoride in vapor phase are drawn through the obtained points.

The lines of constant content of vapor for UF_6 and IF_5 are shown in Fig. 6. Content of the third component, BrF_3 , may be determined from the condition:

$$y_{\text{UF}_6} + y_{\text{IF}_5} + y_{\text{BrF}_3} = 1.$$

The obtained diagram, Fig. 6, describes the change of saturated vapor composition depending on liquid composition. The given diagram may be used not only for calculation of separation processes of the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$ by distillation techniques but also for calculation of other technological processes where the data on vapor phase composition being in equilibrium with the condensed system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$ of any composition are required.

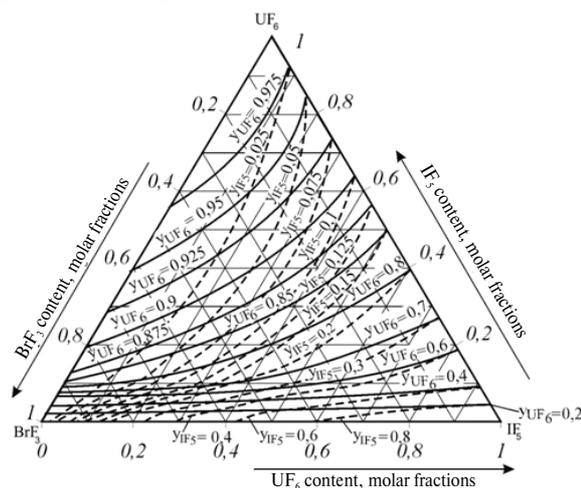


Fig. 6. Lines of UF_6 and IF_5 constant content in vapor phase of the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$

As a result of investigations of phase equilibrium in the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$ at 353,15 K the dependences of saturated vapor pressure on composition of condensed and vapor phase of the system were obtained, the character of system deflection from the ideal behavior was analyzed, lines of constant content of uranium hexafluoride and iodine pentafluoride in vapor phase were plotted. All obtained data may be used for calculation and design of separation processes of the system $\text{UF}_6\text{-IF}_5\text{-BrF}_3$ by distillation techniques.

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