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PHYSICO-CHEMICAL AND ENGINEERING PRINCIPLES OF BORON ISOTOPES SEPARATION BY USING BF_3-ANISOLE·BF_3 SYSTEM

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PHYSICO-CHEMICAL AND ENGINEERING PRINCIPLES OF BORON ISOTOPES SEPARATION BY USING BF_3–ANISOLE·BF_3 SYSTEM

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ABSTRACT

This review is devoted to consideration of physico-chemical and engineering data required for realization of boron isotopes separation by the method of chemical isotope exchange between BF_3 and the complex anisole·BF_3. The properties of the initial substances and anisole·BF_3 complex required for calculation of the separation process are considered. The data on phase equilibrium in the system, isotope equilibrium, kinetics of interphase isotope exchange, and implementation of phases conversion are presented. This article considers comprehensively the reasons for anisole decomposition and the measures for its prevention. The problem of hydrody-

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namics and choice of packing are investigated. The conditions of initial substances preparation are treated. Perspective trends of separation process improvement are discussed.

GENERAL CHARACTERISTICS OF BORON ISOTOPES AND AREAS OF THEIR APPLICATION

Boron ranks 5th in the periodic system of elements. It has two stable isotopes, ^{10}B and ^{11}B. Basic nuclear and nuclear-physical properties of boron isotopes are listed in Table 1. Table 1 shows that ^{10}B is more rare in occurrence. Hence, all separation processes are performed just for the purpose of its extraction from the natural mixture of isotopes. It is essential that the natural concentration of ^{10}B (the initial isotope concentration in separation processes) is rather high, 19.3%. It should be noted that this value is typical for most boron sources. The literature data for this value range between 18 and 20% of ^{10}B, which is probably associated with geochemical processes of salts formation at the sources. This fact is important, because the initial isotope concentration (denoted as X_o) strongly affects the economics of the separation process.

As follows from Table 1, ^{10}B effectively absorbs neutrons. The ^{10}B isotope ranks below ^{157}Gd ($242{,}000 \times 10^{-28}$ m^2), ^{113}Cd ($20{,}000 \times 10^{-28}$ m^2), ^{155}Gd ($61{,}000 \times 10^{-28}$ m^2), ^{151}Eu ($7{,}700 \times 10^{-28}$ m^2), ^{182}Ta ($8{,}000 \times 10^{-28}$ m^2) by the

Table 1. Main Properties of Boron Isotopes

	Isotope	
	^{10}B	^{11}B
Mass number	10	11
Atomic mass, (^{16}O = 16)	10.016116	11.012796
Abundance, %	19.3	80.7
Nuclear spin, I	3	3/2
Absorbing capability compared with ^{13}C–^{C}R	22.1	7.54×10^2
Electric quadrupole moment, $Q \times 10^{-28}$ m^2	8.5×10^{-2}	4.1×10^{-2}
Cross-section capture for thermal neutron, 10^{-28} m^2:		
(n, α)	3837	<0.05
(n, γ)	0.5	<0.05
Energy of γ-radiation, MeV	4.47–11.43	0.95–5.73
Reactions of interaction with neutrons:	^{10}B(n,α)^{7}Li + 2.31 MeV ^{10}B(n,γ)^{11}B + 0.47 MeV	^{11}B(n,γ)^{12}B ($\tau_{1/2}$ = 0.019 s)

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ability to absorb thermal neutrons ($E = 0.025$ eV). However, these isotopes display resonance peaks in a wide range of neutron energies: an effective cross-section increases abruptly only at the specific neutron energies. The ^{10}B isotope exhibits cross-section capture, which is reciprocal of velocity (according to the "1/V" law) in a wide range of energies, and hence, boron-containing neutron absorbents are rather effective.

This ability of the ^{10}B isotope to absorb neutrons is used in the rods of the control and protection systems (CPS) of the reactor as "depleting additive" inserted in the active zone of the reactor to compensate for a surplus of reactivity (in the form of elementary boron, boron carbide, hexaboride, and aluminum dodecaboride). The use of depleting absorbents of neutrons considerably improves the operating conditions of fuel elements (FE) and offers the possibility of reducing the number of controlling rods. The ^{10}B isotope is also effective as a neutron-shielding material used for anti-activation covering to prevent activation during the neutron exposure. The absence of highly penetrating γ-radiation, which is typical for elements of medium and high masses, is the essential merit of the ^{10}B. It is also widely used in nuclear-physical equipment, particularly in neutron counters based on the reaction $^{10}B(n,\alpha)^{7}Li$, which is written as follows:

$$^{10}B + n \rightarrow [^{11}B] \rightarrow {}^{7}Li(0.87\ \text{MeV}) + {}^{4}He(1.52\ \text{MeV}) \tag{1}$$

High ability of α-particles and ^{7}Li nuclei formed by neutron capture for ionization is used in medicine for combating cancer ("neutron capture" therapy). When irradiating a tumor by neutrons, the formed α-particles and ^{7}Li nuclei destroy cancer cells. The ^{10}B isotope is preferable to other isotopes, because it can be injected into a human organism more easily and safely than other neutron absorbents.

The ^{11}B isotope is used far less, because it does not absorb neutrons. Nevertheless, it is used as an additive to steels that are used in the construction of reactors to enhance their heat and radiation resistance without destroying the neutron physics of the reactor-active zone. Uranium and plutonium borides (UB_2 and PuB_2) containing ^{11}B show enhanced heat conductivity, and when using fuels of the ^{15}N type, Pu reproduction appears to be improved in the presence of ^{11}B. It should be emphasized that ^{11}B can become an important potential thermonuclear fuel. The energy release in reaction $^{11}B + p \rightarrow 3^{4}He$ comprises 8.7 MeV. Such a reaction is of prime importance considering the very high ^{11}B content in the natural boron compounds. Both ^{10}B and ^{11}B are employed in research by the NMR-spectroscopy technique.

Brief Review of Development of Boron Isotopes Separation Processes

Design and realization of boron isotopes separation processes began as early as the Second World War. A large industrial plant with productivity of up to 300 kg of elementary boron with 95% ^{10}B content per year was put in operation in 1944 (1). The plant used the process of chemical-exchange rectification of the complex compound of BF_3 with dimethyl ether. The process is called the chemical-exchange rectification, because the vapor phase over the liquid complex contains vapors of the complex itself and its dissociation products, i.e., BF_3 and $(CH_3)_2O$. Separation of the vapor phase components is impossible, because the liquid complex forms again when cooling. The rectification of the complex is carried out in the column. The separation factor, α (see List of Symbols), characterizing this process is equal to 1.000. Isotope exchange between BF_3 and gaseous $(CH_3)_2O \cdot BF_3$ proceeds simultaneously, and for this process, $\alpha = 1.016$–1.025 (according to different authors' measurements by various methods).

The properties of $(CH_3)_2O \cdot BF_3$, and the $(C_2H_5)_2O \cdot BF_3$ complexes are well documented (2). These complexes decompose at boiling point (401 K for $(CH_3)_2O \cdot BF_3$), and this requires performing the separation process at reduced pressure. For the above-mentioned cascade (1), the pressure at the bottom and at the top of the column comprised 152 and 91 mm Hg (20.216 and 12.103 kPa), respectively. The need to operate under vacuum considerably reduces productivity of the plant, without completely overcoming the problem of complex decay. In industrial plants, this value reaches 2–4% of the loaded complex amount per day depending on both temperature and purity of the complex itself and installation. Attempts to suppress reversible thermal decomposition by injection of fluoromethane (one of the dissociation products) have failed (3). Industrial plants for ^{10}B production by chemical-exchange rectification operated in the United States (1,4), the USSR (5), and England (6). Critical analysis of operation of pilot and established plants for chemical-exchange rectification of boron isotopes is given in reviews (7,8). At present, it seems that no industrial plant applies the process of chemical-exchange rectification.

From 1971, a French company, ISOBOR, exploited a plant, yielding 200 kg of ^{10}B with concentration of 90 % per year and 800 kg of ^{11}B (9). The technology was based on the following isotope exchange reactions:

$$R^{*11}BO_2 + H^{10}BO_2 \Leftrightarrow R^{*10}BO_2 + H^{11}BO_2 \qquad (2)$$

performed on an anion-exchanger Amberlite IRA-410 (denoted by R* in reaction 2). Information on this plant operation is not presently available.

Rectification is widely used for production of ^{10}B and ^{11}B isotopes of concentrations of 99% and over, mainly by using BF_3. Thus, a cascade comprising two columns (filled with packing), 56- and 44-mm in diameter and the height of 17.4 m has been built in England for producing 25 kg of boron with ^{10}B concentration up to 95% annually (10). A similar plant was constructed in the USSR in 1965. It included a column 49.5 m in height and 57-mm in diameter and operated under pressure of 0.4 MPa. The annual productivity of the plant was 20–25 kg of boron with 85% ^{10}B content in the final product. The concentration of ^{10}B in the waste did not exceed 14%. The major amount of ^{11}B isotope with a concentration over 99.5% is also produced by BF_3 rectification.

Other methods of B isotopes separation investigated in laboratories included electromagnetic, thermodiffusion, diffusion in a flow of inert carrier, laser techniques, and extraction. However, they have not found any practical application. The sole exception is the chemical exchange method between BF_3 and its complex with anisole considered in this study.

SEPARATION OF BORON ISOTOPES BY CHEMICAL EXCHANGE METHOD: MOLECULAR ADDITION COMPOUNDS

Thermodynamics of Boron Isotope Exchange Reactions

Strictly speaking, chemical isotope exchange methods, as applied to the task of boron isotopes separation, can be realized using a large variety of systems. A selection of literature data on possible systems and their components should be considered to justify the choice of the BF_3–anisole·BF_3 system. The case in question is primarily the values of separation factor attainable by using one or another system and is calculated by β-factors or experimentally found.

Calculations of β-factor values performed by the method of statistic thermodynamics show that among various boron compounds the following have the maximum β-factors at 298 K: BF_3 ($\beta = 1.2349$), $B(OH)_3$ ($\beta = 1.2336$), BO_3^{3-} ($\beta = 1.2098$) (12). Minimal β-factors, in accordance with the results of calculations, are inherent in BI_3 (1.092), BH_4^-(1.1142), and BBr_4^-(1.0817). Isotope exchange reactions involving the above-mentioned pairs of compounds would ensure α of the order of 1.13–1.15. However, the constraints caused by the necessity of flow reversal at the ends of the separation column do not permit the majority of thermodynamically effective systems, such as BF_3–BBr_4^-, $B(OH)_3$–BH_4^-, and others. The flow reversal can be realized without considerable consumption of chemicals for the following effective systems: BF_3–BBr_4^-($\alpha = 1.036$), $B(OCH_3)_3$–$B(OH)_4^-$($\alpha = 1.022$), $B(OCH_3)_3$–BO_2^-($\alpha = 1.045$), $B(OH)_3$–$B(OH)_4^-$($\alpha = 1.056$). The use of systems based on BF_3 and its liquid molecular addition compounds in reactions of isotope exchange permits excluding the chemical method of flow reversal and replacing it with a thermal one, which is cheaper and ecologically preferable. In this case, αvalues can reach 1.030–1.050.

The property of BF_3 (and other boron halides) to form molecular addition compounds is explained by the features of their electron structure. Boron atom is surrounded by six electrons on the hybrid sp^2-orbits and has a vacant p-orbit perpendicular to the plain of three sp^2-bonds. This is the reason why all boron halides exhibit a clearly defined tendency to add atoms having undivided pairs of electrons and are part of other compounds. Among such atoms are O, N, S, Se, and Te, which are donors of d-electrons. The acceptor, i.e. boron atom, is surrounded in such compounds by eight electrons located on the orbits close to the sp^3-type. The liquid or solid complexes formed with donor compounds, D (particularly with nitrogen-containing constituents), are able to exchange with BF_3 by the following isotope exchange reactions:

$$D\cdot{}^{11}BF_{3(1)} + {}^{10}BF_{3(g)} \Leftrightarrow D\cdot{}^{10}BF_{3(1)} + {}^{11}BF_{3(g)}{}^{*} \qquad (3)$$

Separation factors characterizing reaction 3 vary in a wide range from 1.010 to 1.080 depending on the electron nature of the donor atom, the structure and chemical composition of molecules involving donor and other factors. Liquid complex compounds are of particular interest for separation processes based on chemical exchange technique. They can be formed with both liquids and gases, particularly at low temperatures. Thus, at $P = 0.1$ MPa and $T = 195$ K the formation of liquid complex $BF_3\cdot SO_2$ is observed.

Liquid complex compounds can be subdivided into two groups according to their physico-chemical properties. The compounds of both groups are used in various processes for separation of boron isotopes. The first group involves complex compounds possessing vapor pressure lower than that of the individual donor compound D. These substances in a liquid state are characterized by the mole ratio of composing components (r = mole of BF_3/1 mole of D), which equals to 1 in the whole temperature range of their existence. Compounds of the first group possess constant boiling points, which enables their distillation. Complexes in the vapor phase are only partially dissociated, and hence, BF_3 cannot be separated from other vapor components. The phase equilibrium in the system can be described as follows:

$$D\cdot BF_{3(l)} \Leftrightarrow D\cdot BF_{3(v)} \Leftrightarrow D_{(v)} + BF_{3(g)} \qquad (4)$$

As seen, the uptake of BF_3 is required to perform the isotope exchange according to reaction (3). BF_3 can be formed only as the result of vapor phase dissociation. Hence, the isotope exchange is to be followed by rectification, and the separation process as a whole is referred to as chemical-exchange rectification. The first industrial separation of boron isotopes based on the use compounds of the first group refers to 1944 (see above) when the process of chemical-exchange rectification of complex compound BF_3 with dimethyl ether $(CH_3)_2O\cdot BF_3$ has been realized.

The second group comprises complex compounds with vapor pressure higher than that of the donor compound D, which almost completely dissociate in the vapor phase. The vapor pressure of D is, as a rule, very low so that the vapor phase contains pure BF_3, which can be easily separated both from the liquid complex and the vapor of D. This fact enables the exchange between liquid $D\cdot BF_3$ and gaseous BF_3 according to reaction (3), i.e., by using a classic variant of chemical-exchange systems.

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*Coordination bonds in neutral complex compounds are usually denoted by a single point: $(C_2H_5)N\cdot BF_3$.

The liquid complex compound, $D{\cdot}BF_3$, does not have any fixed boiling point. Upon heating it starts to dissociate, releasing BF_3 into the gas phase. The mole ratio r appears to be a function of temperature, varying in a very wide range from 1 at $T = 298$ K to approximately $(50–60) \times 10^{-6}$ at the boiling point of D (complex compounds are liquids at room temperature). This particular property of complex compounds is used as a basis for the boron isotopes separation processes using flow reversal according to the following reaction:

$$D{\cdot}BH_{3(1)} \underset{\text{cooling}}{\overset{\text{heating}}{\longleftrightarrow}} D_{(1)} + BF_{3(g)} \tag{5}$$

Thus, to separate boron isotopes by thermal method of flow reversal, the complex compounds of the second type are applied, because they do not require chemical consumption and allow reuse of the donor compound.

A short lifetime is a common feature of all liquid complex compounds. According to the data of ^{19}F NMR spectroscopy, the lifetime of $D{\cdot}BF_3$ molecules is around $10^{-5}-10^{-3}$ s (13). This feature of BF_3 complexes requires a substantial increase in the rate of isotope exchange.

It is known that BF_3 forms complex compounds of the second group with the following substances: ethers, thioethers, phenol ethers, chloroalkanes, amines, and many of their derivatives. Table 2 presents some of these substances and val-

Table 2. Separation Factor Values for Complex Compounds of BF_3 with Some Donors

No.	Compound	T, K	α	$\lg \alpha = a/T + b$	Ref.
1	$(C_4H_9)_2O{\cdot}BF_3$	293	1.029		13
2	$(CH_3)_2S{\cdot}BF_3$	298	1.036	$16.9/T–0.0440$	14
3	$(CH_3)_2Se{\cdot}BF_3$	298	1.033	$8.13/T–0.0131$	15
4	$(C_2H_5)_3N{\cdot}BF_3$	298	1.023		16
5	$(ClC_2H_4)_2O{\cdot}BF_3$	298	1.040	$15.323/T–0.03447$	17
6	$C_6H_5OH{\cdot}BF_3$	298	1.027	$10.315/T–0.02423$	18
7	$C_6H_5OCH_3{\cdot}BF_3$	298	1.030	$9.87537/T–0.02005$	19
8	o-CH_3-$C_6H_4OCH_3{\cdot}BF_3$	298	1.029		20
9	m-CH_3-$C_6H_4OCH_3{\cdot}BF_3$	298	1.033		20
10	p-CH_3-$C_6H_4OCH_3{\cdot}BF_3$	298	1.022		20
11	p-Cl-$C_6H_4OCH_3{\cdot}BF_3$	300	1.039		20
12	$C_6H_4(OCH_3)_2{\cdot}BF_3$	298	1.048		21
13	$C_6H_5OC_2H_5{\cdot}BF_3$	298	1.042	$12.918/T–0.02573$	22
14	$C_6H_5OC_2H_4Cl{\cdot}BF_3$	298	1.054		20
15	$CH_3COOC_2H_5{\cdot}BF_3$	298	1.036	$32.50/T–0.09354$	23
16	$CH_3Cl{\cdot}BF_3$	165	1.021		24
17	$CHClF_2{\cdot}BF_3$	165	1.017		24
18	cis-2-$C_4H_8{\cdot}BF_3$	165	1.020		25
19	$trans$-2-$C_4H_8{\cdot}BF_3$	165	1.011		25
20	$SO_2{\cdot}BF_3$	177	1.022		24
21	$CH_3NO_2{\cdot}BF_3$	273	1.081	$\ln \alpha = 38.45/T–0.0627$	26

ues of the separation factor. As seen, the number of classes of organic substances forming complex compounds with BF_3 is very high, showing considerable distinctions in their properties.

The ability of complex compound to separate boron isotopes depends basically on the nature of atom being a donor of electrons. A more comprehensive analysis of the literature along with the data of Table 2 shows that, in terms of achievable isotope effects in reaction (3), sulfur is the most favorable donor atom. However, thioethers are toxic, corrosive, and quite unstable, which hinders their application for technological purposes. Compounds containing nitrogen as a donor atom are of no interest in terms of boron isotopes separation because the majority of complex-forming compounds are solid and characterized by low separation factors. This ranks them below others in the isotope exchange rate.

Considering all the properties that different donors are required to have to be used for boron isotopes separation (thermodynamics and kinetics of isotope exchange, aggregation state, separation factor, physico-chemical properties of the ether compound and corresponding complexes), oxygen-containing donor molecules, mostly ethers, stand out as being of primary interest. Introduction of different substituents, electron-donating and electron-withdrawing provides a way to vary the α factor for the newly formed complex compounds (20). One needs to note that the following properties of the complex compounds may change simultaneously: mole ratio *r*, melting point, vapor pressure, and viscosity. Thus, an increase in the separation factor is achieved by the introduction of electrically negative substituents, mainly halogens, into the molecule of the donor. However, the complex compounds thus obtained often have high melting points, considerable viscosity, lower *r* (compared with the initial complex). Commonly, halogen-substituents decrease the chemical resistance of the ethers, particularly at elevated temperatures inherent in the lower flow conversion system. Moreover, some halide ethers are highly toxic. Taking into account the preceding, complex compounds of BF_3 with ethers containing halogen substituents cannot be used in processes of boron isotopes separation despite the high separation factors.

As shown in Table 2, complex compounds of BF_3 with halo-alkanes and other substances formed at low temperatures exchange with BF_3 with relatively low separation factors. Hence, they have not found any use, except for SO_2BF_3. This compound is regarded as more useful due to the chemical stability of SO_2 and its technological convenience: no pumps are required for the donor compound transport.

In 1954, Georgii M. Panchenkov, Vladimir D. Moiseev, and Anatolii V. Makarov from the Laboratory of Stable Isotopes of Lomonosov Moscow State University, proposed using complex compound of BF_3 with anisole (hereafter denoted as An), - $C_6H_5OCH_3$ (27). In succeeding years a great number of BF_3 complex compounds with various types of organic substances were explored, including systems having high separation factors. Nevertheless, the first Soviet pilot plant for separation of boron isotopes by chemical exchange technique applied complex compounds of BF_3 with anisole and phenetol ($C_6H_5OC_2H_5$) (28). The pilot plant study showed the superiority of anisole over phenetol in both separation efficiency (lower HETP values) and chemical stability.

SEPARATION OF BORON ISOTOPES USING MOLECULAR ADDITION COMPOUND OF BF_3 WITH ANISOLE

Physico-Chemical Properties of Anisole, BF_3, and Their Complex

Physico-chemical properties of the initial substances and the complex itself are listed in Tables 3, 4, and 5.

Anisole (phenylmethyl ether, methoxybenzene) is a colorless liquid with a pleasant odor, extremely insoluble in water (see Table 3). It is absolutely soluble in acetone, benzene, alcohol, and ether. It is usually produced from sodium phe-

Table 3. Physico-Chemical Properties of BF_3

No.	Property	Value or Temperature Dependence
1	Molecular mass	67.81
2	T_{melt}, K	146
3	T_{boil} (0.1 MPa), K	172
4	T_{crit}, K	260.75
5	P_{crit}, MPa	4.92
6	Vapor pressure, mm Hg	$lgP = (-1174.4/T) + 1.75\ lgT - 0.01335T + 8.0536$
7	ρ_g, kg/m^3 (273 K)	3.07666
8	ρ_l, kg/m^3 (172 K)	1590
9	ρ_s, kg/m^3	1870
10	$\eta_g \times 10^{-7}$, Pa·s	$0.7844T-(4.223 \times 10^{-4})T^2-27.95$
11	$\eta_l \times 10^{-3}$, Pa·s	0.519 (168 K), 0.620 (163 K), 0.740 (158 K)
12	$c_{P(g)} \times 4.19$, J/mol·K	$6.293 + 22.988 \times 10^{-3}\ T - 11.266 \times 10^{-6}\ T^2$
13	$c_{P(l)} \times 4.19$, J/mol·K	25.05 (170 K), 24.84 (160 K), 24.64 (150 K)
14	$\sigma \times 10^{-3}$, N/m,	$20.29\text{-}0.22(T + 117.0)$
15	ΔH_{evap}, kJ/mol	18.94
16	Thermal conductivity of liquid BF_3, J·cm^{-1}·s^{-1}·deg^{-1} (171–147 K)	203.6×10^{-5}
17	Gas state equation	$PV(1 + 0.01657P) = RT$

Table 4. Physico-Chemical Properties of Anisole ($C_6H_5OCH_3$)

No.	Property	Value or Temperature Dependence
1	Molecular mass	108.13
2	T_{melt}, K	235.62
3	T_{boil}, K	429
4	T_{crit}, K	657
5	P_{crit}, MPa	3.88
6	Vapor pressure, mm Hg	$lgP = 7.35950 - [1718.7/(T - 7)]$
7	$\rho^t \times 10^3$, kg/m^3	$1.2680 - 9.32 \times 10^{-4}\, T$
8	Vapor density $\times 10^3, \rho_v$, kg/m^3	$lg\rho_v = 1.70652 - [1611.6/(T - 7)$
9	$\eta_l \times 10^{-1}$, Pa·s	$lg\eta_l = (636.8/T) - 4.139$
10	$C_p \times 4190$, J·kg^{-1}·deg^{-1} (297 K)	0.442
11	$\sigma \times 10^{-3}$, N/m	$\sigma = 36.43(1 - 0.00306T)$
12	ΔH_{evap}, kJ/mol, T_{boil}	36.87
13	ΔH_{burn}, kJ/mol	3793
14	Flash-point, K	221
15	Self-ignition temperature, K	541
16	Dielectric permittivity ε, 298 K	4.33
17	Dipole moment, D	1.20
18	Conductance, ohm^{-1}, 298 K	1×10^{-13} (298 K)
19	dT/dP, deg/mm	0.04896
20	n_D^{20}	1.51700
21	Aqueous azeotrope, 368.5 K	A = 59.5 % mass An
22	Water solubility in An, %mass	0.15
23	An solubility in water, %mass	0.36

nolate by the following reaction:

$$2C_6H_5ONa + (CH_3)_2SO_4 \Leftrightarrow 2C_6H_5OCH_3 + Na_2SO_4 \quad (6)$$

The product contains up to 0.1% of water, phenol, and cresols. Anisole is heat-resistant, it does not decompose when boiling, even in the presence of water.

Boron trifluoride BF_3 is the gas with a choking odor. It fumes in the air due to the interaction with water vapor (limiting maximum concentration, LMC = 1 mg/m^3). It is produced by reaction between either boron or borates with F_2 or HF. The BF_3 molecule is extremely chemically active and it reacts with many classes of both organic and inorganic substances.

The interaction of BF_3 with water is of special interest. At present, the properties of BF_3 mono- and dihydrate ($BF_3 \cdot H_2O$ and $BF_3 \cdot 2H_2O$, respectively) are well known. By its chemical properties $BF_3 \cdot H_2O$ is an acid, to which the following formula can be ascribed: HBF_3OH. The structure of BF_3 dihydrate can be presented as $H_3O^+BF_3OH^-$. The composition and the properties of aqueous solutions of BF_3 of intermediate concentrations are essentially more intricate. The equilibrium composition of the BF_3-H_2O system in the range of BF_3 concentrations from 0.01 to 15.6 M has been studied only at 298 K (29). Under these conditions, interaction with water goes through several stages:

$$BF_3 + H_2O \rightarrow HBF_3OH \tag{7}$$

$$HBF_3OH + H_2O \rightarrow HF + HBF_2(OH)_2 \tag{8}$$

$$HBF_2(OH)_2 + H_2O \rightarrow HF + HBF(OH)_3 \tag{9}$$

$$HBF(OH)_3 \rightarrow HF + H_3BO_3 \tag{10}$$

Reactions (7)–(10) proceed rapidly unlike the following reaction:

$$HBF_3OH + HF \rightarrow HBF_4 + H_2O \tag{11}$$

The final solution in the equilibrium state contains the following molecules: HBF_4, HBF_3OH, $HBF_2(OH)_2$, and H_3BO_3. All these acids, except H_3BO_3 and HF, are strong. By their strength HBF_4, HBF_3OH, and $HBF_2(OH)_2$ can be compared with HCl, trichloroacetic acid, and dichloroacetic acid, respectively. BF_3 interacts actively with anisole resulting in the $BF_3 \cdot$An complex formation proceeding by reversible reaction in the liquid phase:

$$C_6H_5OCH_3(l) + BF_3(sol) \Leftrightarrow C_6H_5OCH_3 \cdot BF_3(l) \tag{12}$$

Table 5. Physico-Chemical Properties of An·BF_3 Complex

No.	Property	Value or Temperature Dependence
1	Molecular mass	175.94
2	T_{melt}, K	275
3	ΔH_{form}, kJ/mol	-51.53
4	Saturation pressures of An·0.9BF_3, P, mm Hg	$lg\, P = 10.1 - (2140/T)$
5	$\rho^t \times 10^3$, kg/m^3	$\rho^t = 2.3092 - 36.98 \times 10^{-4}\, T$
6	$\eta \times 10^{-1}$, Pa·s	$lg\eta = (1644.5/T) - 6.934$
7	$r = a_0 + a_1Z + a_2Z^2 + a_3Z^3 + a_4Z^4 + a_5Z^5$ $Z = (2T - 721)/(-135)$ $403 > T > 298$ $a_0 = 0.14457$, $a_1 = 0.55658$; $a_2 = 0.81900$; $a_3 = 0.25880$; $a_4 = -0.472080$; $a_5 = -0.326720$ T, K 283 298 313 323 343 353 363 383 398 413 r 1.01 0.99 0.92 0.66 0.33 0.21 0.11 0.036 0.025 0.007	
8	Thermal dissociation: 430 K $P = 0.105$ Mpa, $r = 69 \times 10^{-6}$ mol BF_3/mol An 436 K $P = 0.123$ Mpa, $r = 42 \times 10^{-6}$ mol BF_3/mol An 439 K $P = 0.139$ Mpa, $r = 55 \times 10^{-6}$ mol BF_3/mol An	

The peculiarity of the liquid phase is that the two substances involved in the reaction (anisole and its complex) are liquid, and the third one (BF_3) is gaseous. This provides the constancy of the total number of moles of anisole and the complex in the liquid phase. The number of moles of BF_3 existing in the liquid in the free state depends on the equilibrium constant K of reaction (12) and also on BF_3 solubility in the system, which varies with temperature and pressure. As a result, the molar concentrations of all three components of the liquid phase appear to depend on both the K value and BF_3 solubility.

Let us denote the concentrations of the free anisole, non-associated BF_3, and the complex compound in the liquid phase as n_{An}, n_B, and n_{AnB} (mol/dm^3), respectively. The temperature dependence of n_{An}, n_B, and n_{AnB} at $P_{BF3} = 0.1$ MPa is shown in Fig. 1. The following expression can be derived for the equilibrium constant:

$$K = n_{AnB}\,(n_{An} + n_B + n_{AnB})/(n_{An} \cdot n_B) \qquad (13)$$

The equilibrium constant computed from the experimental data is described well by the following exponential relation:

$$K = 7.19424 \times 10^{-7} \exp(5847/T) \qquad (14)$$

The data presented in Fig. 1 characterize the phase equilibrium in the system at $P = 0.1$ MPa. They show that approximately 5–10% of free BF_3 (non-associated

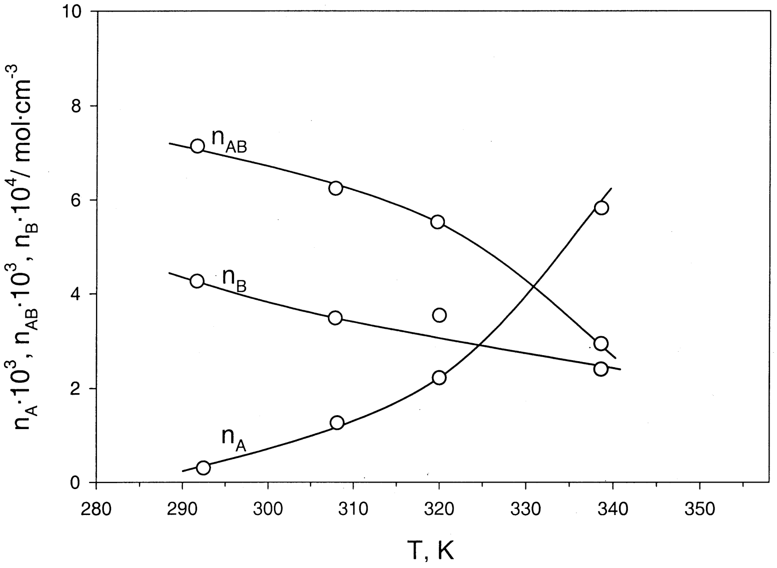

Figure 1. Temperature dependence of equilibrium concentrations of anisole·BF_3 complex, anisole, and BF_3 in liquid phase.

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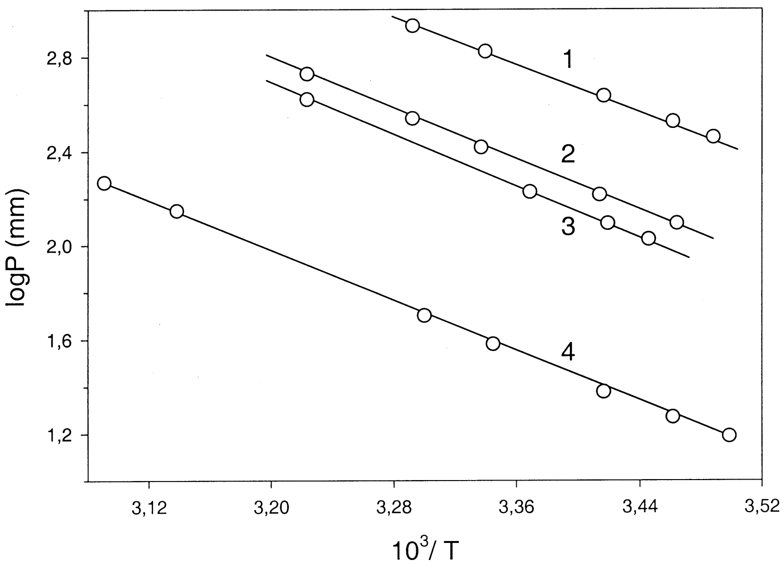

Figure 2. Temperature dependence of logarithm of vapor pressure over anisole·BF_3 complex at different *r* values (see text): $r = 0.92$ (1); $r = 0.75$ (2); $r = 0.70$ (3); $r = 0.21$ (4).

with anisole) always exists in the mixture, more precisely, in the liquid phase. This fact should be taken into account when calculating the effective separation factor α^*. When designing a separation plant only α^* are used and, hence, it is not necessary to subdivide BF_3 in the liquid phase into a dissolved and chemically associated form. As mentioned above, the total content of BF_3 in the liquid phase is commonly denoted as the molar ratio *r*, which constitutes the number of BF_3 moles in the liquid phase per single mole of anisole. The *r* values (in the form of their temperature dependence at $P_{BF3} = 0.1$ MPa) are summarized in Table 5 in the whole range of complex existence, from room temperature to the real operating temperatures occurring in the decomposing reactor. Figure 1 shows the residual BF_3 concentration in anisole leaving the decomposing reactor. The results of calculations show that the degree of complex dissociation under such conditions ensures sufficiently high efficiency of flow conversion for producing ^{10}B of any concentration.

Figure 2 presents the dependence of vapor pressure over the liquid An·BF_3 complex on temperature and *r* (30). The vapor phase existing over the liquid complex constitutes the products of the vapor dissociation of An·BF_3. The dissociation degree of the complex in the vapor phase varies from 0.980 to 0.992 as temperature changes from 353 to 433 K. The heat of complex dissociation in vapor phase is −18.8 kJ/mol in the same temperature range.

As noted above, the vapor pressure of anisole at room temperature is low. Considering the high dissociation degree of the complex in the vapor phase, one may assume that it is composed solely of BF_3. Under such conditions, the equilibrium constant of reaction (12) is proportional to the vapor pressure over the complex. The heat of the complex formation calculated from the data shown in Fig. 2 appears to equal 51.53 kJ/mol (30).

Isotopic Equilibrium in BF_3-Anisole·BF_3 System

The isotope exchange reaction proceeding in the BF_3-anisole·BF_3 system can be written as follows:

$$^{10}BF_3 + A\cdot{}^{11}BF_3 \Leftrightarrow {}^{11}BF_3 + A\cdot{}^{10}BF_3 \qquad (15)$$

As a result, the light boron isotope is concentrated in the liquid phase. The equilibrium constant of this reaction (which is equal to the separation factor α) obtained by Palko and Drury (31) by using the single equilibration technique and taking into account $r > 1.0$ correction, is expressed by the following equation:

$$lgK = lg\alpha = (10.5/T) - 0.022 \text{ at } 273 < T < 305 \text{ K} \qquad (16)$$

Hence, the thermodynamic characteristics of the isotope exchange reaction have been found to equal: $-\Delta F^o = 75.42$ J/mol, $-\Delta H^o = 201.1$ J/mol, $-\Delta S^o = 0.419$ J/K·mol (31). Table 2 gives an expression for the temperature dependence of separation factor in the An·BF_3-BF_3 system (see Eq. 7), which in reality reflects the dependence of the effective separation factor α^* on temperature: $\lg\alpha^* = 9.87537/T - 0.02005$. Numerical comparison of this expression with Eq. 16 shows a negligibly small difference (in the 4th digit after the point) between α and α^* values in the system under consideration. This difference confirms the insignificant contribution of the dissolved BF_3 to α^*. Comparison of α for the BF_3-anisole·BF_3 system with those for other systems shows that it is not the highest (see Table 2). Table 2 also contains the α values for isotope exchange reactions of BF_3 with complex compounds of BF_3 with the following products of anisole decay: phenol, cresols, and methylanisoles.

Kinetics of Interphase Isotope Exchange

The detailed study of kinetics of the isotope exchange reaction in the BF_3-anisole·BF_3 system was not carried out. Nevertheless, the results of experiments on studying the isotope equilibrium of BF_3 (containing 40% of ^{10}B) with An·BF_3 of natural boron isotope composition have shown that exchange is fully completed in periods less than 12 s (30). The half-exchange times calculated from these data

Table 6. Geometrical Characteristics of Packing No. 1 and No. 2

Packing	Fractional Free Space, V_f, m^3/m^3	Specific Geometrical Surface Area, a, m^2/m^3	Equivalent Diameter $d_e \times 10^3 = 4V_f/a$, m
No. 1	0.81	3350	0.97
No. 2	0.88	2600	1.35

were found to be shorter than 3 s indicating a very high rate of the isotope exchange reaction. Some additives such as, benzene, methylbenzene, and chlorobenzene in amounts of 10 vol% have been shown to reduce the half-exchange times to 1.5, 1.5, and 1.4 s. at $T = 294$ K, respectively.*

The mass-exchange in the BF_3-An·BF_3 system was investigated in a laboratory column of height 0.86 m and diameter of 16 mm filled with packings No. 1 (spiral-prismatic elements of 2 × 2 × 0.2 mm size) and No. 2 (net-made) with the element size of 2.5 × 2.5 × 0.12 mm). The geometrical characteristics of packings of both types are given in Table 6.

The mass-exchange kinetics was studied in the temperature range from 278 to 338 K. The experimental results are given in Fig. 3 (32). Analysis of the data on HETP dependence on the loading and temperature shows that the mass-exchange in the system under study is characterized by a considerable contribution of the chemical component h_{chem} to the HETP values, h, which is expressed as follows:

$$h = h_g + \lambda h_l/\alpha + \lambda h_{\text{chem}}, \tag{17}$$

where h_g and h_l are the contributions to HETP (HETP constituents) determined by resistance of the gas and the liquid phases to the mass transfer, respectively; h_{chem} is the contribution to HETP determined by the rate of isotope exchange reaction; and $\lambda = G/L$ is the ratio of the gas to the liquid phase flows.

The contribution of h_{chem} component increases sharply with temperature due to the increase of both the rate of isotope exchange and the rate of BF_3 diffusion in the liquid. At the same time, the diffusion component of HETP slightly decreases from 0.014 to 0.008 m when the temperature increases from 278 to 338 K. Hence, despite some advantages of operation at low temperature, a possibility of substantially increasing the relative loading at elevated temperature in the course of isotope exchange process must also be emphasized. Figure 3 shows, for example, that packing No. 2 (despite the lower specific geometrical surface) exhibits approximately equal separation ability.

The effect of chlorobenzene additives on the efficiency of mass-exchange in the BF_3-An·BF_3 system was investigated by using packing No. 2. The results ob-

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*According to the data obtained in cooperation with N.E. Sizov.

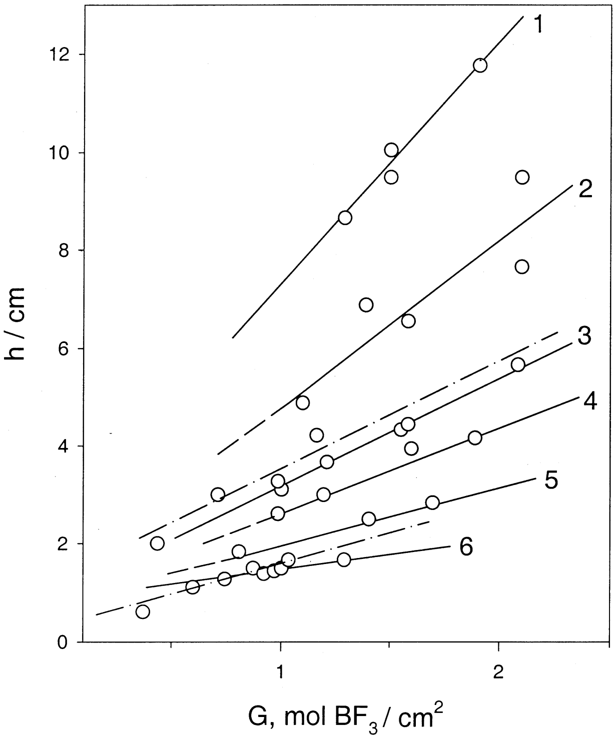

Figure 3. Dependence of HETP on temperature and specific gas loading for complex doped with chlorobenzene (packing No. 2): 1, $T = 278$ K, 10% chlorobenzene; 2, $T = 288$ K, 10% chlorobenzene; 3, $T = 288$ K, 20% chlorobenzene; 4, $T = 298$ K, 20% chlorobenzene; 5, $T = 308$ K, 20% chlorobenzene; 6, $T = 318$ K, 20% chlorobenzene.

tained in this series of experiments are presented in Fig. 4 and clearly show that the additive increases the mass-exchange. All the data on mass-exchange can be described by equation $h = h_o e^{E/T}$, where h_o and E are the coefficients reflecting the influence of temperature on HETP. This equation along with the temperature dependence $\ln \alpha = A/T + B$ was used to calculate the optimal temperature for realization of the separation process by using equation $T_{\mathrm{opt}} = 2AE/(2A - BE)$ as described elsewhere (33). It has been found to be $T_{\mathrm{opt}} = 318$ K. In accordance with Katalnikov et al. (33), the minimal specific volume of the separation unit is the main criterion for optimization.

The modern industrial processes for boron isotopes production are based on the use of columns with a diameter of 100–150 mm. These columns should be filled with highly effective wire packing. In this regard it seems essential to know the hydrodynamic characteristics of the packing such as, the flow resistance ΔP, and the limiting flows of the liquid, L_{lim}, and gas, G_{lim}, phases. Semi-empirical equations are used in rectification processes to calculate ΔP and the limiting velocity, W_{lim} (34). Such equations are not applicable for chemical isotope exchange, where the liquid and the gas phases differ significantly. For this reason these equations (related to rectification) are used after modification by fitting with corresponding coefficients. We also used this approach to treat the data obtained with packing No. 1 and No. 2. The limiting flow of the complex with the liquid phase is described in this case as follows:

$$L_{\mathrm{lim}} = 9.3 - 4.3\,(d_e \rho_v \rho_l)^{1/2} \text{ for packing No. 1} \tag{18}$$

$$L_{\mathrm{lim}} = 18.4 - 7.3\,(d_e \rho_v \rho_l\,)^{1/2} \text{ for packing No. 2} \tag{19}$$

where ρ_v and ρ_l are the density of the vapor and the liquid, respectively, and d_e is the effective diameter of the packing.

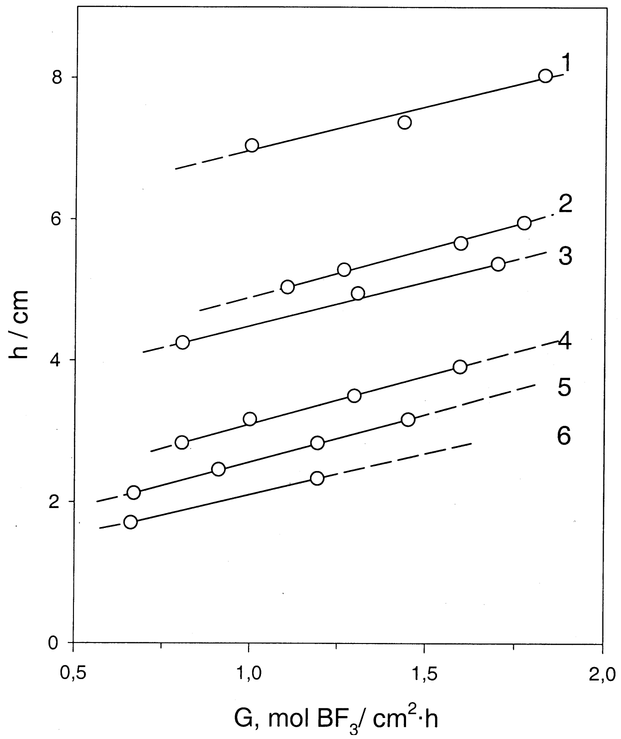

Figure 4. Dependence of HETP on temperature and specific gas loading for isotope exchange columns filled with packing No. 1 (dotted line) and packing No. 2 (solid line): 1, $T = 278$ K; 2, $T = 288$ K; 3, $T = 298$ K; 4, $T = 308$ K; 5, $T = 318$ K; 6, $T = 328$ K.

The accuracy of calculation of L_{lim} [kg/(m^2 s)] by these equations is of the order of ±10%. Calculation of specific flow resistance $\Delta P/l$ [N/m^2] is performed by the following equation:

$$\Delta P/l = \xi \, W_{o,v}^2 S \rho_v / (8(V_f - H_o)^3) \tag{20}$$

where l is the height of the separation column, m; W_v is the vapor velocity related to the entire column cross-section area, m/s; S is the specific geometrical surface area of packing, m^2/m^3,ρ_v is the vapor density, kg/m^3, V_f is the free space of packing, m^3/m^3, ξ is the friction coefficient in the system vapor (gas) − liquid, $\xi = m/Re_v^n$, where Re_v is the Reihnolds criterion for the vapor, m and n are the numerical coefficients, and H_o is the holdup of the packing, m^3/m^3. From the experimental data obtained, the following values of m and n coefficients were calculated: $m = 130$, $n = 0.72$ for packing No. 1, and $m = 330$, $n = 0.83$ for packing No. 2. By using these coefficient values, Eq. (20) describes the experimental data in terms of the $\Delta P/l = f(G)$ dependence with 20% accuracy for the given temperature range.

When selecting the packing, their characteristics must be considered such as, mass-exchange efficiency, limiting flows, flow resistance, and metal consumption. The intensity factor is a generalized criterion of such a choice. The intensity factor $\Phi = 0.8L_{\text{lim}}/h_{0.8}$ or $\Phi' = 0.8L_{\text{lim}}/h_{0.8}\gamma_p$, where $h_{0.8}$ is HETP at a relative loading of 0.8, and γ_p is the poured mass of packing. The values of factors Φ and Φ' for the investigated types of packing are presented in Table 7. Considering the lower flow resistance of packing No. 2, the data of Table 7 display obvious merits of the latter in terms of efficiency of boron isotope separation by the anisole method.

Flow Reversal in Boron Isotope Separation by Anisole Method

A schematic diagram of a single-stage cascade comprising the concentrating and the depleting sections for boron isotope separation by the anisole method is presented in Fig. 5. The peculiarity of this diagram consists of the presence of the depleting section, which is attributed by high initial boron concentration in na-

Table 7. Intensity Factors for Packing No. 1 and No. 2

		Temperature, K					
Packing	Parameter	278	288	298	308	318	338
No. 1	Φ	27	21	31	—	58	55
	$\Phi' \times 10^2$	—	—	2.6	—	—	4.1
No. 2.	Φ	17	24	39	50	69	84
	$\Phi' \times 10^2$	1.6	2.3	3.7	4.8	6.6	8.0

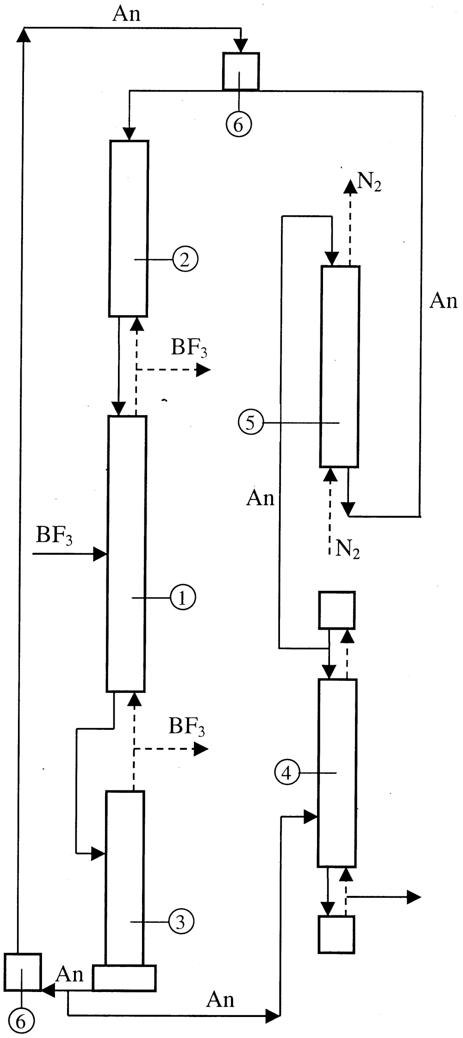

Figure 5. Schematic diagram of plant for boron isotopes separation by anisole method: 1, isotope exchange column; 2, recombiner; 3, decomposer; 4, rectification column; 5, anisole dehumidification column; 6, anisole tanks.

ture. For this reason and due to the high price of source materials, all boron isotope separation plants include the depleting part. This results in the need to supply the separation unit with two flow conversion systems, the upper and the lower. These systems use the thermal method of flow conversion, which is based on the property of components to associate upon cooling and dissociate upon heating.

The upper unit, waste end-refluxer, is referred to as the recombiner. It performs the formation of the liquid complex from anisole and BF_3 leaving the upper end of the depleting column. This process is followed by the energy release of 51.53 kJ/mol, which should be removed to avoid anisole decomposition. Therefore, the recombiner comprises the counter-current column filled with packing supplied with a cooling jacket. Anisole is fed through the upper end of this column, and BF_3 feeds the column from the bottom. The complex is formed in the center of recombiner. The zone of its formation, depending on the anisole flow rate, is determined by a thermocouple. The control of zone position is required to prevent BF_3 leakage into the air. The operating temperature of the complex entering the separation column can be easily fixed by varying the flow rate of cooling water. The recombiner is then operating without any serious problems.

The operation of the lower flow conversion unit—product end-refluxer also called the decomposer—is complicated by a number of problems. In fact, this apparatus is not a decomposer in the true sense because the process, which proceeds in it, is the complex dissociation. The decomposer fulfills the following functions: 1) to extract BF_3 quantitatively from the anisole through the complex dissociation, 2) to separate it from the anisole vapor, and 3) to direct it to the bottom part of the separation column. As a result, anisole must be recovered for reuse in the separation process.

The optimal construction of the decomposer (in the context of the above-listed functions) comprises a column filled with a packing and equipped with a still at the bottom. Such a counter-current multi-stage apparatus is capable of separating BF_3 and anisole more completely, especially in the presence of a temperature gradient along the column. In practice, decomposers of the column type were solely used in a laboratory scale (28) whereas those of the film-type were used in industrial pilot plants (35).

To avoid additional withdrawal of the enriched product, the residual BF_3 concentration in the anisole leaving the decomposer should be as small as possible. It can be estimated by the following equation:

$$B/L = \Theta \varepsilon X_o(1 - X_o)/(X_B - X_o) \tag{21}$$

where $X_o = 0.193$, $X_B = 0.99$ is the atomic fraction of ^{10}B in the product B, $\varepsilon = \alpha - 1 = 0.030$, and $\Theta = 0.8$ is the relative withdrawal. With the proviso that additional withdrawal constitutes 1% of the main one, $B/L = 5\times10^{-5}$ mol BF_3/mol An. According to this estimation and as follows from the data of Table 5, the degree of thermal dissociation of the complex is high enough, and the additional product withdrawal is practically absent.

The problem in question can be successfully solved in both column and film type units (preferably having a reboiler) if the BF_3 and anisole used in the process are sufficiently pure. Water and HF are the basic impermissible impurities. Water can enter the plant together with anisole, whereas HF usually accompanies BF_3 or can form as a product of BF_3 hydrolysis according to the overall reaction:

$$BF_3 + 3H_2O \Leftrightarrow 3HF + H_3BO_3 \tag{22}$$

Reaction (22) proceeds rapidly at high temperatures, i.e., in the decomposer. Hence, one might expect the following reaction to proceed in the decomposer:

$$C_6H_5OCH_3 + HF \rightarrow C_6H_5OH + CH_3F \tag{23}$$

Since BF_3 and HF are effective catalysts in reactions of the aromatic ring alkylation, the following chain of subsequent transformations is possible to proceed:

$$C_6H_5OCH_3 + CH_3F \xrightarrow{BF_3} o\text{-}(p)\text{-}CH_3\text{-}C_6H_4OCH_3\cdot \; + HF \tag{24}$$

$$C_6H_5OH + CH_3F \xrightarrow{BF_3} \rightarrow o\text{-}(p)\text{-}CH_3\text{-}C_6H_4OH\cdot + HF \tag{25}$$

The products of reaction (24) can also be formed as a result of the in- and inter-molecular rearrangement induced by BF_3 and HF as catalysts. All mentioned products of decomposition can also react with BF_3-forming viscous complexes. These complexes are not able to dissociate completely at the anisole boiling point and, hence, they leave the decomposer together with practically fully dissociated anisole. This leads to an increase of the observable BF_3 concentration in the anisole, i.e., it results in essential additional ("parasite") withdrawal of the enriched product. This necessitates the quantitative determination of BF_3 in the anisole leaving the decomposer. When contaminated anisole or BF_3 is used, the anisole phase forms highly boiling tars, which make the subsequent separation process impossible. Since water is the main reason for these conversions (if BF_3 itself does not contain HF), the realization of the separation process requires dehumidification of the anisole feed down to water concentrations of the order of 0.003–0.005%.

It emerges, however, that under such conditions the anisole decomposition observed in the decomposer appears to be of the order of 0.01% per cycle. Phenol, methylanisole, and trace amounts of *o*-(*p*)-cresols are the products of this decomposition. It was found that anisole decay under these conditions is the result of a two-step catalytic (due to the action of BF_3) anisole conversion according to reactions (26) and (27):

The first step is the intramolecular rearrangement of anisole to *o*- and *p*-cresols proceeding by the following equation:

$$C_6H_5OCH_3 \xrightarrow[k_1]{BF_3} o\text{-}(p)\text{-}CH_3\text{-}C_6H_4OH \tag{26}$$

The second step is the interaction of cresols with anisole leading to formation of phenol and methylanisoles:

$$\begin{aligned} o\text{-}(p)\text{-}CH_3\text{-}C_6H_4OH + C_6H_5OCH_3 &\xrightarrow[k_2]{BF_3} \\ &C_6H_5OH + o\text{-}(p)\text{-}CH_3\text{-}C_6H_4OCH_3 \end{aligned} \tag{27}$$

The rate constants of reactions (26) and (27) equal: $k_1 = 0.68 \times 10^{-4}$; 2.2×10^{-4}, and 5.6×10^{-4} h^{-1} at $T = 323$; 343, and 363 K, respectively; and for the second step $k_2 = 0.11$ and 0.39 h^{-1} for *o*- and *p*-cresols, respectively at 363 K.

From the considered mechanism of anisole decomposition, one can derive the following time dependence of the cresols concentration:

$$[K_p] = (k_1/k_2)(1 - \exp(-k_2\tau))$$

Hence, the maximal concentration of *o*- and *p*-cresols in anisole corresponds to 0.51 and 0.14% at 363 K, respectively, which is frequently observed in practice. The presence of minor cresol amounts in the products of catalytic anisole decay due to the action of BF_3 testifies that formation of cresols from anisole proceeds far slower (by intramolecular rearrangement) than their subsequent reaction with the anisole.

Temperatures of around of 363 K are kept in the decomposer. The column is usually kept at room temperature. However, the contact of large amounts of BF_3 with anisole also takes place in the isotope exchange column and in the recombiner. The residence time of the complex in the column is short and does not exceed ~1 h. Under these conditions considerable anisole decay cannot be expected, although the catalytic anisole decomposition proceeds continuously at any temperature.

The complex formation occurs in the recombiner when passing BF_3 through the layer of packing moistened with anisole and is accompanied by the heat release. A local overheating on the surface of gas bubbles observed at non-intensive heat removal can enhance the donor decay. The local overheating should be excluded by using intensive cooling of the recombiner to prevent anisole decomposition.

In summary, two basic routs of the anisole decay must be emphasized:

1. anisole decomposition by the action of HF primarily formed due to BF_3 hydrolysis by water access into the plant in one way or another (see reaction 22 and 23);
2. anisole decomposition by the action of BF_3 primarily taking place in the decomposer: the higher the BF_3 concentration in the high-temperature zone, the more intense are reactions (26) and (27).

These two routs of donor decomposition define the measures required to prevent this process. The basic one is the anisole dehumidification up to the water concentration of ~0.003–0.005%. The anisole decomposition provoked by the action of BF_3 can be reduced in two ways: 1) reduction of temperature in the zone of high BF_3 concentration, or 2) reduction of BF_3 concentration in anisole in the high-temperature zone that can be provided through a proper design of the product-end refluxer, which must be based on a counter-current column mode of operation.

The use of a pure anisole and dry BF_3 (see Table 5) ensures the required completeness of flow conversion. Side reactions occurring mainly in the decomposer not only lead to decomposition of anisole but also impair the completeness of flow conversion. Calculations show that to produce ^{10}B of 85–90% concentrations, the concentration of any phenol impurity (whose complexes are less dissociated compared with the $An{\cdot}BF_3$ complex at 429 K) should not exceed 0.2–0.3%.

The complete flow reversal requires the boiling of anisole in the decomposer compartment, despite the enhancement of anisole decay. The same is true when using other less-resistant donors. The necessity to boil the donor component in the product-end refluxer is a particularly important fact that hinders the use of the thermal method of flow conversion for chemically and thermally unstable ethers. It must be especially emphasized that the limiting BF_3 concentration in the donor at flow conversion is constant (an equilibrium value). It is defined by the boiling point of ether and, hence, is unchangeable in principle.

The noted drawbacks can be partially eliminated through the use of another method of BF_3 isolation from the donor, which is based on the shift of the equilibrium reaction: $D{\cdot}BF_{3(l)} \Leftrightarrow D_{(l)} + BF_{3(g)}$. This shift of the equilibrium is achieved by the BF_3 removal from the reaction zone with any gas or vapor of substance having a low boiling point. The temperature reduction during desorption slows down the donor decomposition. When using vapors of a volatile liquid, they can be easily separated from BF_3 by condensation in a refrigerator. The lower flow conversion unit comprises a counter-current column. Vapors of volatile liquid are formed in the still of the column. The vapor passing through the column (decomposer) from the bottom to the top counter currently to the complex flowing down from the isotope exchange column is saturated with BF_3. The mixture of vapor and BF_3 is separated in the refrigerator. BF_3 is directed to the isotope exchange column and the volatile liquid can be reused in the product-end refluxer. This method has been tested under laboratory conditions using nitrogen and dichloromethane (DCM) as an additive to the initial anisole. The results are presented in Table 8.*

Here $[H_2O]$ is the water concentration in the initial anisole, $\lambda$is the ratio of DCM vapor and BF_3 flows in the decomposer, Δ[phen.] is the increment of phenol concentration after passing anisole through the plant.

The following conclusions can be derived from the data of Table 8:

1. BF_3 separation from the donor can be performed at essentially lower temperatures than when using a pure donor.
2. residual boron content in the anisole withdrawn from the decomposer still depends on λ value, and temperature in the still, i.e., on the DCM content in anisole.

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*According to the work performed in collaboration with L.L. Dmitrevsky.

Table 8. Results of Experiments on BF_3 Desorption from the Complex by DCM Vapors

No.	[DCM], %vol.	T_{still}, °C	[H_2O], %	λ, mol. DCM/mol BF_3	[*B*],γ *B*/ml *A*	Δ[phen.], %
1	0	150	0.003		8	0.003
2	10	107	0.003	3.34	40	0.003
3	10	107	0.003	9.24	23	0.003
4	10	107	0.003	16.70	16	0.003
5	20	85	0.003	2.92	70	0.003
6	20	85	0.003	15.20	29	0.003
7	20	85	0.009	20.90	18	0.003
8	10	107	0.060	2.33	165	0.003
9	10	107	0.060	17.70	100	0.003
10	10	107	0.10	2.92	260	0.005
11	10	107	0.10	18.10	140	0.005

3. completeness of BF_3 isolation from the anisole is not followed by enhancement of the decomposition of the anisole, even at a relatively high water content in the anisole.

It should be mentioned that addition of DCM to anisole enhances not only the operation conditions in the decomposer but also those in the column itself due to considerable reduction of HETP values.

Molecular addition compounds of BF_3 with phenols have viscosity 3 to 5 times higher than that of complex An·BF_3. Therefore, the presence of considerable amounts of phenols in anisole can change the hydrodynamic and mass-exchange characteristics of the plant. The preceding results, by necessity, involve a rectification column in the technological flowsheet for continuous or intermittent separation of the anisole and products of its decomposition.

Preparation of Initial Substances

The initial substances used in the separation process must be carefully purified and dried (see above). Purification of BF_3 from HF can be performed by HF being frozen out or by BF_3 rectification in a column involving one to two separation stages. Although expensive, it is a sufficiently reliable method of BF_3 purification.

Anisole should be purified from water and products of decomposition, namely, phenol, *o*-(*p*)-methylanisole, and *o*-(*p*)-cresols. As is known, an anisole-water system is a heteroazeotrope in the range of water concentrations from 0.4 to 99 mass%. The composition of the vapor phase is constant and is equal to 40.5

Table 9. Liquid-Vapor Equilibrium in Anisole-Water System (37)

P, kPa	P_1^O, kPa	P_2^O, kPa	T_{boil}, K	$[H_2O]_{liquid}$, mass%	$[H_2O]_{vapor}$, mass%	Γ_{exp}/ Γ_{calc}
98.7	532.8	96.0	427	0.0025	0.0134	5.36/5.55
				0.0062	0.029	4.68
				0.0070	0.040	5.71
				0.011	0.063	5.73
				0.022	0.130	5.91
				0.077	0.364	4.73
	518.6	93.3	425	0.143	0.630	4.40/5.56

mass% of H_2O. It is important that the heteroazeotropy does not depend on pressure. In the range of extra-low water concentrations (<0.03 mass%), the anisole-water system behaves as an ideal solution (37). Table 9 presents the experimental and calculated distribution factors, Γ, for water in the vapor and the liquid phases.

Data on the liquid-vapor equilibrium in the anisole-water system are required to calculate the parameters of columns used for anisole drying. Corresponding data on liquid-vapor equilibrium are summarized in Table 10 for binary mixtures involving anisole and one of the decomposition products.

Commercial-grade anisole or anisole circulating through the column is rectified under vacuum ($P = 0.4 \times 10^5$ Pa). As a result, anisole with a water content of 0.02–0.03% is produced. Further anisole dehumidification (up to water content of 0.002–0.003%) should be performed in a column filled with packing that is fed from the bottom by nitrogen obtained by evaporation of the liquid N_2. According to Beradze et al. (38), the temperature dependence of the distribution factor for water in the liquid and gas phases is described by the following equation: $\lg\Gamma = -6.970 + 2830/T$, which is valid for the range of low concentrations of water in

Table 10. Liquid − Vapor Equilibrium in Anisole-Phenol, Anisole-*o*-Cresol, Anisole-*p*-Cresol, Anisole-*o*-Methylanisole, and Anisole-*p*-Methylanisole Systems*

	$P = 0.1$ MPa		Vacuum		
System	Γ_{exp}	Γ_{id}	P, MPa	Γ_{exp}	Γ_{id}
Anisole-phenol	2.23	2.25	0.0376	2.55	2.58
Anisole-*o*-cresol	2.70	2.78	0.0367	3.20	3.21
Anisole-*p*-cresol	4.35	4.37	0.0382	5.06	5.08
Anisole-*o*-methylanisole	1.8		0.0395	2.83	
Anisole-*p*-methylanisole	2.0		0.0395	2.90	

* According to the work performed in collaboration with L.J. Dmitrevskaya.

anisole in the temperature range from 273 to 363 K. Dehumidification is quite effective, since $\Gamma = 336$ at room temperature. Thus, it appears possible to dry 6 L of anisole per hour from the initial water concentration of 0.04% to 0.003% in the column with diameter of 126 mm and working height of 1.5 m at $\lambda = 6$ mol of N_2/mol of anisole (38).

The successful operation of a separation plant is impossible without a corresponding control. The anisole used in the separation process should be tested to determine water content (e.g., by using the Fisher reagent). The anisole leaving the decomposer should be checked for a residual content of boron and phenol. The necessity to determine the mole ratio r arises from the need to control the recombiner operation. It is advisable to measure the isotope composition of boron in the source material, in the product, and in the waste after conversion of BF_3 into trimethylboron $(CH_3)_3B$, which, unlike BF_3, is not adsorbed by the plant walls (39). The method of boron isotopes analyses used in this work is analogous to that applied in the industrial plant (4).

Prospects of Anisole Method of Boron Isotopes Separation

The anisole method of boron isotopes separation has been known since 1954. The results obtained by studying BF_3-anisole·BF_3 system are described in numerous publications. This method has been realized in industrial scale. Nevertheless, the actual possibilities of this fractionation technique are essentially wider. Let us consider two directions in which the further work on development of this process could be carried out.

The first direction deals with the development of separation process under elevated pressures. Pressure as one of the factors affecting most chemical processes, is widely used in the chemical industry. Operation under pressure has the following merits: 1) increase of limiting flows in the specified installation, and 2) substantial improvement of the process kinetics. The main drawback in the use of elevated pressure is the deterioration of equilibrium characteristics.

We explored the phase equilibrium between the liquid An·BF_3 complex and BF_3 under pressures of 0.3, 0.5, and 0.8 MPa in the temperature range between 281 and 443 K in a special unit made from stainless steel. The mole ratio r was determined in the liquid phase. The value of r at all temperatures and $P = 0.1$ MPa was assumed to relate to the chemically bound BF_3. All excessive r (in comparison with r at $P = 0.1$ MPa) related to BF_3 dissolution in the complex followed by the isotope effect corresponding to $\alpha_{ph} \leq 1.003$. The r values obtained are summarized in Table 11.

Effective separation factors for boron isotopes were measured by a single equilibration of An·BF_3 complex and BF_3 under pressure. They are equal to 1.028 (0.12 MPa, 298 K); 1.029 ± 0.002 (0.29 MPa, 288 K); 1.027 ± 0.005 (0.29 MPa,

Table 11. Results of Mole Ratio *r* Measurement at Different *P* and *T* (40)

	T, K								
P, Mpa	281	298	313	333	353	373	393	413	443
0.1	1.02		0.86	0.51	0.22	0.03			
0.3	1.18	1.12	1.04	0.86	0.62	0.37	0.17	0.05	0.03
0.5	1.25	1.21	1.11	0.97	0.74	0.48	0.23	0.09	0.07
0.8	1.60		1.33	1.18	0.98	0.62		0.25	0.10

298 K), and 1.028 ± 0.002 (0.5 MPa, 288 K). A comparison of the experimental α^* values with those computed by equation $\alpha^* = \alpha_x X_x + \alpha_{ph} X_{ph}$ (where α_x is the separation factor at $P = 0.1$ MPa and corresponding temperature, X_x and X_{ph}, are the fractions of BF_3 in the liquid related to α_x and α_{ph}, respectively) is shown in Table 12.

Good agreement between the experimental and calculated data makes it possible to assume that values of α^* for exchange between $A{\cdot}BF_3$ and BF_3 under pressure can be computed with high accuracy using corresponding α values determined at $P = 0.1$ MPa and the data on phase equilibrium at specified *P* and *T*. The α and *r* changes are minor because they actually compensate each other (in terms of liquid phase flow). Hence, the advantage of high limiting gas flows becomes clear. Nevertheless, a comprehensive analysis of the possibilities of operation at pressure is limited due to the lack of data on the kinetics of interfacial mass-transfer under those conditions.

The second direction to be considered to improve the separation process consists in the practical realization of the so-called ideal temperature cascade (ITC) (41). It is known that the theory of ideal cascade assumes a decrease of the flow in the cascade as the isotope concentration increases. The possibility of

Table 12. Values of α, α_{ph} and α^* (Computed/Experimental) (40)

	T, K			
α, *r*	288	298	308	318
α	1.033	1.030/1.028	1.028	1.026
α_{ph}	1.003	1.003	1.003	1.003
r 0.1 MPa	1.002	0.99	0.91	0.77
r 0.3 MPa	1.15	1.13	1.08	1.01
r 0.5 MPa	1.22	1.20	1.14	1.07
α^*, 0.3 MPa	1.029/1.029	1.027/1.027	1.024	1.020
α^*, 0.5 MPa	1.028/1.028	1.025	1.022	1.018

realizing ITC results from the condition of constancy of the net isotope transfer, which is determined at the feeding point. The separation factor should be increased to increase the net transfer. This can be achieved by the reduction of temperature at the feeding point. As the isotope concentration in the cascade increases, the temperature can also be increased throughout the column height. The temperature increase in the anisole-BF_3 system results in a decline of the following process parameters: 1) boron flow in the liquid phase, 2) α, and 3) HETP. Therefore, an improvement of the separation process kinetics is achieved due to the temperature increase related to the rise in the required isotope concentration. This permits achieving the pre-assigned enrichment in a shorter column or increasing the relative withdrawal Θ. The relationship between temperature and concentration, as applied to isotope separation, is discussed by Katalnikov et al. (42). A comparison of the isothermal and non-isothermal conditions, as applied to the chemical isotope exchange is presented by Khoroshilov et al. (43). Three cases of the optimal temperature regime are considered in the last quoted work as an optimum criterion: 1) minimal flow, 2) minimal column height, and 3) minimal unit (cascade) volume. As follows from these criteria, realization of the separation process in a temperature cascade, i.e., under non-isothermal conditions, allows for achieving: 1) the increase of productivity of separation process, 2) the decrease of both a column height and a cascade volume, and 3) to lower the cost of flow conversion. Therefore, all of the above lead to the overall reduction of the specific cost of production. The above quantitative calculations have been performed with the data on separation of boron, nitrogen, oxygen, and sulfur isotopes. The process of boron isotopes separation using the anisole·BF_3-BF_3 system has been successfully realized in the pilot scale in the Laboratory of Stable Isotopes at the Department of Physical Chemistry, Chemical Faculty, Lomonosov Moscow State University.

CONCLUSION

The material described in this review demonstrates the unique physicochemical properties of the anisole·BF_3-BF_3 system, which permits the successful application of this system under industrial conditions with relatively simple engineering design. The use of a chemically active reagent, such as BF_3, appears to be possible by using an appropriately designed separation process flowsheet. The completeness of thermal dissociation of the complex in flow conversion units prevents the additional withdrawal of the enriched product. The achievable chemical decomposition of anisole is of the order of 0.01% of a single-cycle flow that corresponds to the technologically acceptable level. The proposed methods of BF_3 separation from the complex through the use of gaseous or volatile liquid additives allow one to increase the completeness of the flow conversion and to reduce the donor decay. Realization of the process under non-isothermal conditions gives some additional advantages compared with the isothermal version of the process.

The study of physico-chemical properties of the anisole·BF_3-BF_3 system being carried out in parallel with the search of the optimal engineering designs allows the use of systems with higher separation factor values. For example, as it is shown above, these systems have not been previously used due to the poor chemical stability of the donors under conditions of the product-end refluxer. The reduction of temperature during the desorption process or creation of a temperature gradient in the course of the separation process can help bypass these restrictions. The economical advantages of using such systems are evident as the technological space of isotope separation plants is inversely proportional to ε^2 ($\varepsilon = \alpha - 1$) at the same magnitude of other process parameters.

LIST OF SYMBOLS

An	denotes anisol;
a	is coefficient of temperature dependence;
B	is value of product flow;
b	is coefficient of temperature dependence;
c_p	is specific heat capacity, J/mol·K;
D	denotes compound of donor type;
d	is diameter of packing, m^2;
G	is flow density of gas phase, kg/m^2·c;
ΔH	is enthalpy, kJ/mol;
h	is height equivalent to theoretical plate (HETP), m;
K	is the equilibrium constant;
L	is flow density of liquid phase, kg/m^2·c;
l	is height of separation column, m;
n	is molar concentration, mol/dm^3;
P	is pressure, Pa, atm;
R	is universal gas constant, $R = 0.082$ L·atm/mol·K;
r	is molar ratio of BF_3 to compound of donor type in their complex;
S	is specific surface area of packing, m^2/m^3;
T	is temperature, K;
V	is molar volume, L/mol;
W	is velocity, m/s;
X	is atomic fraction of ^{10}B in total boron of liquid phase;
X_o	is atomic fraction of ^{10}B in total boron of feeding flow (natural concentration of ^{10}B);
Y	is atomic fraction of ^{10}B in total boron of gas phase;

Greek

α	is separation factor determined as $\alpha = \dfrac{X(1 - Y)}{Y(1 - X)}$;
α^*	is effective separation factor;
ε	$= \alpha - 1$;
η	is viscosity coefficient, Pa·c;
λ	is ratio of gas to liquid flows;
σ	is surface tension coefficient, N/m;
ρ	is the density of phase, kg/dm^3;
ξ	is friction coefficient;
Φ and Φ'	are intensity factors;

Subscripts

B	designates values related to BF_3;
boil	denotes boiling;
burn	designates burning;
crit	denotes critical values;
evap	designates evaporation;
form	designates formation;
g	denotes values related to gas phase;
l	designates values related to liquid phase;
lim	designates limiting values;
melt	designates melting;
opt	designates optimal;
s	designates values for BF_3 dissolved in liquid phase;
v	designates values for vapor phase;

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REFERENCES

1. Conn, A.; Wolf, J. Ind. Eng. Chem. **1958**, *50*, 1231.
2. Kilpatrick, M.; Hutchison, C.A.; Taylor, E.H.; Judson, C.M. *Separation of*

Boron Isotopes, Nat. Nucl. Eng., Ser., Vol. 1–5; McGraw-Hill: New York, 1952.
3. Kaminskiy, V.A.; Karamian, A.T.; Nikolaev, Yu.V.; Oziashvili, E.D.; Parzachashvili, G.L. Isotopenpraxis **1967**, *3*, 26.
4. Muller, G.T.; Kralik, R.J.; Belmore, E.A.; Drury, J.S. In *Proceedings of the 2nd UN International Conference on Peaceful Use of Atomic Energy*, Vol. 4. United Nations, Geneva, 1958, p. 585.
5. Bondarenko, B.R.; Vlasenco, V.A; Gverdtziteli, I.G.; Gagua, T.A.; Kiladse, N.Sh. Isotopenpraxis **1967**, *3*, 97.
6. Edmunds, A.O.; Loveless, F.C. In *Proceedings of 2nd UN International Conference on Peaceful Use of Atomic Energy*, Vol. 4. United Nations, Geneva, 1958, p. 576.
7. Sevrugova, N.N.; Uvarov, O.V.; Javoronkov, N.M. Atomnaja Energia (Atomic Energy) **1960**, *9*, 110. (in Russian)
8. Katalnikov, S.G.; Nedzvetscki, V.S.; Pisarev, V.S.; Voloshuk, A.M. Isotopenpraxis **1968**, *4*, 341.
9. Blum, J.M.; Marteau, S. Energie Nucleaire **1972**, *14*, 33.
10. Nettley, P.T.; Cartwright, D.K.; Kronberger, H. In *Proceedings of International Symposium on Isotope Separation*; North-Holland Publ. Co.: Amsterdam, 1958, p. 385.
11. Bachtadse, A.B.; Tevzadse, G.A.; Oziaschvili, E.D. Izotopy v SSSR (Isotopes in USSR), Kaloshin, V.M., Ed., **1978**, *59*, 61. (in Russian)
12. Voloshuk, A.M.; Katalnikov, S.G.; Knyasev, D.A. Kernenergie **1974**, *17*, 20.
13. Ribnikar, S.V. Bull. Inst. Nucl. Sci., Boris Kidrich (Belgrade) **1958**, *8*, 31.
14. Palko, A.A.; Drury, J.S. J. Chem. Phys. **1960**, *33*, 779.
15. Palko; A.A.; Drury, J.S. J. Chem. Phys. **1967**, *46*, 2297.
16. Ribnikar, S.V.; Bootsma, G.A. Bull. Inst. Nucl. Sci. Boris Kidrich (Belgrade) **1959**, *9*, 91.
17. Katalnikov, S.G.; Pisarev, V.E.; Franzkevichute, D.I. Zh. Fiz. Khim. **1969**, *43*, 1207. (in Russian)
18. Palko, A.A.; Drury, J.S. J. Chem. Phys. **1961**, *35*, 103.
19. Merriman, J.R.; Pashley, J.H.; Snow, N.W. US AEC Rep., K-1653, 1966.
20. Katalnikov, S.G.; Voloshuk, A.M.; Kozik, T.A. Zh. Fiz. Khim. **1974**, *48*, 2874. (in Russian)
21. Katalnikov, S.G.; Dmitrvsky, L.L.; Ivanova, I.Yu. Zh. Fiz. Khim. **1974**, *48*, 995. (in Russian)
22. Katalnikov, S.G.; Paramonov, R.M. Zh. Fiz. Khim. **1966**, *40*, 401. (in Russian)
23. Katalnikov, S.G.; Chgi-Cin, Gun. Zh. Fiz. Khim. **1965**, *39*, 1393. (in Russian)
24. Nakane, R.; Kurihara, O. Sci. Papers Inst. Phys. Chem. Res. **1962**, *56*, 161.

25. Nakane, R.; Watanabe, T.; Kurihara, O. Bull. Chem. Soc. Japan **1964**, *37*, 381.
26. Herbst, R.S.; McSandlerss, S.P. Sep. Sci. Technol. **1994**, *29*, 1293.
27. Panchenkov, G.M.; Moiseev, V.D.; Makarov, A.V. Dokl. Akad. Nauk SSSR **1957**, *112*, 659. (in Russian)
28. Voloshuk, A.M.; Dgigiyshvili, Sh.I.; Katalnikov, S.G.; Nedzvetzkii, V.S.; Oziaschvili, E.D. In *Proizvodstvo Izotopov (Production of Isotopes)*, Bochkarev, V.V., Ed.; Atomizdat: Moscow, 1973, p. 443. (in Russian)
29. Wamser, C. J. Am. Chem. Soc. **1951**, *73*, 409.
30. Palko, A.A.; Begun, G.M.; Landau, L. J. Chem. Phys. **1958**, *28*, 218.
31. Palko, A.A.; Drury, J.S. In *Advances in Chemistry*, Ser. 89; Spindel, W., Ed.; Washington, DC, 1969; p. 40.
32. Katalnikov, S.G.; Sizov, N.E.; Sobolev, A.S.; Malzev, K.A. Trudy Moskovskogo Khimiko-Tekhnologicheskogo Tnstituta imeni Mendeleeva (Proceedings of Moscow Mendeleev Chemical Technological Institute) **1989**, *156*, 123. (in Russian)
33. Katalnikov, S.G.; Khoroshilov, A.V.; Sobolev, A.S.; Timashev, A.P. Isotopenpraxis **1982**, *18*, 208.
34. Kafarov, V.V. *Osnovy Massoperenosa (Fundamentals of Mass Transfer)*, Vischaya Shkola, Moscow, 1979. (in Russian)
35. Polevoy, A.S.; Asatiani, P.Ya.; Kudziev, A.G. Vysokochistye Vetshestva (High Purity Substances) **1991**, *No. 1*, 47. (in Russian)
36. Katalnikov, S.G.; Sobolev, A.S. Zh. Obshch. Khim. **1993**, *63*, 191. (in Russian)
37. Giorgadze, N.A. Russ. J. Appl. Chem. **1985**, *58*, 504.
38. Beradze, D.G.; Dmitrevsky, L.L.; Zelvenski, Ya.D.; Katalnikov, S.G.; Tevzadze, G.A. Trudy Moskovskogo Khimiko-Tekhnologicheskogo Tnstituta imeni Mendeleeva (Proceedings of Moscow Mendeleev Chemical Technological Institute) **1977**, *96*, 93. (in Russian)
39. Katalnikov, S.G.; Dubrovin, A.V.; Kuzmina, L.A. Abh. Dtsch. Ak. Wiss. Berlin, Kl. Chem., Geol., Biol. **1964**, *No. 7*, 339.
40. Katalnikov, S.G.; Sizov, N.E. In 2nd International Symposium of Countries-Members of SEMA on Stable Isotopes, Tbilisi, Abstracts; 1989; p. 89.
41. Katalnikov, S.G.; Sobolev, A.S.; Hachischvili, G.V.; Khoroshilov, A.V. Dokl. Akad. Nauk SSSR **1980**, *251*, 1190. (in Russian)
42. Khoroshilov, A.V.; Katalnikov, S.G.; Sobolev, A.S. Dokl. Akad. Nauk SSSR **1981**, *256*, 922. (in Russian)
43. Khoroshilov, A.V.; Andreev, B.M.; Katalnikov, S.G. In *Proceedings of the International Symposium on Isotope Separation and Chemical Exchange, Uranium Enrichment*. Tokyo Inst. of Technol.; 1992; p. 486.

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