TOMSK POLYTECHNIC UNIVERSITY

Applied Physics & Engineering

Chare of Chemical Technology of Materials in Modern Power Engineering

Fluorination process, halogen fluorides and perspective forms of using bromine thrifluoride

Associate professor
Ostvald Roman

Self information

- *Graduated from Tomsk polytechnic university in 2003, the department of Applied Physics & Engineering, Chare of Chemical Technology of Materials in Modern Power Engineering.*
- *In 2004 defend qualification to PhD in chemistry science in Tomsk Polytechnic University.*
- *At now moment – associate professor of chare, and deputy of the departments dean.*
- *General science interest is chemical technology of rare and Nobel metals, process of fluorination and halogen fluorides.*

Application fluorine process

Fluoride processes is important in the technology of rare elements.

- *production of fluoric compounds for rare metals getting.*
- *complex compounds production to separation of attendant rare and rare-earth elements.*
- *oxidative fluorination of ores and technologic materials*

Fluoric compounds of rare elements

Berillium technology

Magnesium thermal reduction of BeF_2

$BeF_2 + Mg = \mathbf{Be} + MgF_2 + 150.5\ kJ$

Tantalum & Niobium technology

Sodium thermal reduction of $K_2Ta(Nb)F_7$

$K_2TaF_7 + 5Na = \mathbf{Ta} + 2KF + 5NaF + Q\ kJ$

Tantalum & Niobium technology

Electrolysis of melt mixture 70% KCl + 30% K_2ZrF_6

$K_2ZrF_6 + 4KCl = \mathbf{Zr} + 6KF + 2Cl_2$

Separation of attendant rare elements

Separation of Zr and Hf

Factional crystallization of $K_2\mathbf{Zr}F_6 : K_2\mathbf{Hf}F_6$

Separation of Nb and Ta

Factional crystallization of $K_2\mathbf{Nb}OF_5 \cdot H_2O : K_2\mathbf{Ta}F_7$

Based on difference in solubility complex salt in water solutions

Oxidative fluorination

$Ag + BrF_3 \rightarrow Ag[BrF_4] + Br_2$,

$Au + BrF_3 \rightarrow [BrF^{2+}][AuF^{4-}] + Br_2$,

$Me + BrF_3 \rightarrow [BrF^{2+}][MeF^{6-}] + Br_2$,

Where Me – Ru, Os, Ir, Pt, Rh.

$Pd + BrF_3 \rightarrow PdF_3 \cdot BrF_3 + Br_2$

The interaction between BrF_3 and the group of Nobel metals is accompanied by the formation of well-dissolving complexes

Fluorination reagents

F_2, HF, NH_4F, NH_4HF_2 and other fluorinating reagents are applied for the simple fluorination. But if it is necessary to carry out the oxidative fluorination then metal fluorides in the highest oxidation level, fluorides of noble gases or halogen compounds of fluorine are applied.

ClF, ClF_3, BrF_3, BrF_5, IF_5 and IF_7

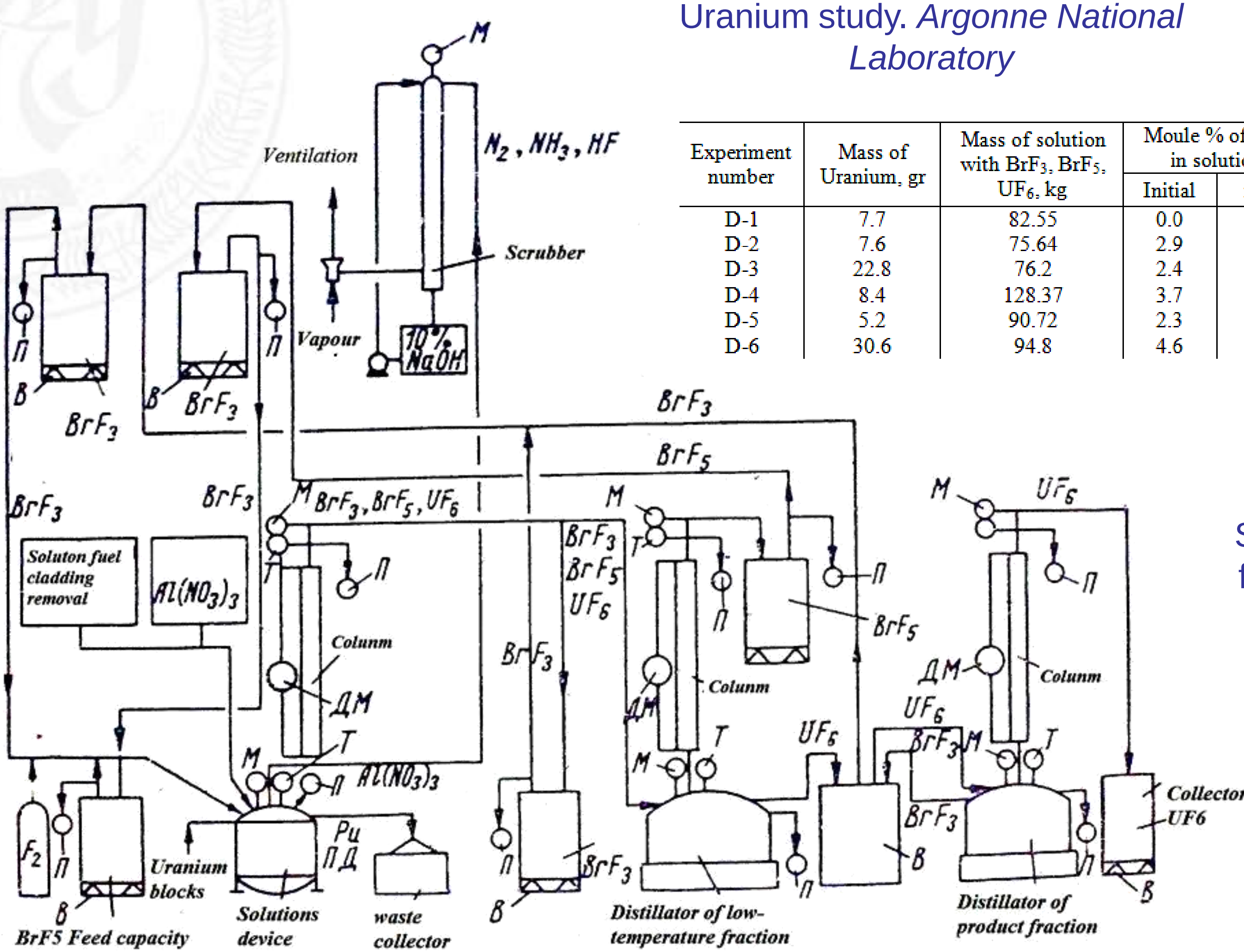
Using of halogen fluorides for uranium compounds fluorination

- *Reprocessing of irradiated nuclear fuel;*
- *Fluorination of uranium oxides with chlorine trifluoride, bromine trifluoride;*
- *Fluorination of uranium compounds with bromine trifluoride and iodine pentafluoride.*

Reprocessing of irradiated nuclear fuel

Results of solution and separation Uranium study. *Argonne National Laboratory*

Experiment number	Mass of Uranium, gr	Mass of solution with BrF_3, BrF_5, UF_6, kg	Moule % of UF_6 in solution		Time of process, h	Temperature, °C
			Initial	final		
D-1	7.7	82.55	0.0	2.5	31	125-132
D-2	7.6	75.64	2.9	5.0	8	110-122
D-3	22.8	76.2	2.4	3.0	9	120
D-4	8.4	128.37	3.7	5.1	9	120
D-5	5.2	90.72	2.3	3.7	8	120-140
D-6	30.6	94.8	4.6	3.7	14	120



Scheme of research fluorides distillation. *Argonne National Laboratory*

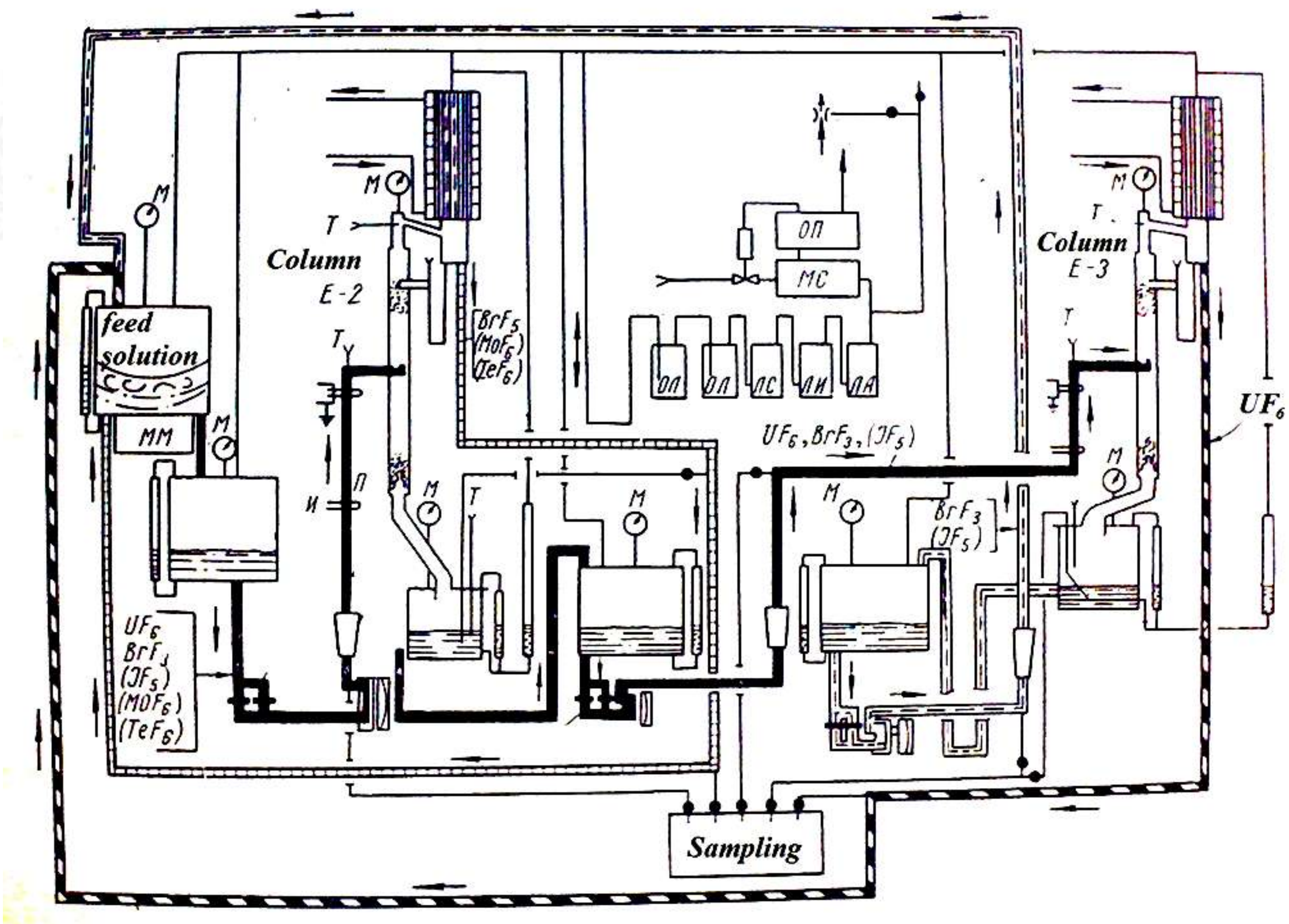
Reprocessing of irradiated nuclear fuel

Two experimental plant was designed in Brookhaven National Laboratory:

- Plant to separation Uranium of light admixture;
- Continuously working plant for uranium solution;

Reproccessing of irradiated nuclear fuel

Brookhaven National Laboratory
Office of Science / U.S. Dept. of Energy
BROOKHAVEN NATIONAL LABORATORY



Plant for separation Uranium of light admixture.
Brookhaven National Laboratory

Continuously working plant for uranium solution

It is a tubular reactor, for 2.27 kg solution of uranium in 1 hour. Rate of solution circulation – 189.3 litre/min

Reprocessing of irradiated nuclear fuel

OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

Process of interaction irradiated uranium with chlorine trifluoride was study in the Experimental plant K-25.

Three general operation was produced:

- Solution of Uranium;
- Distillation of Plutonium and fission products;
- Extraction of Plutonium and fission products in the aqueous solution

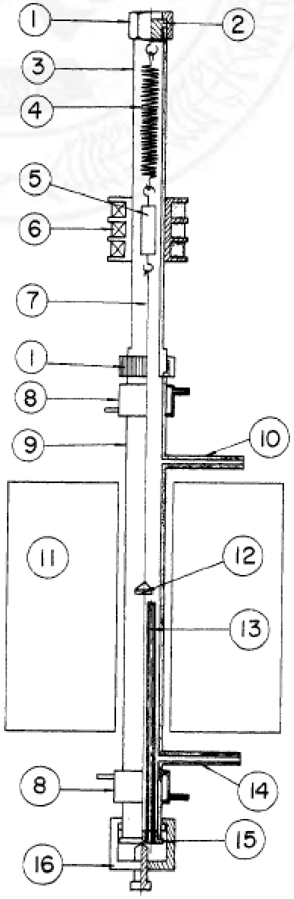
OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

The results of uranium solution show that 2.5 kg of Uranium was dissolved in 4.5 kg of mixture:

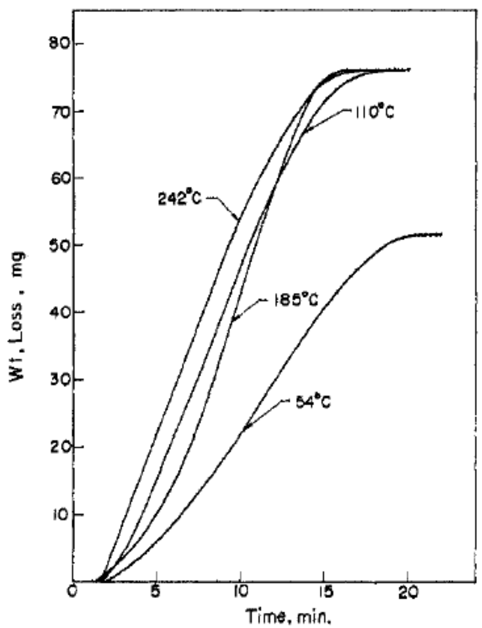
- ClF_3/HF (2/1) at 30 ºC for 5 days,
- ClF_3/HF (0.3/1) at 80 ºC for 19 hours.

Japan Atomic Energy Agency

Division of Research,
Japan Atomic Energy Research Institute



Kinetics and mechanism of the reaction between BrF_3 vapor and UF_4 was research by Tsutomu Sakurai and Matae Iwasaki



Weight loss vs. time curves at different temperatures: initial weight of UF_4 = 77±1 mg, partial pressure of BrF_3=15 mm, gas velocity = 55.4 cm/min.

Reprocessing of irradiated nuclear fuel

RUSSIAN RESEARCH CENTRE KURCHATOV INSTITUTE
РОССИЙСКИЙ НАУЧНЫЙ ЦЕНТР "КУРЧАТОВСКИЙ ИНСТИТУТ"

INSTITUTE OF MOLECULAR PHYSICS

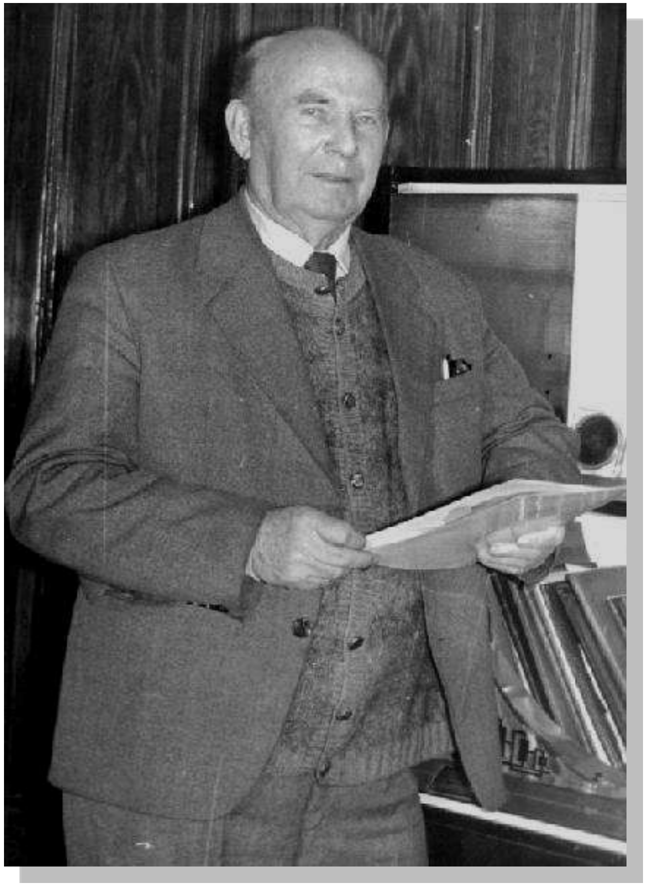
Technological scheme of INF reprocessing was suggested.

It is one of the modification gaseous fluorine process.

After separation UF_6, process of separation plutonium compounds and fission product in fluoride melt is produced.

Fluorination of uranium oxides with chlorine trifluoride, bromine trifluoride

Research of interaction liquid ClF_3-HF and BrF_3-HF with UO_2, and gaseous ClF_3 with U_3O_8 was produce in TPU, professor **Nikolay Kurin** research school.



Interaction of liquid ClF_3-HF with UO_2 tablet

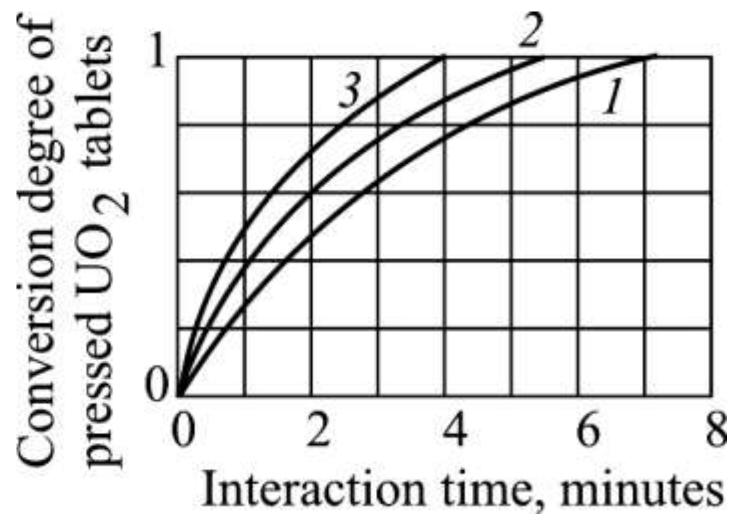
Solution with 23, 35, 48 mass % of ClF_3 was used. The process of fluorination uranium dioxide was produced at 10, 20, 30 ºC.

Time of fluorination process was 3.5 min at 30 ºC and 23 min at 10 ºC.

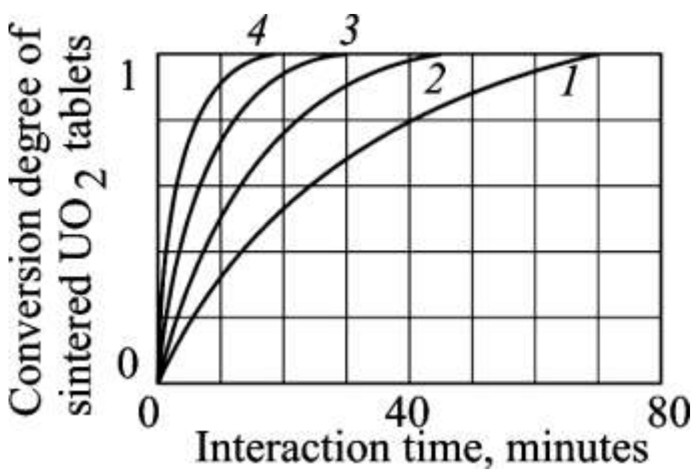
$$UO_2F_2 + 2ClF_3 \rightarrow UF_6 + 2ClF + O_2;$$
$$UO_2 + ClF_3 \rightarrow UO_2F_2 + ClF;$$
$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O;$$
$$UF_4 + ClF_3 \rightarrow UF_6 + 2ClF;$$
$$2H_2O + 2ClF_3 \rightarrow 4HF + O_2 + ClF_3.$$

Interaction of liquid BrF_3-HF with UO_2 tablet

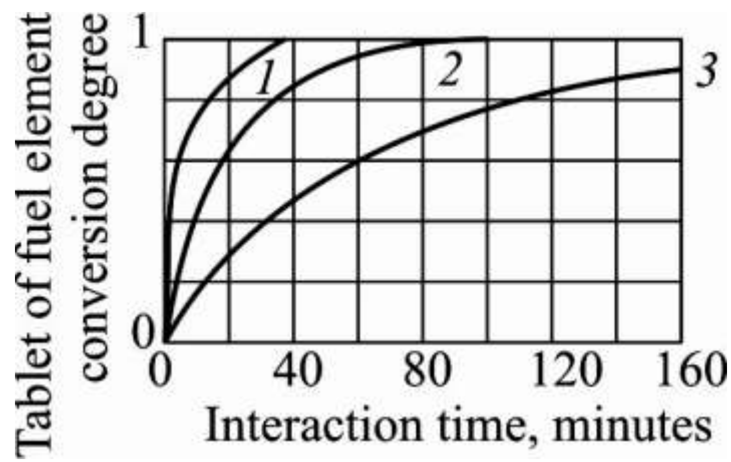
Solution with 20, 33, 50, 66, 80 mass % of BrF_3 was used. The process of uranium dioxide fluorination was produced at temperatures from 10 to 80 ºC.



Conversion degree dependences on time of interaction between pressed UO_2 tablets with mixture BrF3 (66 %) and HF at temperatures: 1 – (+10); 2 – (+20); 3 – (+30)°C



Conversion degree dependences on time of interaction between sintered UO_2 tablets with mixture BrF3 (50 %) and HF at temperatures: 1 – (+20); 2 – (+40); 3 – (+60); 4 – (+80) °C



Conversion degree dependences on time of interaction between tablets of fuel element with mixture BrF3 (50 %) and HF at temperatures: 1 – (+60); 2 – (+40); 3 – (+20)°C

Interaction of liquid BrF_3-HF with UO_2

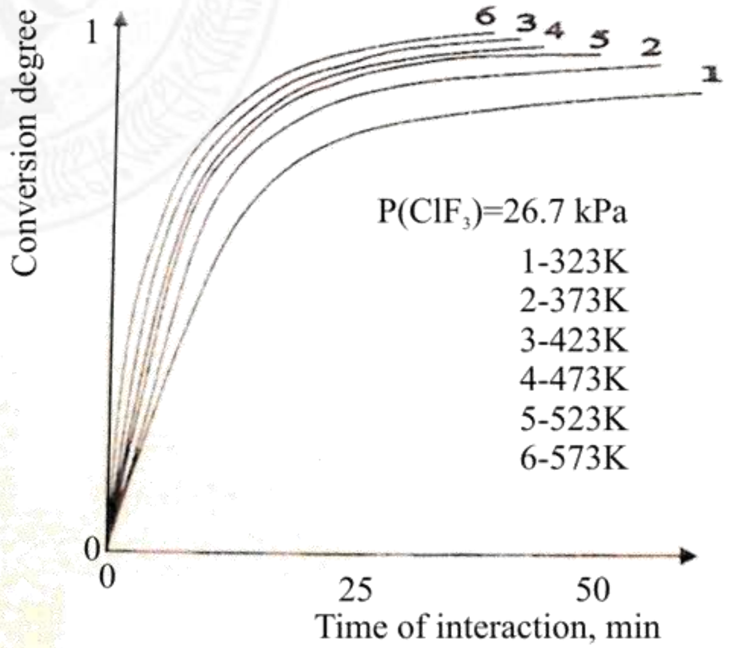
Process of fluorination can be described by following reaction:

$$3UO_2 + 2BrF_3 + nHF \rightarrow 3UO_2F_2 + Br_2 + nHF;$$

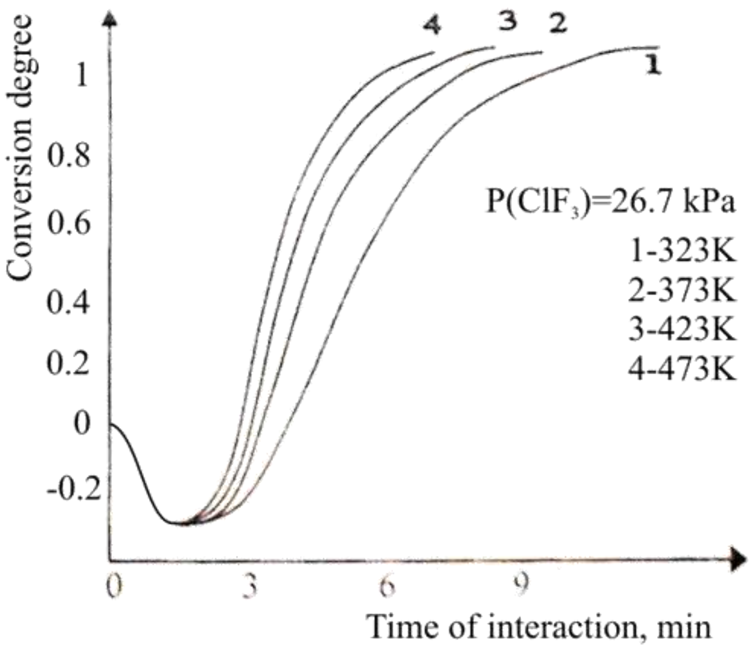
$$3UO_2F_2 + 4BrF_3 + nHF \rightarrow 3UF_6 + 3O_2 + 2Br_2 + nHF;$$

$$BrF_3 + Br_2 \rightarrow 3\ BrF.$$

Interaction of gaseous ClF_3 with U_3O_8 and UO_2



Dependence conversion degree of U_3O_8 at time and temperature



Dependence conversion degree of UO_2 at time and temperature

Interaction of gaseous ClF_3 with U_3O_8 and UO_2

Process of fluorination can be described by following reaction:

$$U_3O_8 + 6ClF_3 \rightarrow 3UF_6 + 3Cl_2 + O_2;$$
$$U_3O_8 + 3ClF_3 \rightarrow UO_2F_2 + 3ClF + O_2;$$
$$UO_2F_2 + 2ClF_3 \rightarrow 3UF_6 + 2ClF + O_2;$$
$$UO_2 + ClF_3 \rightarrow UO_2F_2 + 3ClF;$$
$$UO_2F_2 + 2ClF_3 \rightarrow UF_6 + ClO_2F + ClF;$$
$$ClO_2F \rightarrow ClF + O_2.$$

Fluorination of uranium compounds with bromine trifluoride and iodine pentafluoride

For fluorination of uranium compounds used mixture BrF_3 and IF_7 was suggested by RSC Kurchatov Institute.

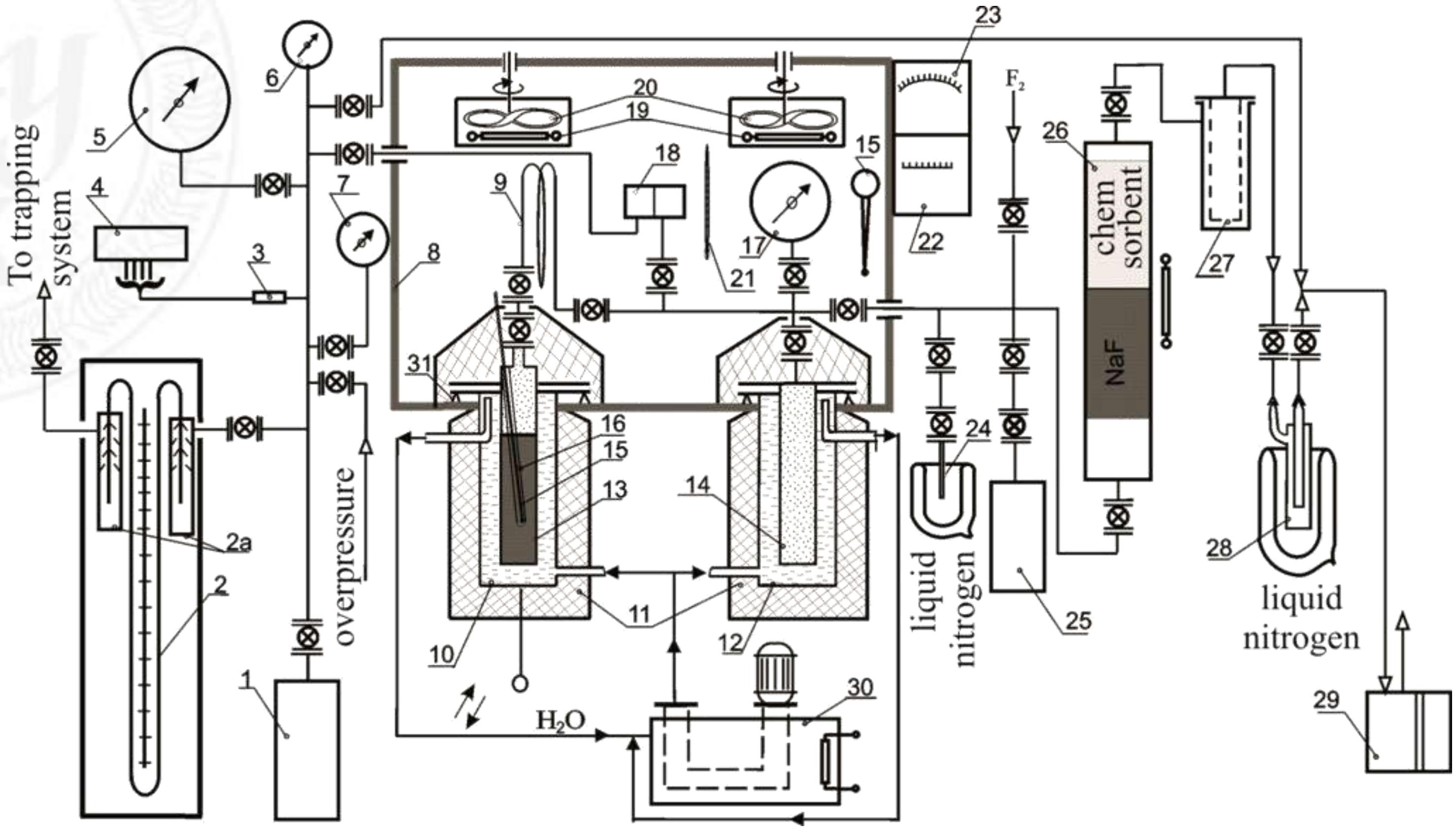
$$3UOF_4 + 2BrF_3 \rightarrow 3UF_6 + Br_2 + 3/2O_2;$$

$$3UF_5 + BrF_3 \rightarrow 3UF_6 + 1/2Br_2;$$

$$3UF_4 + 2BrF_3 \rightarrow 3UF_6 + Br_2;$$

$$3IF_7 + Br_2 \rightarrow 2BrF_3 + 3IF_5.$$

Phase balance in system UF_6-IF_5-BrF_3



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

Phase balance in system UF_6-IF_5-BrF_3

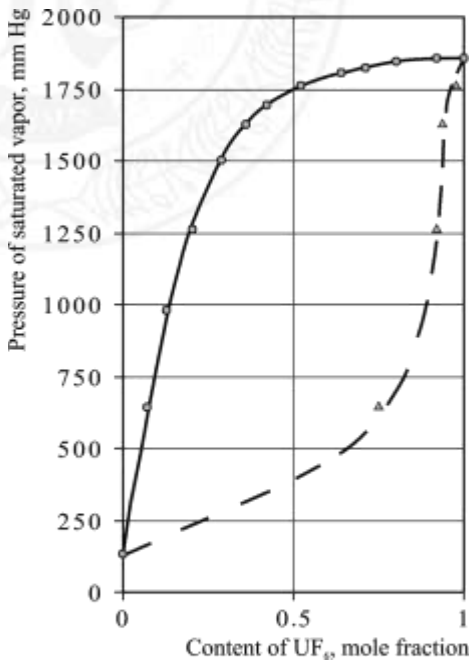
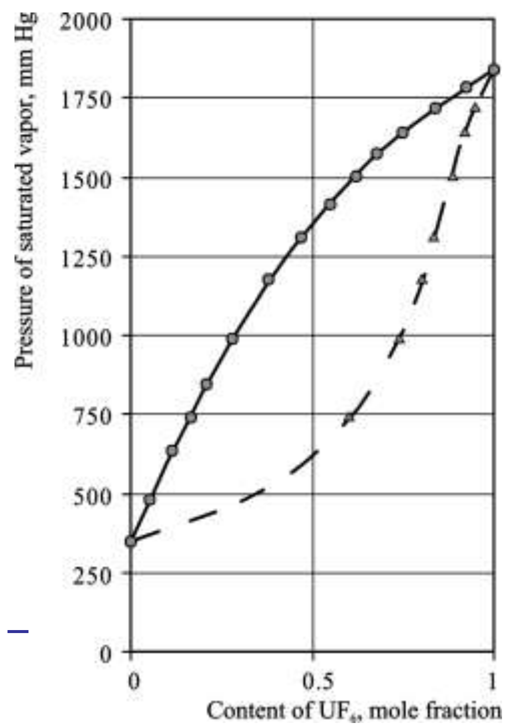


Diagram phase equilibria of liquid – vapour in system UF_6 – BrF_3 at 80 °C

Diagram phase equilibria of liquid – vapour in system UF_6 – IF_5 at 80 °C



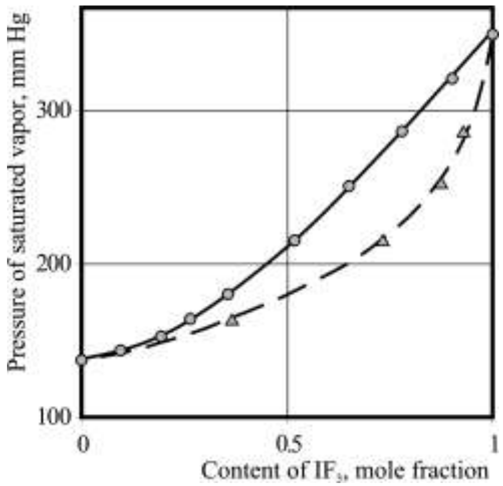
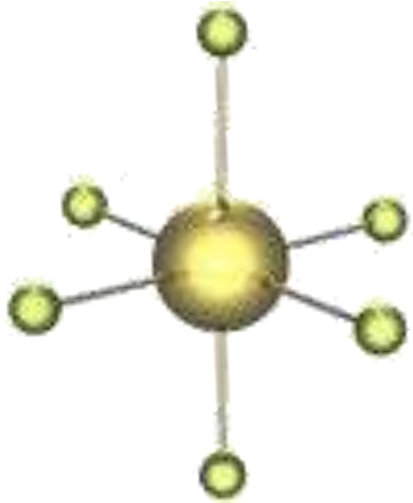
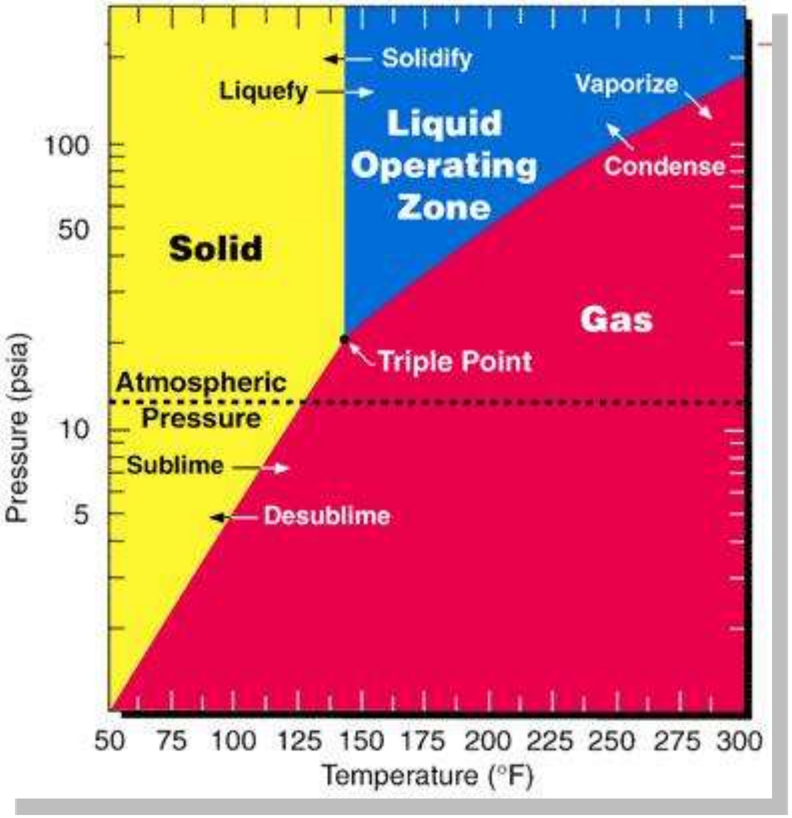
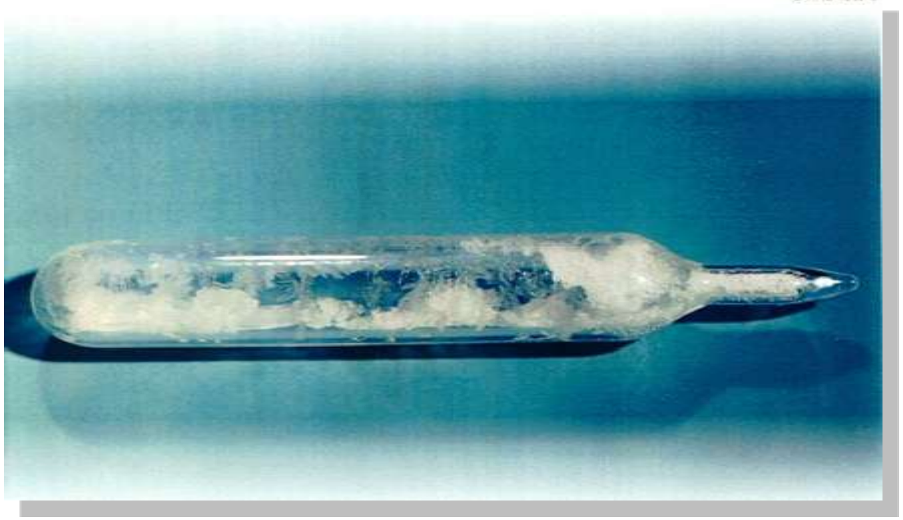


Diagram phase equilibria of liquid – vapour in system IF_5 – BrF_3 at 80 °C

Phase balance in system UF_6-IF_5-BrF_3







Phase balance in system UF_6-IF_5-BrF_3

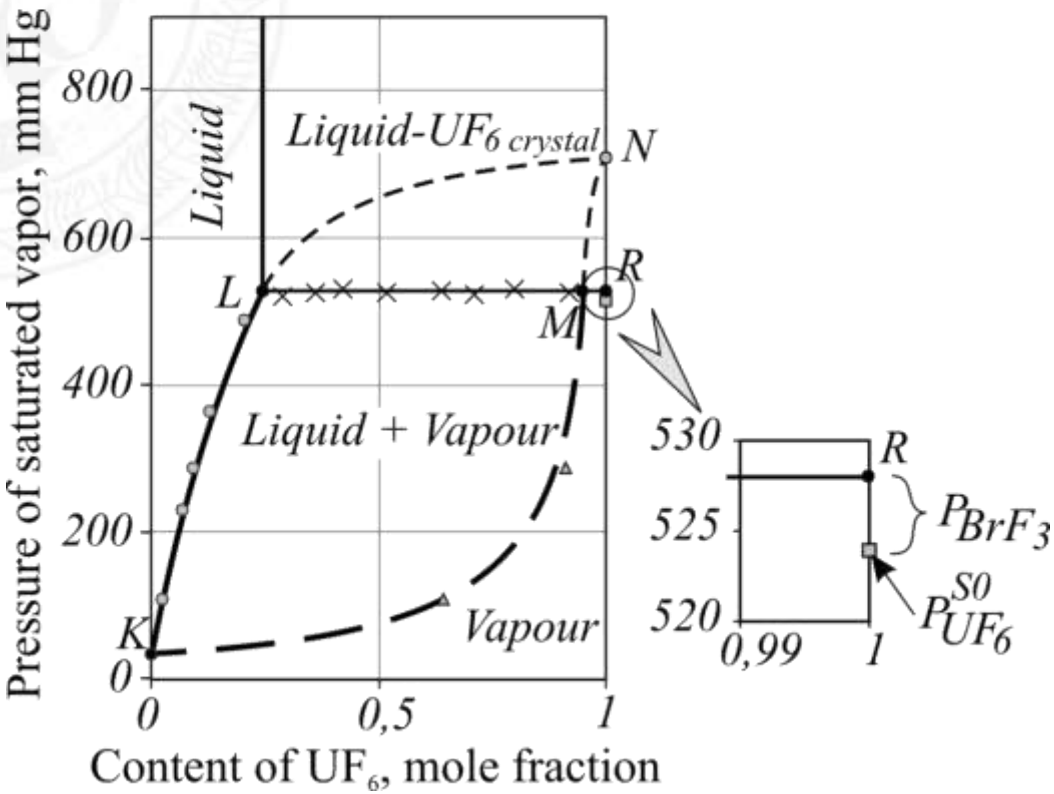


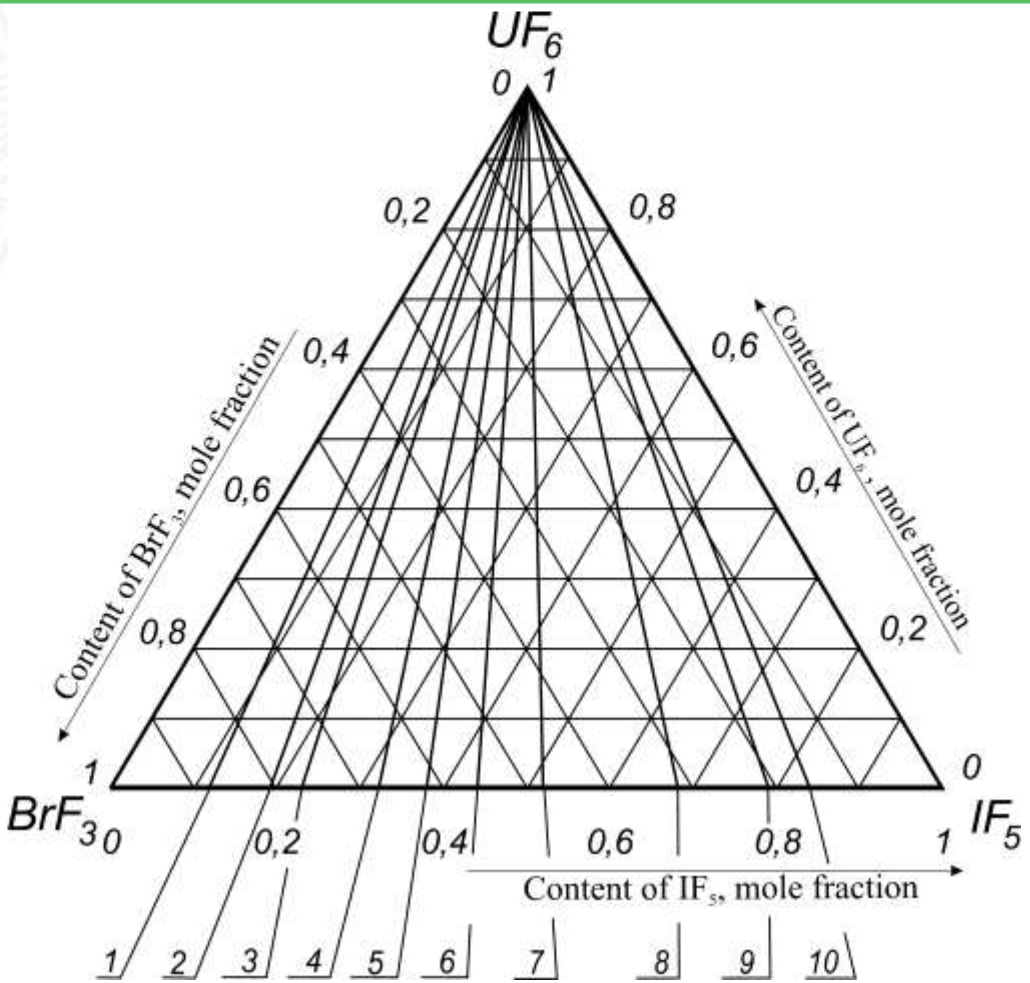
Diagram phase equilibria of condenseted phase – vapour in system в UF_6 – BrF_3 at 50 ºC

- liquid line;
- vapour line;
- experimental data at liquid composition;
- experimental data at vapour composition;
- experimental data in field of solid UF_6

$$P = P_{BrF_3} + P_{UF_6}$$

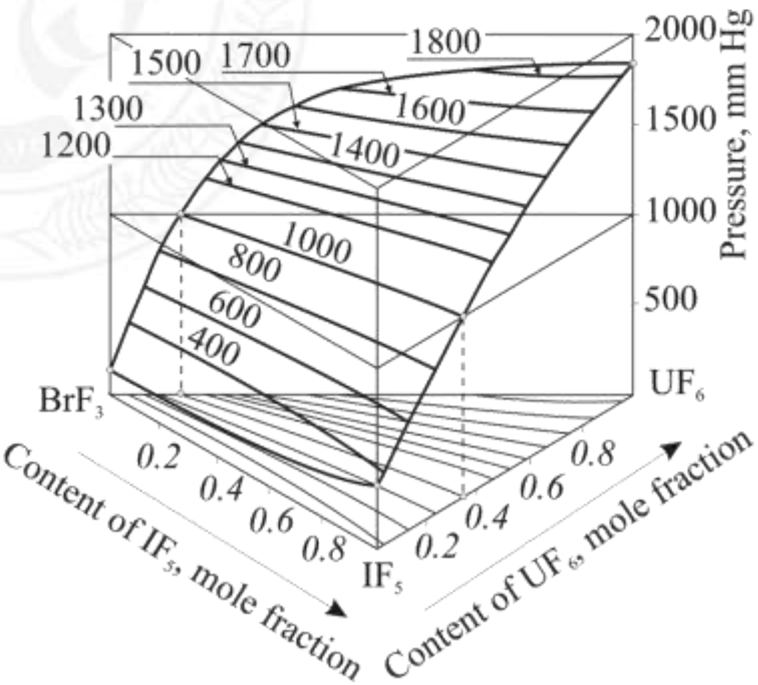
$$P = P_{BrF_3} + P_{UF_6}^{S0}$$

Phase balance in system UF_6-IF_5-BrF_3

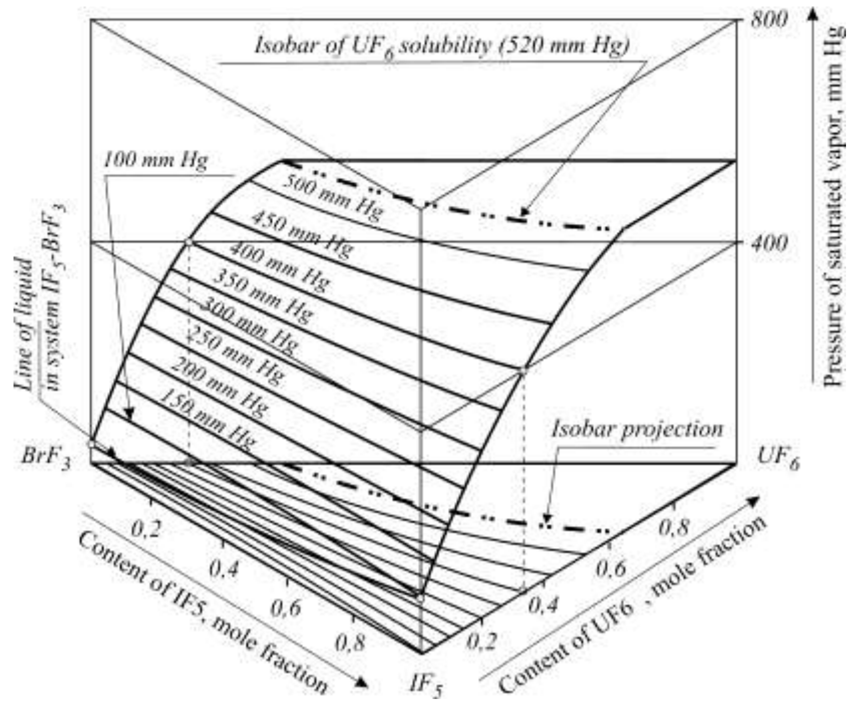


Secants on triangle UF_6 – IF_5 – BrF_3; a_i=x(IF_5)/x(BrF_3)
1) a=0,13; 2) a=0,23; 3) a=0,29; 4) a=0,47; 5) a=0,61;
6) a=0,78; 7) a=1,08; 8) a=2,12; 9) a=3,76; 10) a=5,25

Phase balance in system UF_6-IF_5-BrF_3

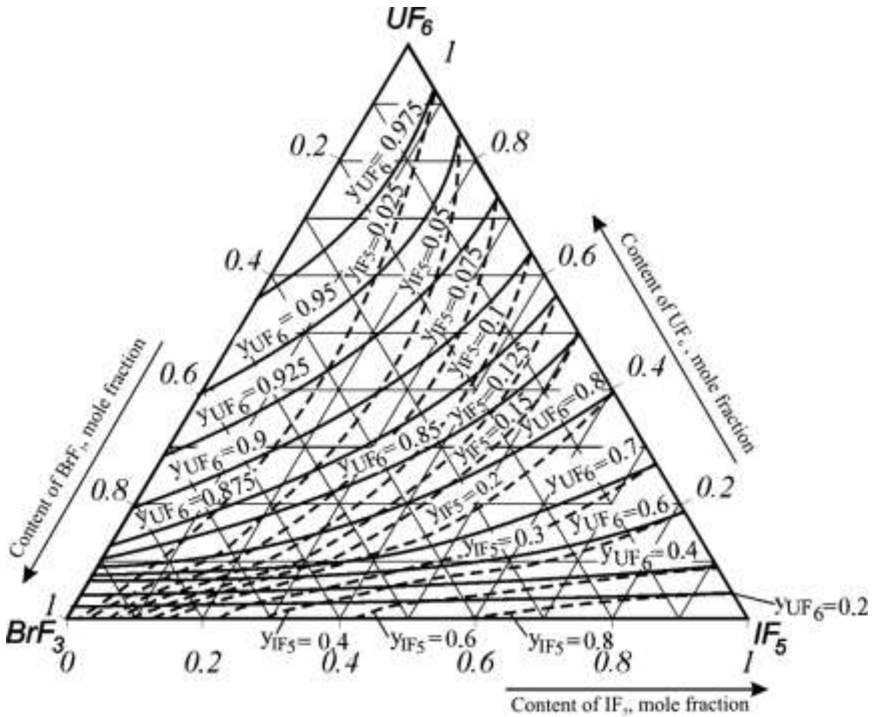


Surface of liquid in system
UF_6 – IF_5 – BrF_3 at 80 ºC

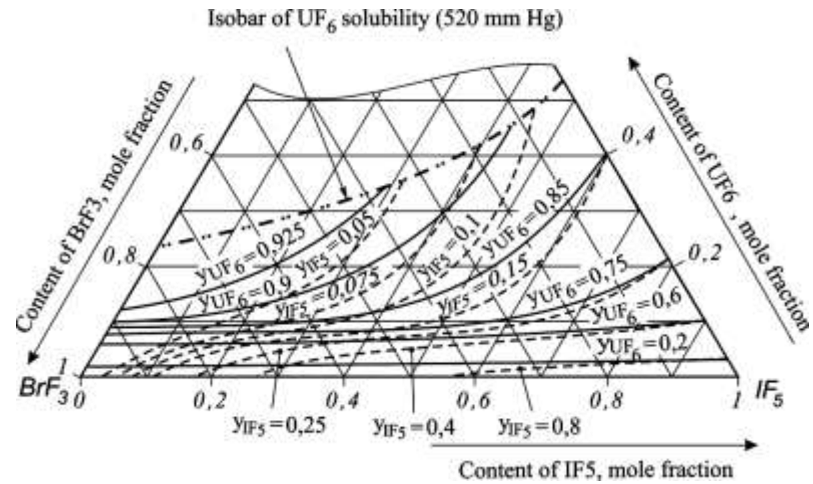


Surface of liquid in system
UF_6 – IF_5 – BrF_3 at 50 ºC,
at limited solubility of UF_6

Phase balance in system UF_6-IF_5-BrF_3



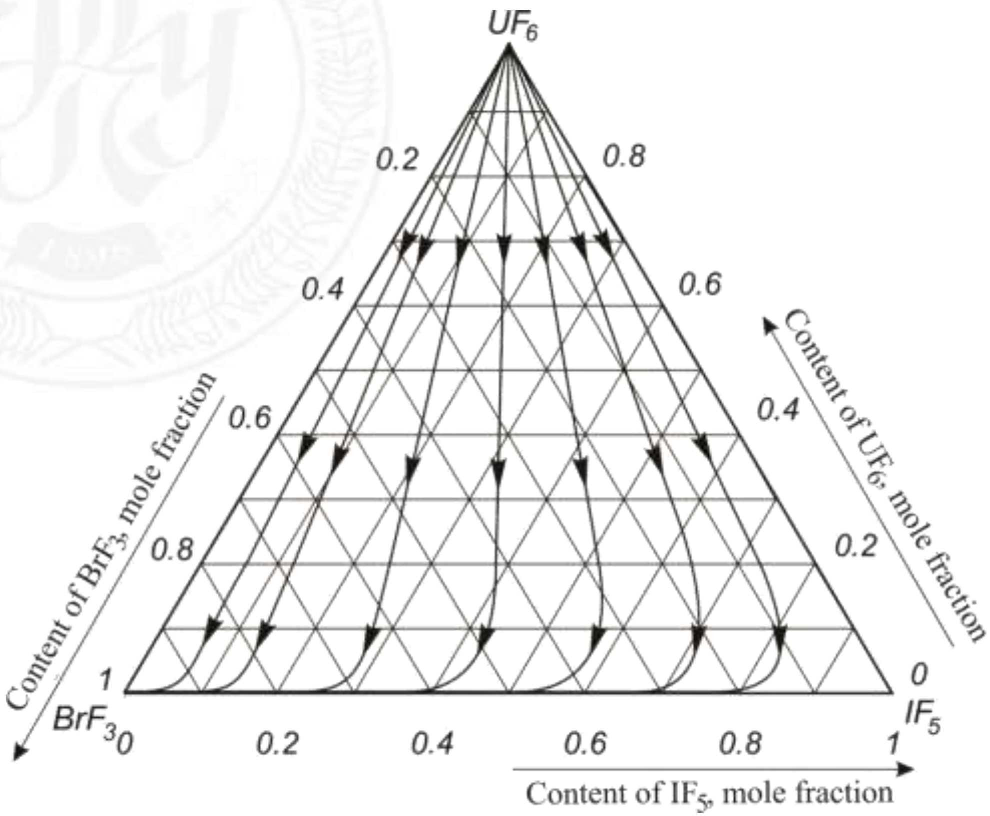
Lines of permanent concentration IF_5 and UF_6 in vapour system
UF_6 – IF_5 – BrF_3 at 80 ºC



Lines of permanent concentration IF5 and UF6 in vapour system
UF6 – IF5 – BrF3 at 50 ºC

$$y_{UF_6} + y_{IF_5} + y_{BrF_3} = 1$$

Phase balance in system UF_6-IF_5-BrF_3



Lines of evaporation
in system UF_6 - IF_5 - BrF_3

UF_6 is extracted from the condensed system practically in full.

After uranium hexafluoride exhaust, rectification in the binary system IF_5 - BrF_3 takes place with pure bromine trifluoride being the final point of the process.

Complex compounds of bromine trifluoride

In spite off all facilities application of halogen fluorides in laboratory and industrial practice is difficult.

To using fluorides of halogen is necessary application some specific skills, providing safety.

As alternative complex compound of BrF_3 can be used with alkaline and alkaline-earth metals.

This reagents, stable at normal conditions, show fluorination properties while heating.

Complex compounds of bromine trifluoride

Barium tetrafluorobromate is the most stable one among alkaline-earth elements. It forms by next reaction:

$$BaCl_2 + BrF_3 \rightarrow Ba[BrF_4]_2 + Cl_2 + Br_2$$

$Ba[BrF_4]_2$ has high thermal stability.

More perspective application of complex compound BrF_3 with alkaline metals. In that work are shown $NaBrF_4$ and $KBrF_4$

Preparation of Sodium and Potassium tetrafluorobromates

interaction between potassium and sodium fluorides and liquid bromine trifluoride

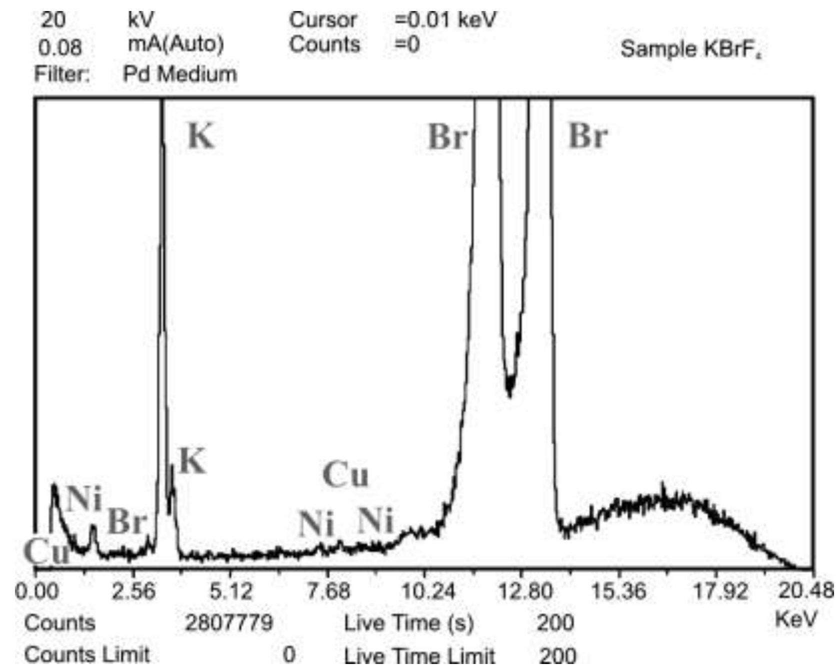
$$KF + BrF_3 \rightarrow KBrF_4$$
$$NaF + BrF_3 \rightarrow NaBrF_4$$

fluorination of potassium bromide and sodium bromide with elementary fluorine

$$KBr + F_2 \rightarrow KBrF_4$$
$$NaBr + F_2 \rightarrow NaBrF_4$$

Complex compounds of bromine trifluoride

Fluorescent spectrometer Quant`X



Spectrum of potassium tetrafluorobromate

Characteristic lines

K Kα=3,04 keV, Kβ=3,9 keV

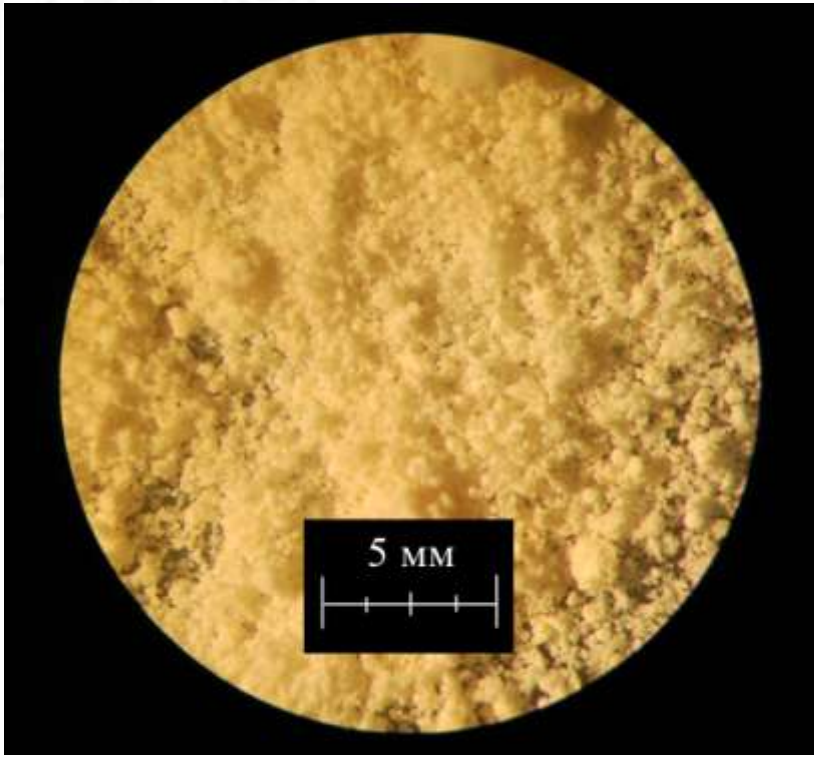
Br Kα=11,92 keV, Kβ=13,29 keV, L3=1,54 keV

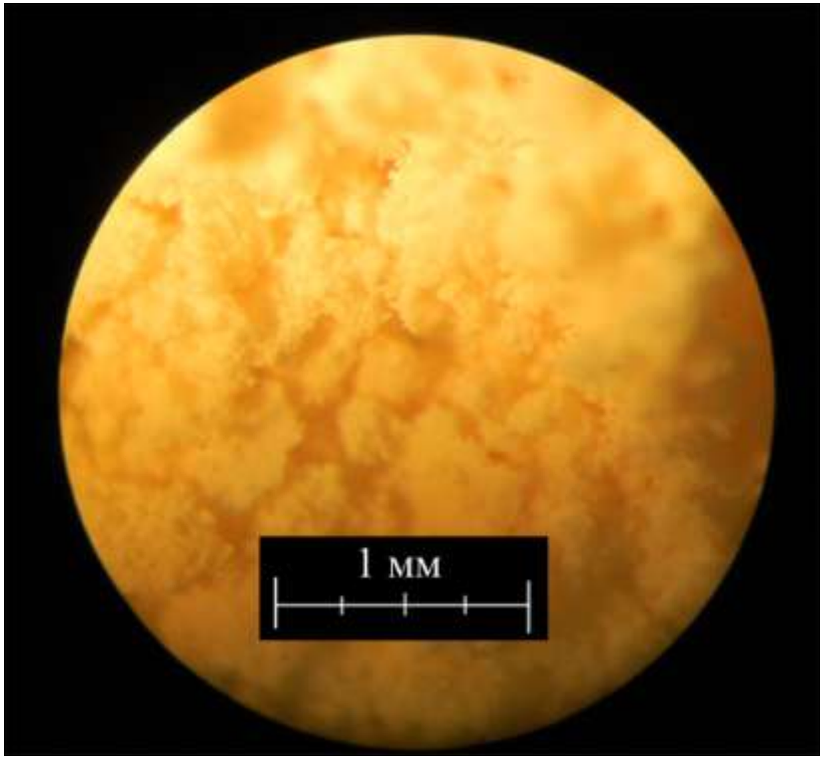
Constructive materials

Ni Kα=7,47 keV, Kβ=8,26 keV, L1=1,01 keV

Cu Kα=8,04 keV, L3=0,85 KeV

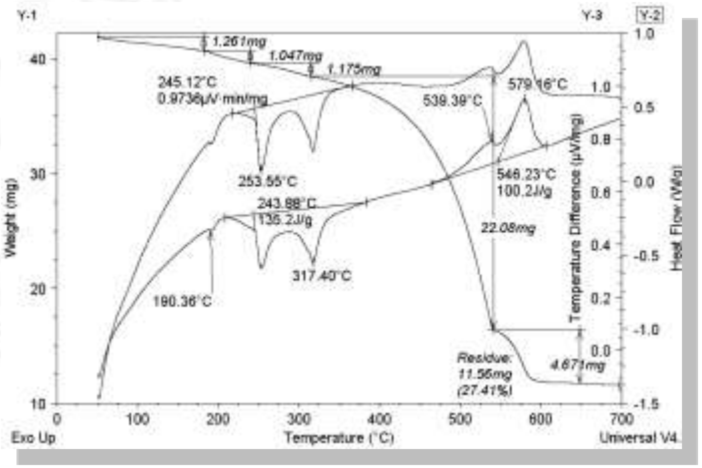
Complex compounds of bromine trifluoride





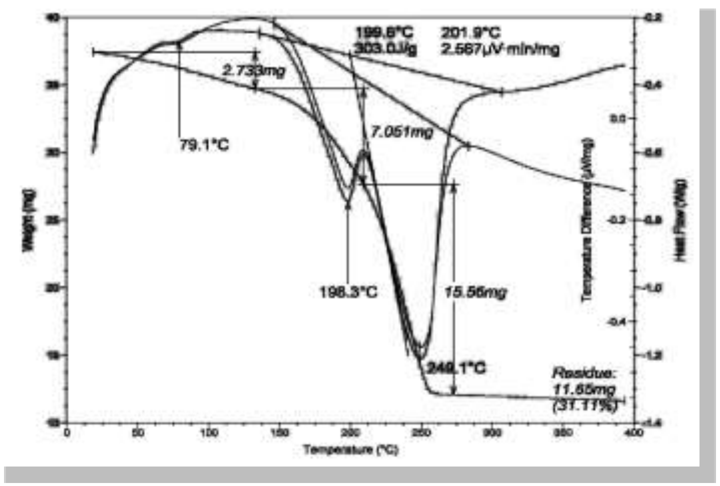
Tetrafluorobromate of potassium

Complex compounds of bromine trifluoride



Thermograms of samples $KBrF_4$

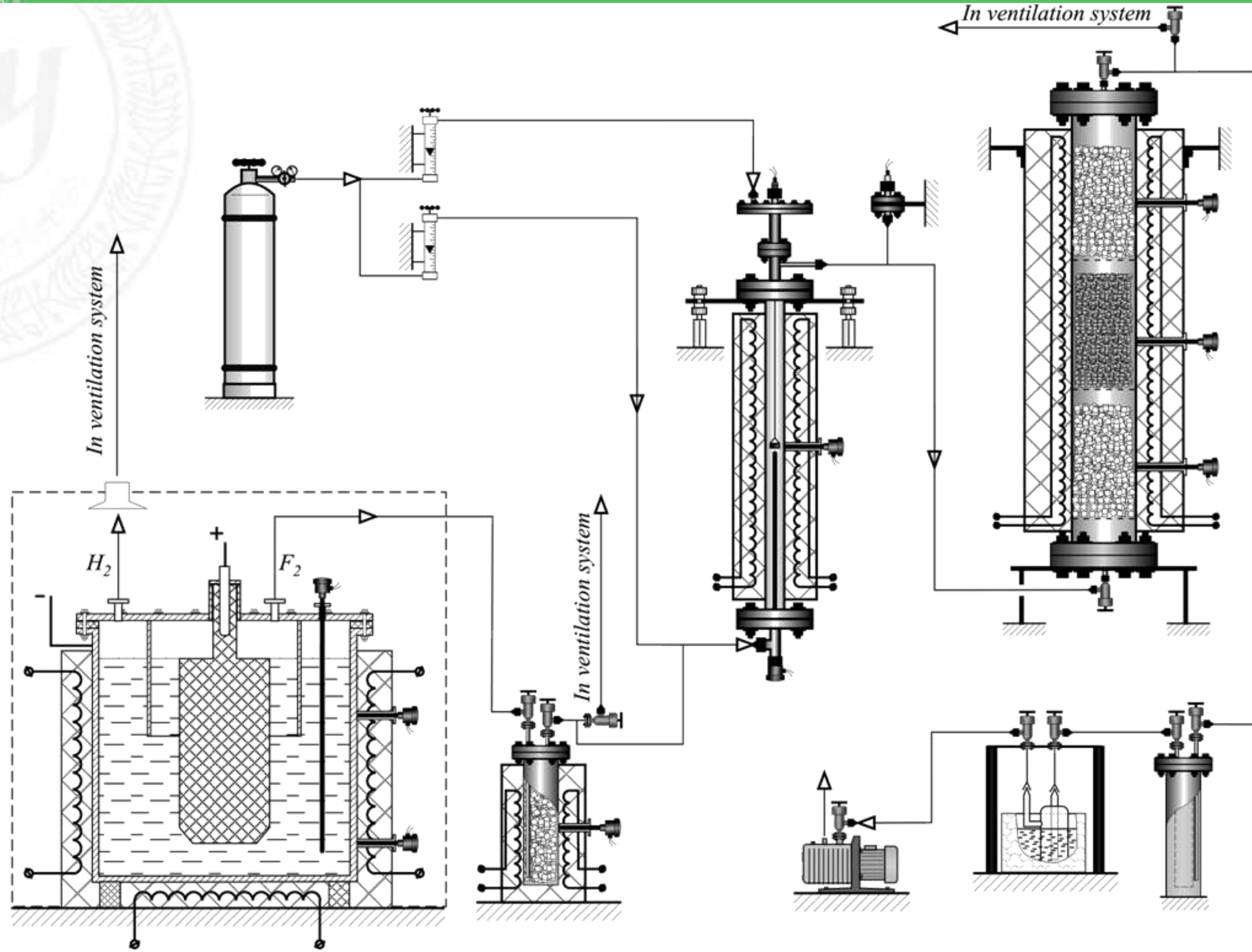
Thermo-analytical investigations (TI) with the application SDT Q 600 thermal analyzer



Thermograms of samples $NaBrF_4$

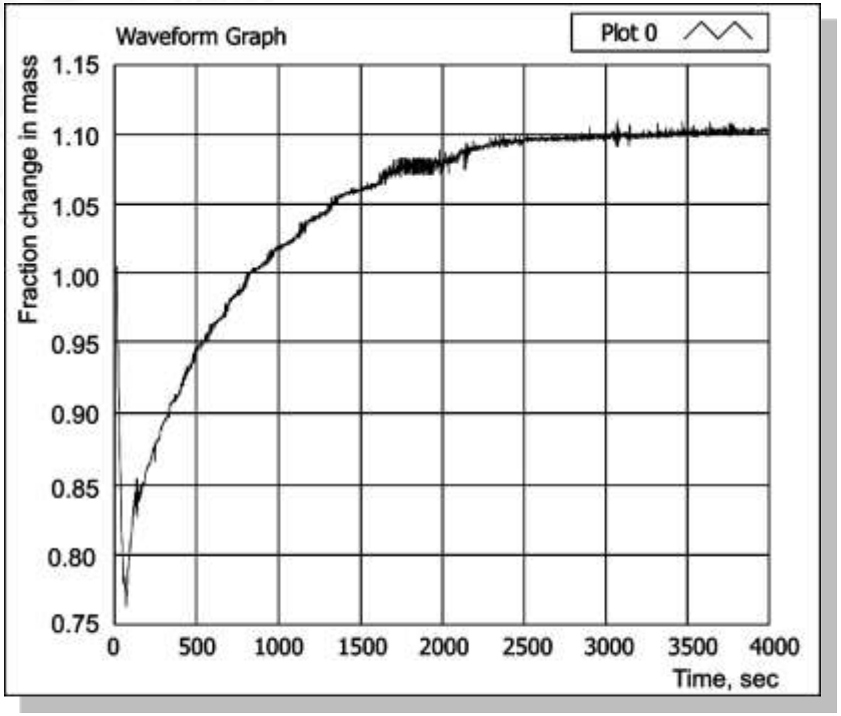
$NaBrF_4$ decomposition temperature (150÷250 ºC) is lower than $KBrF_4$ decomposition temperature (320÷540 ºC). The thermal stability of $NaBrF_4$ is lower than $KBrF_4$ one, though endothermic effect of $NaBrF_4$ decomposition is considerably higher than endothermic effect of $KBrF_4$ decomposition

Kinetic of potassium bromide fluorination



Experimental installation for kinetic fluorination study

Complex compounds of bromine trifluoride



Dependence of KBr and reaction productbs mass change at time in interaction F_2 and KBr at 50 ºC

$$2KBr + F_2 \rightarrow 2KF + Br_2$$

$$Br_2 + F_2 \rightarrow 2BrF$$

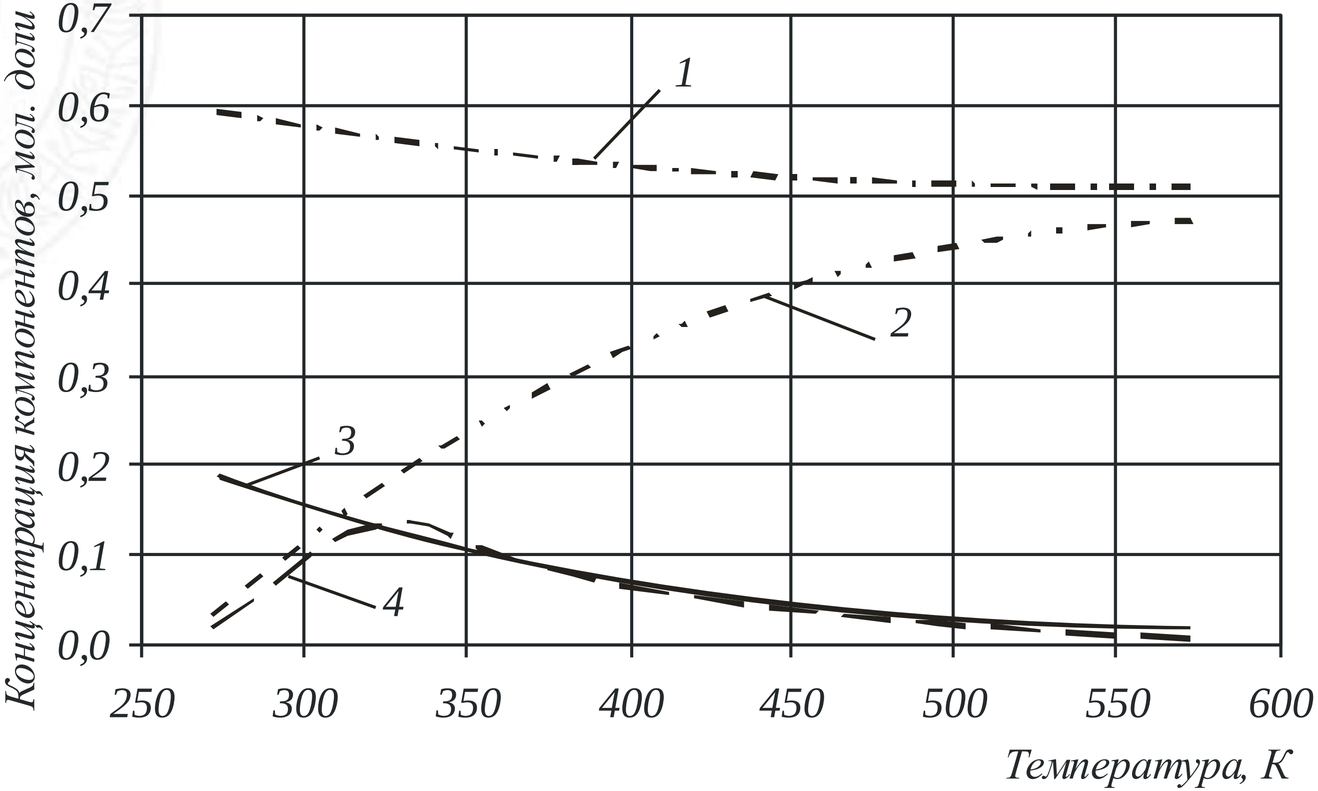
$$Br_2 + 3F_2 \rightarrow 2BrF_3$$

$$Br_2 + 5F_2 \rightarrow 2\ BrF_5$$

$$KF + BrF_3 \rightarrow KBrF_4$$

$$KBrF_4 \rightarrow KF + BrF_3$$

Complex compounds of bromine trifluoride



Calculation result of gaseous products equilibrium concentrations of reaction at pressure 0.1 MPa
1- KF , 2 – BrF, 3 – BrF_3, 4 – Br_2

TOMSK POLYTECHNIC UNIVERSITY

Physical Technical Faculty

Chare of Chemical Technology Rare and Radioactive Elements

Fluorination process, halogen fluorides and perspective forms of using bromine thrifluoride

Associate professor

Ostvald Roman

CESAER

CLUSTER