Journal of Fluorine Chemistry 130 (2009) 108–116

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Separation of systems based on uranium hexafluoride and some of halogen fluorides

R.V. Ostvald [a,*], V.V. Shagalov [a,1], I.I. Zherin [a,1], G.N. Amelina [a,1], V.F. Usov [a,1], A.I. Rudnikov [b,2], O.B. Gromov [c,3]

[a] *Tomsk Polytechnic University, Lenin Avenue 30, Tomsk 634050, Russian Federation*[4]
[b] *Siberian Group of Chemical Enterprise, Kurchatov St. 1, Seversk, Tomsk Region 636000, Russia*[5]
[c] *All-Russian Research Institute of Chemical Technology, Kashirskoye Shosse 33, Moscow 115409, Russia*

ARTICLE INFO

Article history:
Received 28 February 2008
Received in revised form 19 June 2008
Accepted 16 July 2008
Available online 3 August 2008

Keywords:
Uranium hexafluoride
Bromine trifluoride
Iodine pentafluoride
Phase equilibrium diagram
Statistical method of research of phase equilibrium
Lines of extensible evaporation
Processes of sorption and desorption

ABSTRACT

The purpose of this paper is to present the results of the comprehensive study of the phase equilibriums liquid–solid and liquid–vapour in binary and ternary systems, formed by uranium hexafluoride, bromine trifluoride and iodine pentafluoride.

Investigation of the phase equilibriums in condensed systems is done by methods of differential thermoanalysis and visual polythermal analysis. All systems belong to simple eutectics; formation of the compounds is not detected. For all systems under investigation diagrams of the phase equilibrium liquid–solid are plotted.

Phase equilibriums liquid–vapour in studied systems were studied by statistical method. All systems are non-aseotropic. The article presents diagrams of the phase equilibrium liquid–vapour in binary systems, pressure of the saturated vapour dependences on liquid composition, surface of the boiling liquid and lines of the constant content of uranium hexafluoride and iodine pentafluoride in vapour phase of the ternary system UF_6–BrF_3–IF_5.

1. Introduction

Historically, development of the fluorine process engineering is connected with development of nuclear-power engineering. First of all it is connected with production processes for volatile uranium hexafluoride. The processes of fluorination in atomic engineering technologies, however, are not limited only to manufacture of uranium hexafluoride using fluorine and far from all the problems can be solved using the latter. From this point of view, fluorides of halogens (ClF_3, BrF_3, etc.) are rather perspective. By chemical activity they compare well with fluorine, being the strongest fluorinating oxidizers and nonaqueous ionizing solvents, so they can be applied both in liquid and in vapourous states including in the form of synergetic mixes. Now one can single out two most perspective problems to be solved by means of halogen fluorides.

One of them is the problem of removing the uranium-containing deposits in uranium enrichment at centrifuge manufactures. From the beginning of separating manufacture there appeared a problem of accumulation of solid radioactive deposits which formation is caused by interaction of UF_6 with the basic constructional materials and with air moisture which inevitably accumulates in cascades of devices. It causes the deposition of significant amounts of uranium (in the form of fluorides and oxofluorides) resulting in product losses and decrease in nuclear safety of the manufacture, and in the returned fissile material processing, decay daughters accumulate in the deposit: U-232, Th-228, Tc-99 and other elements, which rather aggravates the radiation environment.

As a result of cooperative research of the Institute of molecular physics, RRC “Kurchatov Institute”, the Siberian chemical complex (SCC) and Tomsk Polytechnic University carried out in ninetieth, the technology of removal of uranium-containing deposits from gas centrifuges (GC) working in nominal conditions was developed with use of synergetic mix of BrF_3–IF_7 vapours.

Another field of application of halogen fluorides is the recycling of the irradiated nuclear fuel (INF). Fluorination of INF allows one

---

[*] Corresponding author. Tel.: +7 383 341 89 05; fax: +7 383 341 89 01.
E-mail address: Ostvald@phtd.tpu.ru (R.V. Ostvald).
[1] Tel.: +7 3822 56 34 70; fax: +7 3822 56 38 65.
[2] Tel.: +7 382 272 44 46; fax: +7 382 272 44 46.
[3] Tel.: +7 495 324 61 05; fax: +7 495 324 54 41.
[4] tpu@tpu.ru.
[5] SHK@seversk.tomsknet.ru.

0022-1139/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2008.07.020

to produce UF_6 as early as at the first stage and to separate it from non-volatile fluorides of the fission products. It shortens the INF processing scheme and reduces considerably the volumes of liquid radioactive waste. The fluoride technology can be used for processing any type of INF that allows it to be the principal one in a nuclear fuel cycle. Possibilities of application of halogen fluorides for processing INF are discussed in a number of papers [1,2]; the high efficiency of processes of uranium-containing compounds fluorination with use of BrF_3 and ClF_3 both in gas and liquid phases was shown by the authors. From all fluorinating reagents, the most suitable one is BrF_3 due to its good combination of reactivity and operational characteristics. Bromine trifluoride transforming any uranium compounds in the volatile hexafluoride is thermodynamically capable to fluorinate plutonium and its compounds only to non-volatile PuF_4. It allows a number of problems connected with distribution of plutonium in a technological scheme to be solved already at the fluorination stage.

As a result of carrying out the fluorination processes using halogen fluorides, there formed multicomponent systems of various compositions consisting of UF_6, IF_7, IF_5, BrF_3, HF and other noncondensable gases. To use halogen fluorides in processes of fluorination of uranium compounds and to apply this process in industry, it is necessary to develop a separation technology for the multicomponent systems forming as a result of fluorination processes. For such a technology to be developed, the complete data about physical and chemical properties are necessary including figures of phase equilibrium between the condensed and vapour phases.

This work is devoted to the analysis of phase equilibria between a liquid and a solid phase, a liquid and vapour in the system UF_6–IF_5–BrF_3 with the aim to estimate the possibility of application of distillatory and rectificative methods for separation of the system under study.

2. Results and discussion

2.1. Study of phase equilibria between liquid and solid phases in UF_6–IF_5–BrF_3 system

Analysis of equilibrium between liquid and solid phases was made with the purpose of substantiation of composition and temperature areas for distillatory and rectificative processes, and for estimation of possibility to separate the system UF_6–IF_5–BrF_3 into components by means of the crystallization method.

When studying solubility in binary and ternary systems, the phenomena of significant overcooling were observed in BrF_3 and IF_5, but the value of overcooling varied from experiment to experiment and ranged from 5° up to 30°. For this reason, mixes with compositions belonged to areas of halogen fluoride crystallization, were mainly investigated by means of heating curves.

At the first stage, the solubility of components in binary systems UF_6–IF_5 and BrF_3–IF_5 were studied [3,4]; the solubility of uranium hexafluoride in the system UF_6–BrF_3 is described in paper [5].

Bromine trifluoride and iodine pentafluoride form a simple eutectic system, chemical compounds were not found out in the system (Fig. 1a). A solubility diagram in the system is close to the symmetric one, the eutectic mix contains (0.580 ± 0.005) molar fraction of BrF_3, its melting point is (-27.0 ± 0.5) °C.

Both components of the system show an insignificant negative deviation from the ideal solubility (Fig. 1a). It suggests an intermolecular interaction between the components with formation of heteromolecular solvates or ionic associates. Symmetry of the fusibility diagram structure, similar values of activity factors of the components for corresponding concentrations of substances, insignificant negative deviations of the system from the ideal one, absence of compounds in the condensed state imply that donor–acceptor properties of BrF_3 and IF_5 are similar. Therefore, ionized solvates as $BrF_2^+ IF_6^-$ and $IF_4^+ BrF_4^-$ can be suggested to exist in the liquid phase.

Uranium hexafluoride and iodine pentafluoride form a simple eutectic system with a positive deviation from the ideal one (Fig. 1b). The eutectic contains (0.135 ± 0.005) molar fraction of UF_6 and melts at temperature of (3 ± 0.4) °C. Judging by eutectic curves, one can conclude that the formation of a new chemical compound does not occur in the system UF_6–IF_5.

Activity factors of the components were determined using known equations by Hildebrand–Sketchard with correction introduced by Flory–Huggins, by Margules one-parametrical, by Margules two-parametrical, by van Laar two-parametrical, and by Wilson [6] (Fig. 2).

Values of the components activity factors in condensed system UF_6–IF_5 are shown in Table 1. It was calculated by the following

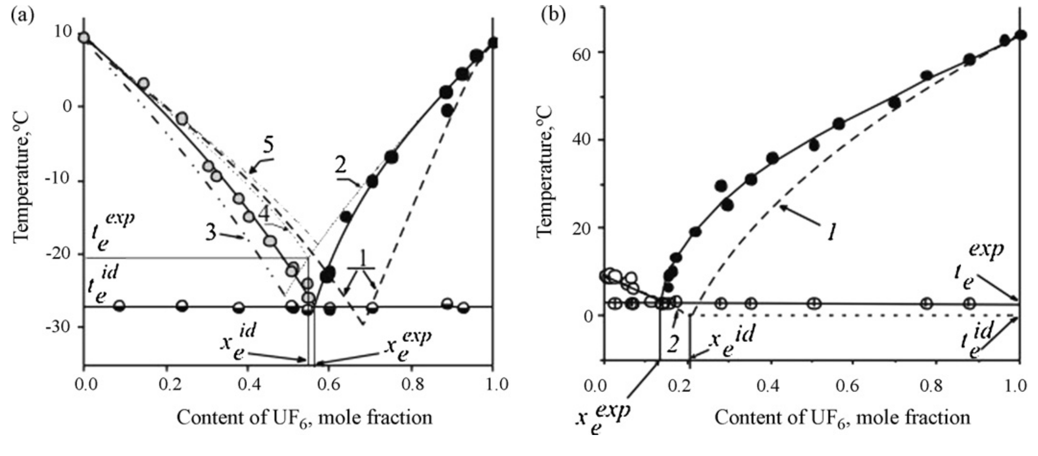

Fig. 1. Experimental data and ideal solubility of components in the systems. (a) The system BrF_3-IF_5; ●—liquidus of BrF_3 (experimental data); ●—liquidus of IF_5 (experimental data); ●—melting temperature of the eutectic mixture, (experimental data); x_e^{exp} and t_e^{exp} —composition and melting temperature of the experimental eutectic; 1—ideal solubility BrF_3 and IF_5 calculated on Raoult equation [6]; 2—ideal solubility BrF_3 calculated on Schroeder–Le Chatelier equation [6]; 3—ideal solubility IF_5 calculated on Schroeder–Le Chatelier equation with melting heat 2.682 kcal/mol; 4 – ideal solubility IF_5 calculated on Schroeder–Le Chatelier equation with melting heat 3.800 kcal/mol; 5—ideal solubility IF_5 calculated on Schroeder–Le Chatelier equation with melting heat 4.010 kcal/mol x_e^{id} and t_e^{id} —composition and melting temperature of the ideal eutectic. (b) The system UF_6–IF_5; ●—liquidus of UF_6 (experimental data); ○—liquidus of IF_5 (experimental data); ⦶—melting temperature of the eutectic mixture, (experimental data); Ideal solubility UF_6 (1) and IF_5 (2) calculated on Schroeder–Le Chatelier equation; x_e^{exp} and t_e^{exp} —composition and melting temperature of the experimental eutectic; x_e^{id} and t_e^{id} —composition and melting temperature of the ideal eutectic.

equation:

$$\gamma_i = \frac{x_i^{\text{ideal}}}{x_i}, \qquad (1)$$

where x_i^{ideal} is the ideal solubility of i-compound, which was calculated on Schroeder–Le Chatelier equation, mole fraction; x_i is the experimental data about solubility of i-compound, mole fraction.

The equations by Margules, van Laar and Wilson are semiempirical, the empirical parameters were used for calculation of activity factors and solubility of the components (Fig. 3). It is evident from the figure that in the system UF_6–IF_5 good correlation of experimental data of UF_6 solubility was observed when the equations by Margules, van Laar and Wilson were used. For the system BrF_3–IF_5 the results of calculations are in agreement with experimental values of solubility. In the system UF_6–BrF_3 none of the equations describes experimental data of UF_6 solubility with high accuracy.

For the experimental study of phase equilibria and interpretation of the data in the ternary system UF_6–IF_5–BrF_3, a method of composition change along the secants going through a top point of UF_6 and through the IF_5–BrF_3 binary system.

For all 11 secants, plots of phase transition temperatures as a function of UF_6 content are constructed (for the secant no. 10 it is presented in Fig. 4). As well as in binary systems with BrF_3 and IF_5, in the ternary system UF_6 shows only a positive deviation

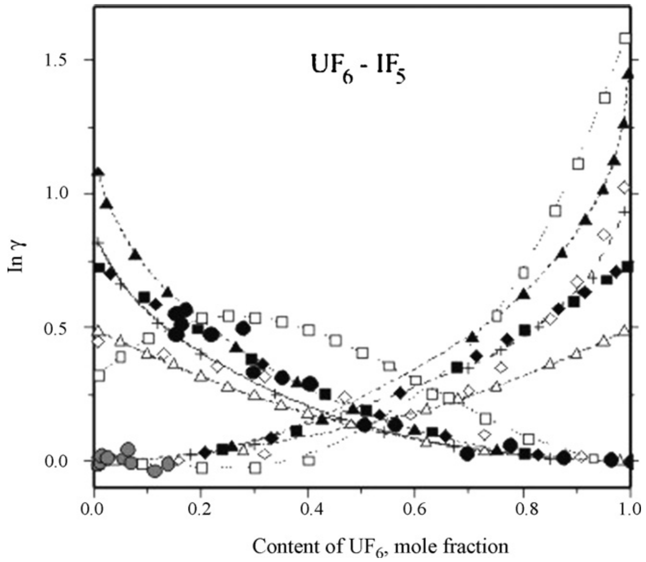

Fig. 2. Dependence of activity factors in the system UF_6–IF_5, which calculated on Margules, Van Laar and Wilson equations; ●: experimental data; ◉: experimental data; activity factors, calculated on equations: - -▲- -: Margules 1-parametric on all experimental data; - -△ - -: Margules 1-parametric on eutectic; - -■ - -: Margules 2-parametric on all experimental data; - - □:- -: Margules 1-parametric on eutectic; - -◆ - -: Van Laar on all experimental data; - -◇- -: Van Laar on eutectic; -+-: Wilson.

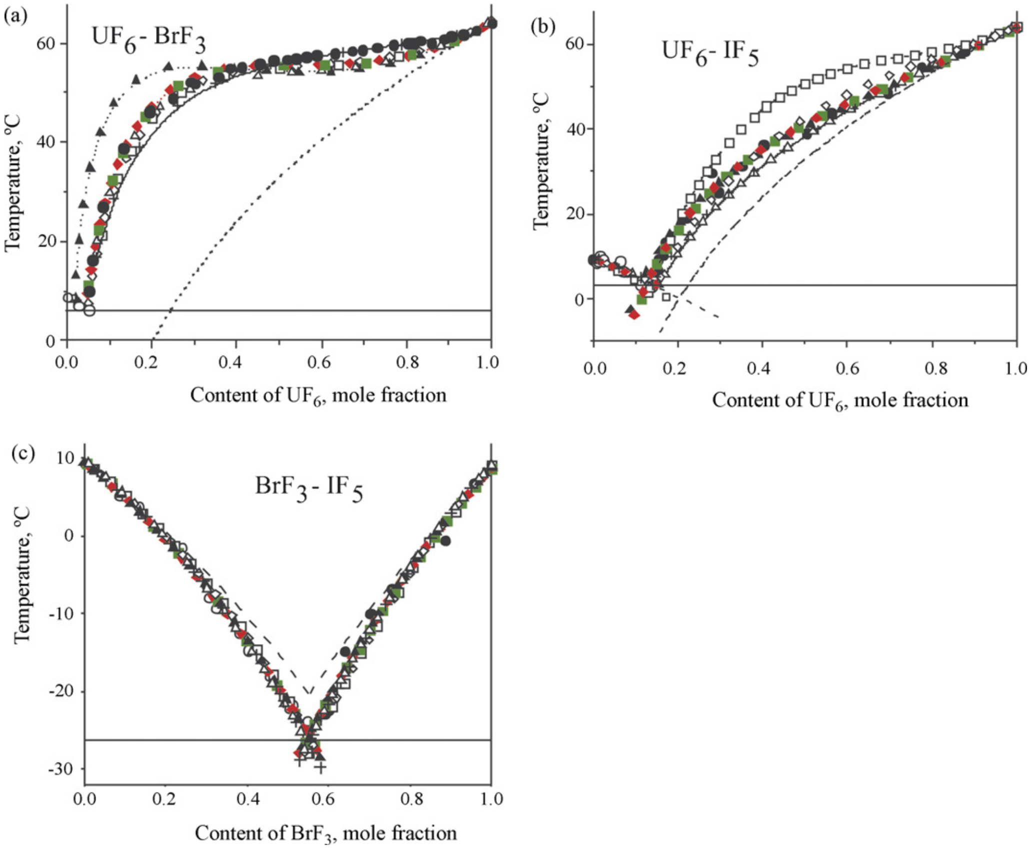

Fig. 3. Solubility of components in the systems UF_6–BrF_3, UF_6–IF_5 and BrF_3–IF_5, calculated on equations of Margules, Van Laar and Wilson, Experimental data: ●—in systems UF_6–BrF_3 and UF_6–IF_5 solubility of UF_6, in system BrF_3–IF_5 solubility of BrF_3; ○—in system UF_6–BrF_3 solubility of BrF_3, in system UF_6–IF_5 solubility of IF_5, in system BrF_3–IF_5 solubility of IF_5; -.-.-.-: ideal solubility of the components, calculated on equation Schroeder–Le Chatelier; solubility of the components calculated for all experimental data on eqs.; ◆: Van Laar 2-parametric; 🟩: Margules 2-parametric; –▲–: Margules 1-parametric; –+–: Wilson; solubility of the components calculated for data about eutectic on eq.: –△–: Margules 1-parametric; ◇: Van Laar 2-parametric; –□–: Margules 2-parametric.

Table 1
Values of the components activity factors in condensed system UF_6–IF_5 in dependence of system composition

Concentration of UF_6 (mole fraction)	Temperature (°C)	Activity factor of UF_6	Concentration of UF_6 (mole fraction)	Temperature (°C)	Activity factor of IF_5
1.000	64.05	1.000	0.000	9.4	1.000
0.900	59.4	1.008	0.045	7.5	1.002
0.800	55.0	1.033	0.100	5.3	1.009
0.700	50.8	1.075	0.135	3.2	1.018
0.600	46.2	1.139	–	–	–
0.500	41.4	1.220	–	–	–
0.400	35.4	1.329	–	–	–
0.300	27.8	1.463	–	–	–
0.200	16.4	1.635	–	–	–
0.135	3.2	1.752	–	–	–

from ideality, whereas BrF_3 and IF_5 both positive and negative deviations.

The method of composition change in the ternary system along the secants allows one to describe solubility of UF_6 using the equations by Margules, Van Laar and Wilson (Fig. 4). Wilson's equation for binary systems showed the highest accuracy of correlation of experimental data concerning UF_6 solubility in pseudo-binary systems UF_6–(BrF_3 + IF_5).

Fig. 5 shows the spatial pattern of equilibrium diagram of the condensed system UF_6–BrF_3–IF_5. The isothermal plane (*ABC*) shows temperature of the triple eutectic point E located on (*ABC*) is a composition of the triple eutectic. Below this plane all the components of the system are in solid state.

Solubility isotherms of uranium hexafluoride are shown in Fig. 6. The system UF_6–BrF_3–IF_5 belongs to the simple eutectic type. The temperature of the triple eutectic determined experimentally from heating curves is equal to −32.2 °C. Composition of the triple eutectic corresponds to the following content of components (in mole fractions): (0.007 ± 0.003) of UF_6; 0.561 of BrF_3 and 0.432 of IF_5. The phenomenon of lamination was not revealed in the examined system. In carrying out the processes of mixes crystallization, to separate completely any component in its pure form is impossible.

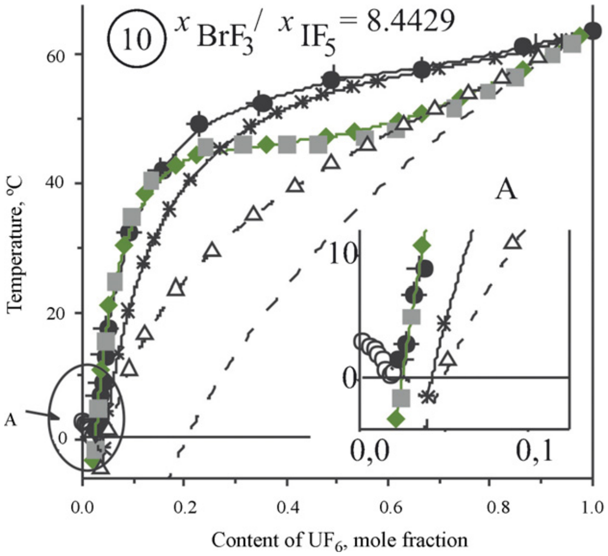

Fig. 4. Solubility of components in the system UF_6–IF_5–BrF_3 calculated on equations of Margules, Van Laar and Wilson. 10 Number of secant; $a = (x_{BrF_3}/x_{IF_5})$: ratio BrF_3 and IF_5 in system, ●: solubility of UF_6, experimental data; ○: solubility of BrF_3, experimental data; – – – –: ideal solubility of UF_6, calculated on equation Schroeder–Le Chatelier; solubility of UF_6, calculated on equations -△-: Margules 1-parametric; —■—: Margules 2-parametric; —◆—: Van Laar 2-parametric; –+–: Wilson for binary systems; –*–: Wilson for plural-component systems.

2.2. Study of phase equilibria of liquid–vapour in ternary system UF_6–IF_5–BrF_3 and in double systems composting at 80 °C

The composition of investigated systems includes the components which are closely like in their physical and chemical properties (BrF_3 and IF_5), and UF_6 with symmetric molecule structure. At temperatures below 64.05 °C the specified systems have limited solubility of UF_6, a static method was used for their study.

Results of study of phase liquid–vapour equilibrium in the system UF_6–BrF_3 at 80 °C are presented in Fig. 7a. The system has no azeotrope and is governed by the laws of vapour–liquid equilibrium.

The system shows a significant positive deviation from Raoult's law [6]. It may be explained by the fact that only dispersive (London) interactions can be the sole possible type of interactions in solutions between UF_6 molecules.

Experimental data for phase equilibria of liquid–vapour at 80 °C in the system UF_6–IF_5 are given in Fig. 7b. At these

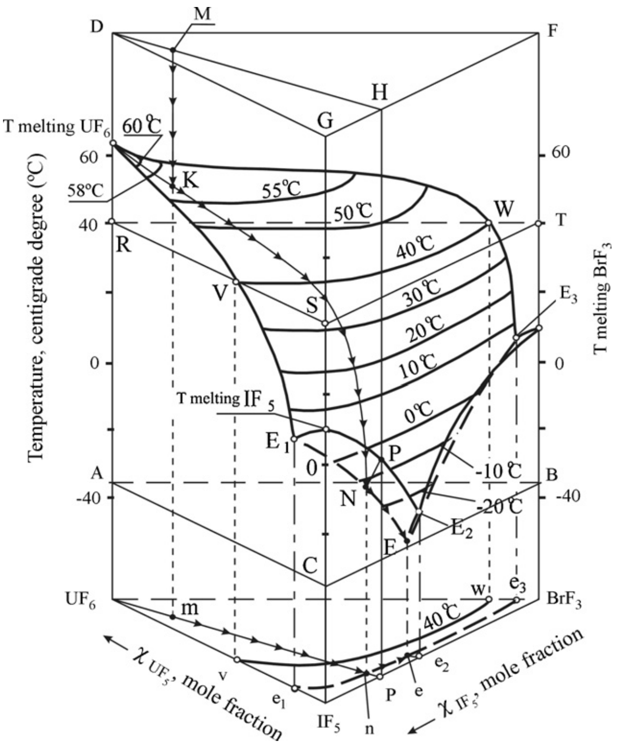

Fig. 5. The spatial pattern of equilibrium diagram of the condensed system UF_6–BrF_3–IF_5. E: eutectic in triple system; E_1, E_2, E_3: eutectics in binary systems; e, e_1, e_2, e_3: projections of eutectic points.

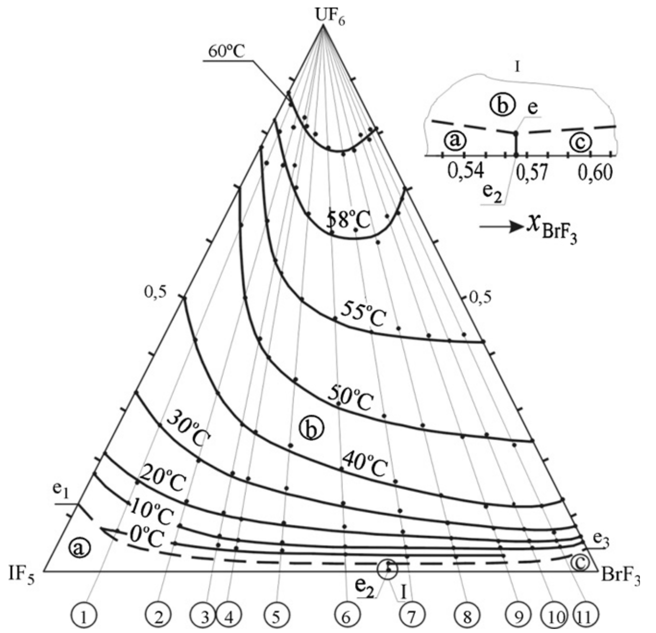

Fig. 6. The isotherms of UF_6 solubility in system UF_6–IF_5–BrF_3. —●—: isotherms of UF_6 solubility; --: line of crossing crystallization fields; e: eutectic in triple system UF_6–IF_5–BrF_3 (−32.2 °C); e_1: eutectic in binary system UF_6–IF_5 (3 °C); e_2: eutectic in binary system BrF_3–IF_5 (−27 °C); e_3: eutectic in binary system UF_6–BrF_3 (6.4 °C); (a) IF_5 crystallization field; (b) UF_6 crystallization field; (c) BrF_3 crystallization field; "1–11": number of secants.

temperatures the system has no azeotrope, the value of positive deviation in the system UF_6–IF_5 is less than a deviation value in the system UF_6–BrF_3, the system is governed by classical thermodynamic laws.

Components of the system BrF_3–IF_5 have mutual unlimited solubility. The diagram of liquid–vapour equilibrium is presented in Fig. 7c. Equilibrium in the system BrF_3–IF_5 is subject to classical laws, an azeotrope in the system was not found out. The system shows negative deviations from Raoult's law, which agrees with the results of study of phase equilibria in liquid–solid. The complete equilibrium diagram of solid–liquid–vapour for the system BrF_3–IF_5 shows the absence of compounds formation.

To prepare mixes of the given compositions of ternary system, there was also used the method of composition change along the secants going through a top point of UF_6 and through the binary system IF_5–BrF_3. Thus, data obtained for each secant represent the diagram of phase equilibrium in the pseudo-binary system in which one of the components is uranium hexafluoride and another—a mix of iodine pentafluoride and bromine trifluoride with a constant ratio of mixture (UF_6–[IF_5:BrF_3]).

Fig. 8 shows plots of saturated vapour pressure as a function of liquid composition along all secants in the system UF_6–IF_5–BrF_3 at 80 °C. In this figure, the area *I* is clearly observable where isotherms represented along secants are crossed, that implies transition from a negative deviation in the ternary system UF_6–IF_5–BrF_3 to a positive one in the process of enrichment of the solution with uranium hexafluoride from the binary system IF_5–BrF_3.

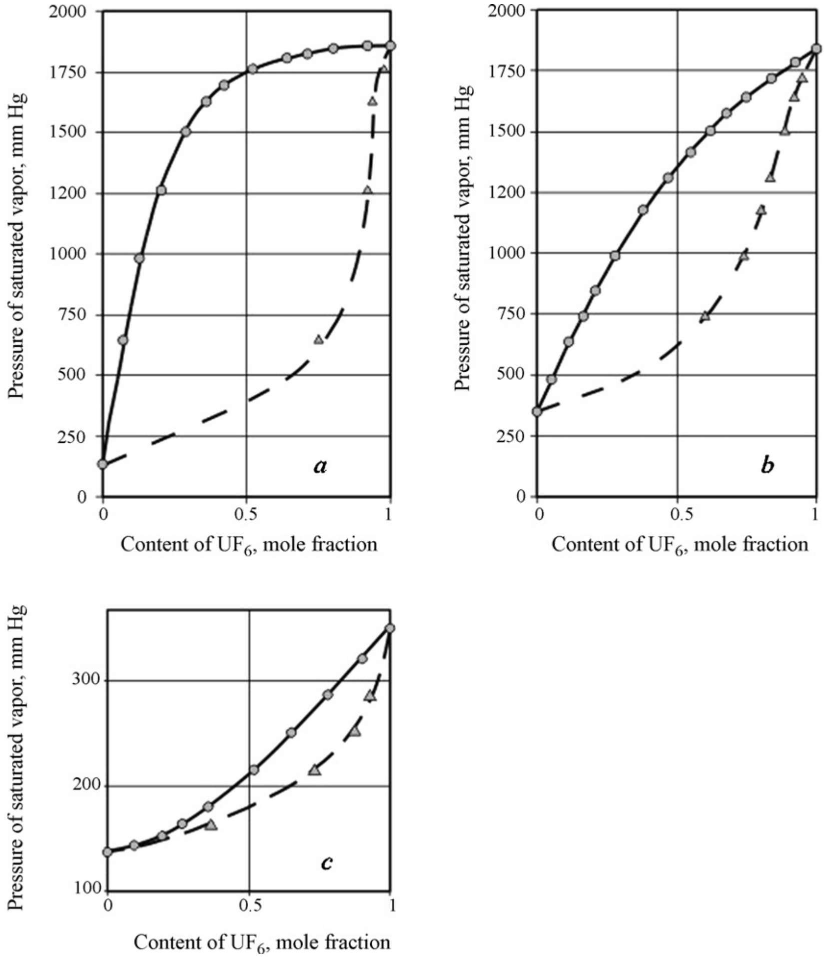

Fig. 7. Diagrams phase equilibria of liquid–vapour in binary systems at 80 °C. (a) In the system UF_6–BrF_3. (b) In the system UF_6–IF_5. (c) In the system IF_5–BrF_3; ▬▬: liquid line; ▬ ▬ ▬: vapour line; experimental data: ●: composition of liquid; △: composition of vapour.

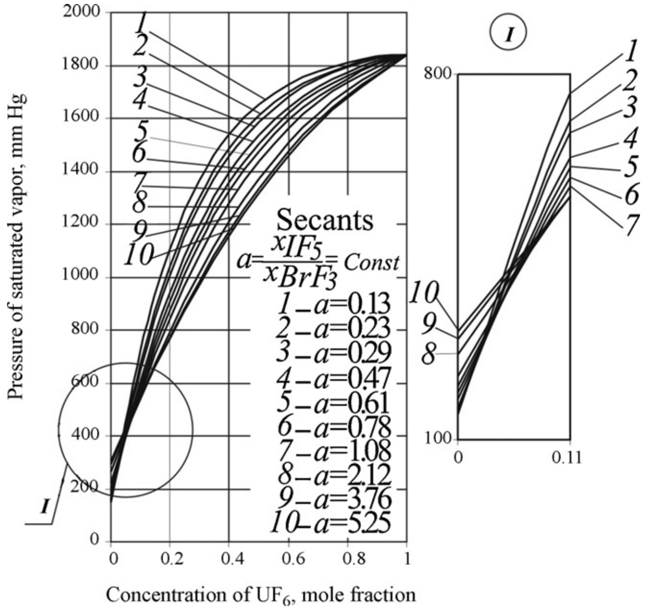

Fig. 8. Dependence saturated vapour pressure from composition of liquid in triple system UF_6–IF_5–BrF_3 at 80 °C by secants $a = x(IF_5)/x(BrF_3)$.

A peculiarity of the system UF_6–IF_5–BrF_3 is its diverse character of deviations from Raoult's law in constituting binary systems. For ternary systems one should take into account that factors influencing the character of deviations from ideal behaviour work simultaneously in the solution, the deviations observable in ternary systems, therefore, result from superposition of opposite in sign deviations introduced by each component. According to paper [7], positive as well as negative deviation can occur in multicomponent systems, depending on the composition.

The valuation of the deviation from Raul's law in the system UF_6–IF_5–BrF_3 was carried out in the following way. Deviations from the ideal behaviour, which are observed in any real systems, when phase balances in isothermal conditions are studied, can be shown as the relation of the pressure of saturated vapour in the system under study to the pressure of ideal saturated vapour. This relation is calculated according to Raul's law and additive Dalton's law [7]. Thus, if we show the deviation of the system on the whole from the ideal behaviour as the coefficient η and call it integral coefficient of activity, we get the following equation:

$$\eta = \frac{P}{P'}, \qquad (2)$$

where P is the pressure of saturated vapour in the real system; P' is the pressure of saturated vapour in the ideal system which is calculated according to Raul's law. But if the deviation coefficient is more than 1 ($\eta > 1$), the real pressure in the system is higher than the ideal one and the deviation in the system is positive. When $\eta < 1$, the deviation from the ideal behaviour in the system is negative.

Fig. 9 shows the dependence of the logarithm of coefficient η on the composition of a three component mixture at 80 °C for all 10 secants, which proves the presence of negative deviation area in the system UF_6–IF_5–BrF_3 (*I*) and positive deviation area from Raul's law. In case uranium hexofluoride prevails in the condensed phase, a positive deviation is observed in the system UF_6–IF_5–BrF_3. The change from positive deviation to negative one is due to the predominance of halogen fluorides in the system UF_6–IF_5–BrF_3. Therefore, properties of a three component system in this area resemble the properties of the system IF_5–BrF_3, which reveals only negative deviations.

Fig. 9 shows the relationship: when a_i increases, coefficient η decreases. The peak so common for the system UF_6–BrF_3 ($x(UF_6) = 0.11$ mole fraction (Fig. 9), when iodine pentafluoride is added to the system UF_6–IF_5–BrF_3, moves to the peak in the system UF_6–IF_5 ($x(UF_6) = 0.32$ mole fraction (Fig. 9). This phenomenon can be explained in the following way. Molecules of bromine trifluoride and iodine pentafluoride react with molecules of uranium hexofluoride in different ways. When the amount of iodine pentafluoride in a liquid phase of the system UF_6–IF_5–BrF_3 increases, forces of intermolecular interactions in the solution become stronger, that results in the decrease of positive deviation of the system from the ideal behaviour.

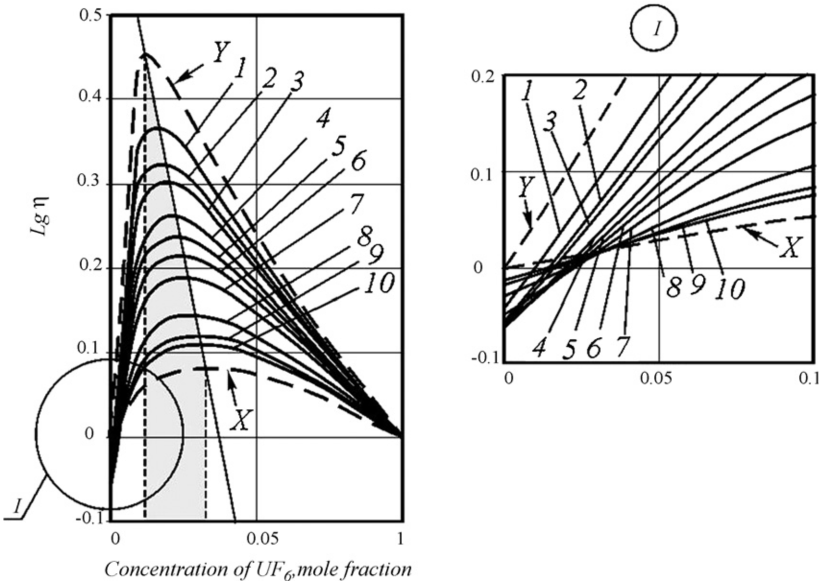

Fig. 9. Dependence of logarithm of coefficient η on concentration of UF_6 in condensed system UF_6–IF_5–BrF_3 by secants $(a_{1-10} = X_{IF_5}/X_{BrF_3})$ at 80 °C: *1*—a_1 = 0.13; *2*—a_2 = 0.23; *3*—a_3 = 0.29; *4*—a_4 = 0.47; *5*—a_5 = 0.61; *6*—a_6 = 0.78; *7*—a_7 = 1.08; *8*—a_8 = 2.12; *9*—a_9 = 3.76; *10*—a_{10} = 5,25. *X*—dependence of lg η from concentration of UF_6 in system UF_6–IF_5; *Y*—dependence of lg η from concentration of UF_6 in system UF_6–BrF_3.

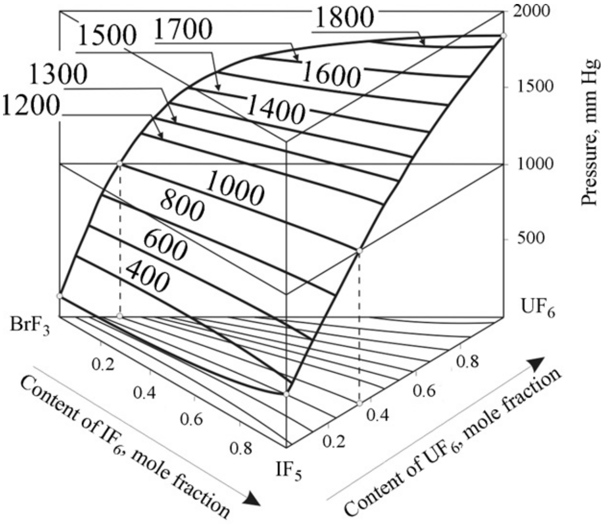

Fig. 10. The surface of boiling liquid in system UF_6–IF_5–BrF_3 at 80 °C.

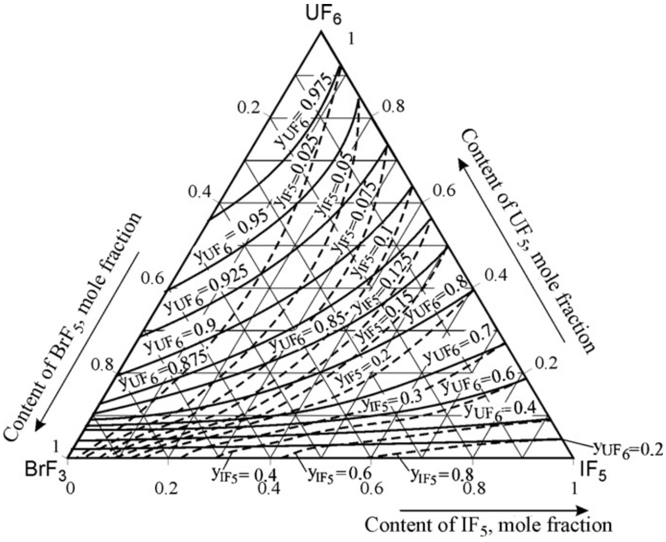

Fig. 11. Lines of permanent concentration IF_5 and UF_6 in vapour.

Fig. 10 presents the volumetric diagram of saturated vapour pressure as a function of the liquid phase composition (the boiling liquid surface) in the system UF_6–IF_5–BrF_3 at 80 °C.

In Fig. 10 various characters of deviation from ideal behaviour in binary systems are well visible. In the systems with uranium hexafluoride a positive deviation and in the system BrF_3–IF_5 a negative deviation from the ideal one are observed, which completely agree with the data obtained at study of equilibrium between liquid and solid phases.

A smooth run of lines of isothermobaric sections can be explained by the fact that both of solvents (IF_5 and BrF_3) in the system are rather similar in their physical and chemical properties like boiling and melting points, polarity, ionizing power and complexing ability.

From Fig. 10 one can see prevalence in volatility of uranium hexafluoride in comparison with a mix of halogen fluorides, it suggests high efficiency of distillation methods for separation of the system in study from the point of view of UF_6 extraction, and the azeotrope absence in all the systems in question implies applicability of distillation methods for separation of the system UF_6–IF_5–BrF_3 into components.

Data for composition of the vapour phase in equilibrium are presented in Fig. 11 as lines of constant content in the vapour phase for UF_6–IF_5–BrF_3, the content of the third component (BrF_3) one can determine from the condition:

$$y_{UF_6} + y_{IF_5} + y_{BrF_3} = 1. \tag{3}$$

Fig. 11 describes the change of saturated vapour composition as a function of liquid formulation. It can be used not only for calculations of separation processes in the system UF_6–IF_5–BrF_3 by distillation methods, but also for calculation of other technological processes where data are required concerning the vapour phase composition, which is in equilibrium with the condensed system UF_6–IF_5–BrF_3 of any composition.

To make the thermodynamic-topological analysis, calculation of lines of open evaporation in the system UF_6–IF_5–BrF_3 was performed.

2.3. Construction of open evaporation lines in system UF_6–IF_5–BrF_3

The concept of the open evaporation process was introduced by Schreinemakers [8,9]. He also derived the differential equation of curves of the open evaporation

$$\left(\frac{dx'_1}{dx'_2}\right)_{P\,\mathrm{or}\,T} = \frac{x''_1 - x'_1}{x''_2 - x'_2}, \tag{4}$$

where x'_i and x''_i are the molar fraction of **i**-th component in liquid and vapour phases respectively.

According to Schreinemakers conclusion, Eq. (4) holds strictly under the following conditions:

1. equilibrium between liquid and vapour phases is kept during the process;
2. the amount of vapour being extracted is much less than the amount of liquid;
3. extraction of the vapour is made infinitely slowly.

Calculation of lines of open evaporation in the system UF_6–IF_5–BrF_3 was performed by the procedure described in [9–11].

If after distillation D moles of vapour phase and R moles of the condensed one were formed from Z moles of the mixture, one can write the equation [11]:

$$Z = D + R. \tag{5}$$

The balance of components distribution between distillate D and residue R is defined by the equation

$$Zx_{i,z} = Dy_i + Rx_i, \tag{6}$$

where y_i and x_i are the molar fractions of ith component in vapour and condensed phases after distillation of infinitesimal amount of the vapour phase; x_i, z are the molar fractions of ith component in the original mixture.

To determine the composition of equilibrium vapour yi, the vapour–liquid equilibrium data from Fig. 11 were used. Fig. 12 presents the lines of open evaporation in the system UF_6–IF_5–BrF_3 calculated from the results of study of the vapour–liquid equilibrium at 80 °C.

The presented lines of open evaporation for the system UF_6–IF_5–BrF_3 allow one to draw a conclusion that hexafluoride is extracted from the condensed system practically in full and during separation the condensed phase is being saturated with bromine trifluoride and iodine pentafluoride. After uranium hexafluoride exhaust, rectification in the binary system IF_5–BrF3 takes place with pure bromine trifluoride being the final point of the process.

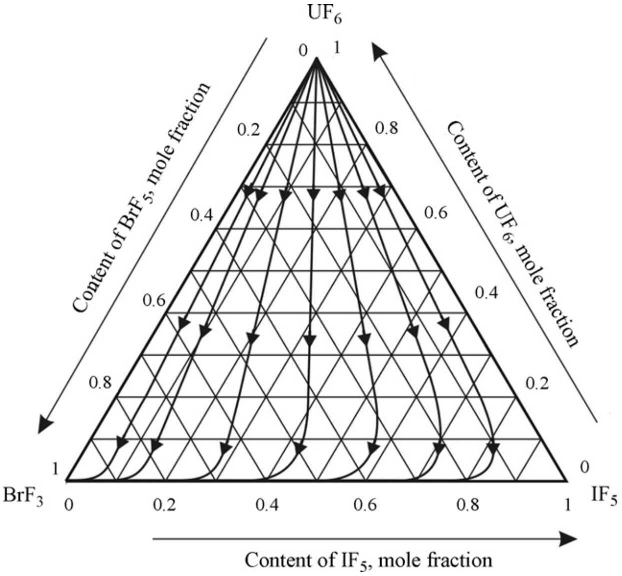

Fig. 12. Lines of evaporation in system UF_6–IF_5–BrF_3.

3. Experimental

3.1. Study of phase equilibria between liquid and solid phases in UF_6–IF_5–BrF_3 system

Analysis of equilibrium between liquid and solid phases was made with the purpose of substantiation of composition and temperature areas for distillatory and rectificative processes, and for estimation of possibility to separate the system UF_6–IF_5–BrF_3 into components by means of the crystallization method. Methods of differential-thermal (DTA) and visually-polythermal (VPT) analyses were chosen for research. The experimental installation for DTA (Fig. 12) consisted of the copper block (1) with two holes for nickel ampoules containing the composition in study (2a) and the standard sample (2b). The block is equipped with a coil for controllable supply of liquid nitrogen and with the programmed electroheater. The rate of temperature change ranged from 1 to 5 degrees per minute depending on the weighted sample mass.

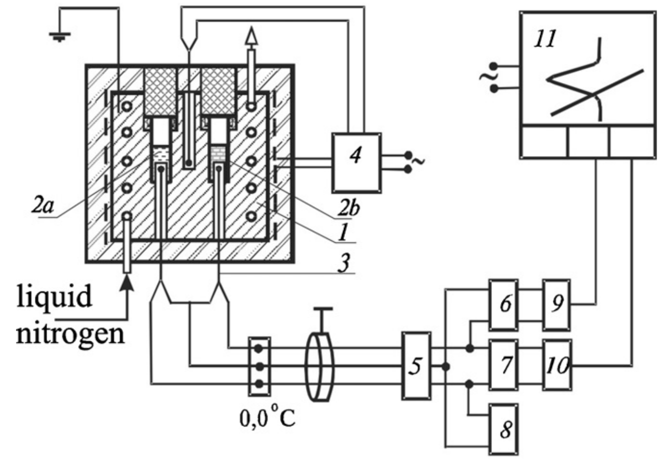

Fig. 13. The experimental installation for DTA. 1—copper block; 2—ampoules; 3—thermocouples; 4—block of temperature control; 5—inlet splitter; 6–8—intensifiers; 9 and 10—outlet splitters; and 11—registering potentiometer.

The unit for visual-polythermal analysis consisted of a tight ampoule provided with a thermocouple, a transparent fluoroplastic-4 being used as the material. The study was carried out in air bath using illumination and a binocular magnifier; the rate of temperature change was about 0.2°/min.

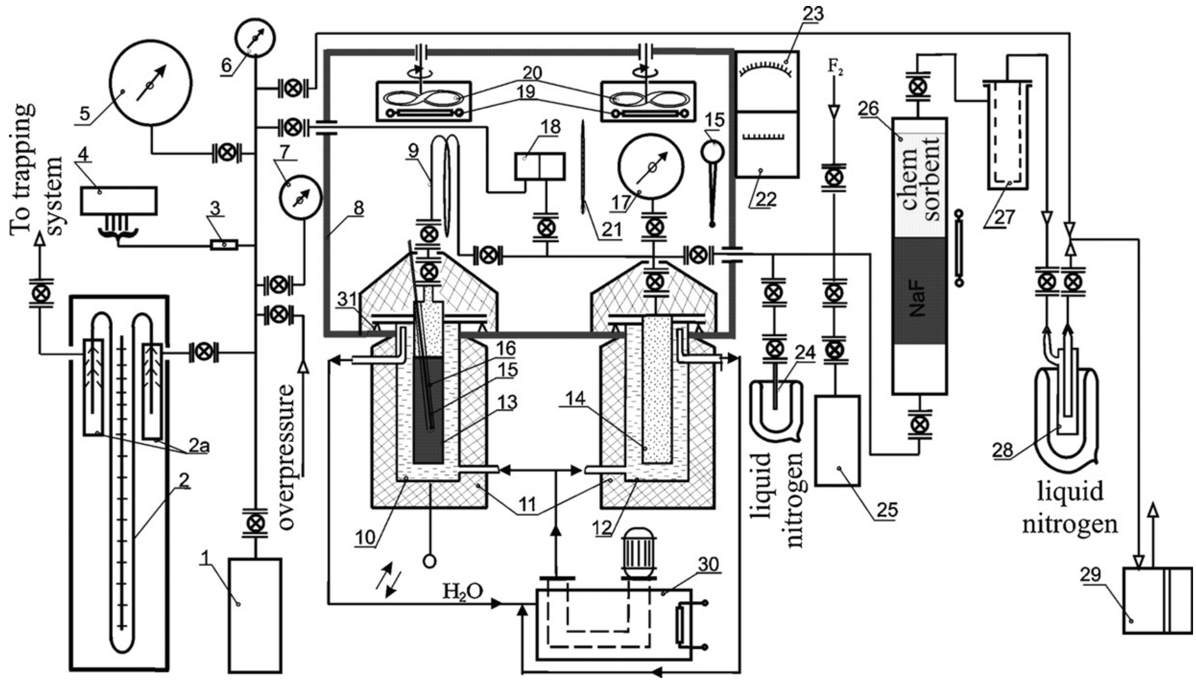

Fig. 14. Experimental installation for phase balance study. 1: calibrated tank; 2: mercury manometer; 3: vacuum lamp; 4: thermocouple vacuum gauge; 5: standard vacuum gauge; 6: absolute pressure gage; 7: standard pressure gauge; 8: air thermostat; 9: spiral compensator; 10: water-jacket; 11: thermo-insulation; 12: water-jacket; 13: tank for studied system; 14: equilibrium calibrated tank; 15: thermocouples; 16: pocket; 17: standard manometer; 18: pressure transducer; 19: heating spiral; 20: ventilators; 21: thermometer; 22, 23: regulative potentiometer; 24, 25: triers; 26: sorption column; 27: metal-pore filter; 28: freeze trap; 29: vacuum pump; 30: hydro thermostat. (For interpretation of the references to colour in the artwork, the reader is referred to the web version of the article.)

Purification of UF_6, IF_5 and BrF_3 from hydrogen fluoride (which is practically always their majority impurity) was carried out by long-term vacuum distillation. For each composition, from four to seven cooling and heating curves were obtained.

Formulations of the produced mixes were determined by masses of their components weighed with error of $\pm 1 \times 10^{-3}$ g; sample weights ranged from 0.7 up to 10 g. All the operations were performed in the hermetic box in dry nitrogen atmosphere (Fig. 13).

3.2. Study of phase equilibria of liquid–vapour in ternary system UF_6–IF_5–BrF_3 and in double systems composing it at 80 °C

To study phase equilibrium of liquid–vapour, a static method was preferred. This method is distinguished by simplicity and reliability, with its help the vapour–liquid equilibrium can be studied in the systems where the condensed phase is heterogeneous.

The layout of experimental installation is presented in Fig. 14.

Pressure measurements in a range up to 10 mm Hg were accurate to within ±0.1 mm Hg, for higher pressures within ±0.3 mm Hg; temperature in reservoirs 13, 14 was held to an accuracy of ±0.1 °C. To prevent partial condensation of the vapour phase, the pressure measurement system and stop valves were located in the air bath (8), the temperature in which was held by 3 °C above that in the water bath (30).

The sampling system for vapour phase consists of the calibrated reservoir (14) and two samplers: (24) and (25) which are further directed to potentiometric and spectrophotometric determination of elements.

On the given composition mix having been prepared, the reservoir (13) was cooled down the temperature of −114 °C and nondensables were pumped out at residual pressure of 10^{-2} mm Hg for a half an hour. Then the reservoir was heated up to 70 °C for removal of the dissolved nondensables, being maintained at this temperature for 1 h, it was cooled again down to −114 °C and pumped out for an hour. When the disposal of gases was completed the reservoir was connected to the installation. With continuous stirring the system was maintained in static conditions within 2–3 h. The achievement of equilibrium was judged by a constant value of saturated vapour pressure for an hour. After the pressure measurement, taking a sample of vapour to samplers (24,25) was performed.

4. Conclusion

Using methods of differential-thermal (DTA) and visual-polythermal analyses (VPA), liquid–solid phase equilibria in the systems UF_6–IF_5, BrF_3–IF_5, UF_6–BrF_3–IF_5 were studied. All the systems belong to a simple eutectic type, the formation of compounds was not revealed. The system BrF_3–IF_5 was found to have a negative deviation from the ideal one. Uranium hexafluoride in all the systems showed positive deviations. In the ternary system BrF_3 and IF_5 showed both negative and positive deviations.

In research, the method of composition change along the secants going through a top point of UF_6 was chosen; it allows ternary system to be transformed into pseudo-binary systems "UF_6-solvent". Among equations of Hildebrand-Sketchard, Margules, van Laar and Wilson, the last one is shown to be the most appropriate for the description of UF_6 solubility.

Using a static method, "liquid–vapour" phase equilibria in systems UF_6–BrF_3, UF_6–IF_5, BrF_3–IF_5, UF_6–BrF_3–IF_5, at temperature of 80 °C were studied. All the systems are non-azeotropic. The character of deviations of the components from ideality is similar to their behaviour in condensed systems.

In the ternary systems, isotherm–isobars and lines of constant component content in the vapour phase were constructed, the thermodynamic-topological analysis was performed, the distillation lines were constructed, and the distillation processes were calculated. Wilson's equation most exactly describes the experimental data.

References

[1] V.I. Scherbakov, V.A. Zuev, A.V. Parfenov, Kinetics and Fluorination Mechanism of the Uranium, Plutonium and Neptunium Compounds by Fluorine and Halogen Fluorides, Energoatomizdat, Moscow, 1985, pp. 28–54 (in Russian language).
[2] R. Richards, S. Stoler, Processing of a Nuclear Fuel, Atomizdat, Moscow, 1964, pp. 116–208 (in Russian language).
[3] I.I. Zherin, G.N. Amelina, R.V. Kalaida, A.M. Tjagelskaja, J. Chem. Technol. 7 (2003) 22–31 (in Russian language).
[4] I.I. Zherin, G.N. Amelina, R.V. Kalaida, in: Proceedings of the First International Siberian Workshop ISIF-2003 on Advanced Inorganic Fluorides INTERSIBFLUORINE-2003, Novosibirsk Russia 2–4 April 2003, Russian Academy of Sciences Siberian Branch, (2003), pp. 4–17.
[5] J. Fischer, R.C. Vogel, J. Am. Chem. Soc. 76 (1954) 4829–4832.
[6] S. Wales, V.S. Beskov, Phase Equilibria in Chemical Technology: vol. I–II, Mir, Moscow, 1989, pp 87–263.
[7] W.B. Cogan, Heterogeneous Equilibriums, Chemistry, Moscow, 1968, pp 192–263 (in Russian language).
[8] F.A. Schreinemakers. Zs. Phys. Chem., 36, 257, 413, 1901; 39, 485,1902; 40, 440,1902; 43, 671, 1902; 47, 445, 1904; 48, 257, 445, 1904 (in English language).
[9] N. Bushmakin, I.N. Kisch, J. Appl. Chem. Moscow 4 (1957) 561–567 (in Russian language).
[10] V.P. Zharov, L.A. Serafimov, Physical–chemical Basis of the Distillation and Rectification Chemistry, St. Petersburg, 1975, pp 80–106 (in Russian language).
[11] A.V. Storonkin, Thermodynamics of the Heterogeneous Systems, Leningrad, St. Petersburg, 1968, pp. 302–360 (in Russian language).