APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS4I8G8

600

1. RYSS, I.G.

2. USSR (600)

"The Thermodynamic Relation Between the Elasticity of Dissociation and the Solubility of Complex Strong Electrolytes," 13, no.4, 1939. Metallurgical Insti., Chair of Gen'l Chem. Dnepropetrovsk. Received 17 June 1938.

9. [redacted] Report U-1613, 2 Jan 1951.

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Virtual entropy of silicon tetrafluoride, calculated from the molecular constants. I. G. Ryss. *Compt. rend. acad. sci. U. R. S. S.* **24**, 568-9(1939)(in German).—Using the available electron diffraction, Raman and infrared data, the entropy (translational, rotational and vibrational) of gaseous SiF_4 was calcd. as follows (°K., entropy in cal./degree mol.): 298.2°, 67.430; 373.2°, 71.560; 400°, 72.870; 473.2°, 76.347; 500°, 77.476; and 573.2°, 80.404. In the above calcns., the Si-F distance was taken as 1.56 A. (cf. Brauae and Pinnow, *C. A.* **31**, 4177⁹); if the distance is taken as 1.54 A. (cf. Brockway and Wall, *C. A.* **29**, 996¹), the above entropy values must each be diminished by 0.069 cal./degree mol. The error in the calcd. entropy values is probably less than ±0.5 cal./degree mol.

George Ayers

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Continuous process for the preparation of chromium oxide. J. G. Ryss and R. Mandel. *Novosti Tekhniki* **1938**, No. 21, 37-8.—Na_2CrO_4 is rapidly reduced by producer gas at 600° and higher. An addn. of soda or NaOH sharply increased the velocity of reaction. The product, after washing with alkali, is calcined at 800° for a short period.

A. A. Podgorny

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Ca

2

Viscosity of solutions of alkali chromates. I. G. Ryss, V. M. Shutova and A. I. Zelyanskaya. *J. Applied Chem.* (U. S. S. R.) 12, 1787-9(1939).—The viscosities were detd. in Ostwald viscometers and the calcns. were made with the formula: $\eta = \eta_0 Pt/P_0 t_0$, where η_0 is the viscosity, P_0 the sp. gr., t_0 duration of discharge of water at the given temp., and η the viscosity, P the sp. gr. and t the duration of discharge of the soln. at the same temp. The closeness of the properties of the hydrated SO_4^{--} and CrO_4^{--} ions justifies the assumption that the viscosity of concd. solns. contg. Na_2CrO_4 and Na_2SO_4 is also given basically by the total molarity of the soln. Partial conversion of Na_2CrO_4 to $Na_2Cr_2O_7$ lowers the viscosity.

A. A. Bochtlingk

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2ND LETTER

1ST AND 2ND LETTER

RYSS, I. G.

"The Velocity of formation of tetrafluoboric acid in mixtures of hydrofluerie and boric acids. H. I. Zhur, Obshch. Khim. 10, 1936-42, (1940) cf. C. A. 44, 415c-- The exptl. kinetic data for the over-all reaction 4HF +3H2O in soln. contradict both the assumption of a rate law k(HF]$^{\lambda}$[H2BO3]2. A rate law in agreement with the expts. can be derived on the assumption of a mechanism involoing the rapid initial step H3BO3 + 3HF $\rightarrow$ [BF3OH]$^-$ + H$^+$, a maintained equil. [BF3OH]$^-$ +H$^+$ $\rightleftarrows$ BF 3HO2 with the equil. const. K = [BF3OH]-+[H$^+$]/[BF3H2O],+ and the rate-detg. step Bf3H2O + HF$\rightarrow$Bf3-H$^-$+ H2O; the over-all rate is then detd. by e the bimol, fate dx/dt - k [HF3H2O] [HF], which leads for the rate of increase of the yield φ of Hf4$^-$ (in fractions of the therotically possible max. yeild), to dφ /dt = (k/K)- M^2(q-^{3}-q) (1-φ)q^2, where M = initial concn. of HF (inmoles/l.), and q = mol. ratio Hf/H2BO3 in the mist. This equation is verified in 2 ways. In the initial stages, it simplifies to dφ /dt = (k/K)M2(q-3/q2, calling for rapid increase with increasing, q, in conformity with the expt. in the integrated form, the rate equation calls for linearity between t and log)(5-3)/(1 -φ)[for q - 8, and with log[φ/(1- φ) for q - 4, verified except for deviations at high φ, owing no doubt to the reverse reaction. For q - 4, M3 - 0,2681 and 0,1388, at 30.058, k//K - 7.3 (const.) and for q = 8, k/K - 9.3 and 8.0 (1 4 Mole 2 Minl), The exptl. data of Wamser (C. A. 42, 4430) at 25 yield the somewhat lower values k/K - 6.34, 4.35, and 3.55, for Mo 0.052, 0.2244, and 0.4422, showing the same trend with the concn. The fore-

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going reaction scheme is applicable only for $q > 3$. Formation of the hydrate $BF_3.2H_2O$, tantamount to the hydrated acid $H[BF_2OH].$-_ H_2O, accounts for the old finding of Thomsen that, on mixing dil. solns. of HF and H_3BO_3, the heat of reaction increases with q only up to q - 3 and then remains const; this indicates that, whereas formation of $Bf_2.2H_2O$ is rapid and stronly exothermal, further addn. of HF to form HFB_4 is only weakly exothermal, and slow. The observation of Abegg, et al. (Z. anorg. allgem. Chem. 35, 129(1903) that the elec. cond. of a mixt. of HF with H_3BO_3 is established momentarily and does not change with time despite the decrease of acidity, is explained by the closeness of the mobilities of the ions $[BF_2OH]^-$ and $[BF]^-$, high dissocn. of BF_3H_2O, and suppression of the dissocn. of HF; owing to these factors, progress of the rate-detg. reaction $BF_3H_2O + HF \rightarrow BF_4^- + H^+ + H_2O$ witll not significantly affect the elec. cond. N. T.

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2

Thermodynamic constants of silicon tetrafluoride. The hydrolysis equilibrium of silicon tetrafluoride. I. G. Ryss. *J. Phys. Chem.* (U. S. S. R.) 14, 571-81(1940).—The thermodynamic functions C_p, translational, rotational and vibrational entropies and free energies of SiF_4 were calcd. from known mol. (spectroscopic, etc.) consts. From various thermochem. data in the literature the heat of hydrolysis of SiF_4 to yield β-quartz is found to be 22.5 cal. and values of the hydrolysis const. are calcd. that differ considerably from the exptl. results of Baur (*Z. Physik. Chem.* 48, 483(1904)) which are considered subject to considerable exptl. errors. F. H. Rathmann

Dnepropetrovsk Metallurgical Inst. im. Stalin

Inst. Phys. Chem. im. Pisarzhevskii AS UkrSSR

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2

Kinetics of the decomposition of fluosilicate ions under the action of alkali. I. G. Ryss and M. M. Slutskaya. *J. Phys. Chem.* (U. S. S. R.) 14, 701-7(1940).—The decompn. of SiF_6 ions in alk. solns. for concns. of fluosilicate from 0.010 to 0.027 *M*, NaOH from 0.000 to 0.026 *M* and at temps. from 10 to 50°, as measured by the time till the reaction $2H_2O + SiF_6^{--} \rightarrow 4H^+ + 6F^- + SiO_2$ neutralizes the base added, as indicated by decoloration of phenolphthalein indicator present, obeys the equation for a unimol. reaction. The values of *k* are given by $\log k = (4248/T) + 13.083$, and $E = 19.44$ Cal.

F. H. Rathmann

Lab. Gen. Chemistry, Metallurgical Inst.

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Ca

18

Preparation of crystallized chromic anhydride from calcium chromate. I. G. Ryss, A. E. Zayarnyi and A. I. Zelyanskaya. *J. Applied Chem.* (U. S. S. R.) 14, 46-61 (in German, 62) (1941).—A boiling mixt. of 456 g./l. Na_2CrO_4, 29.6 g./l. Na_2SO_4 and traces of free alkali was treated with an equiv. quantity of a soln. contg. $CaCl_2$ 33, KCl 2.04, and $KClO_3$ 0.75%. The filtered and washed $CaCrO_4$ was decompd. with H_2SO_4 and the soln. of CrO_3 obtained was filtered and concd. to about 60%. Yield of CrO_3 was 97-98%. The corrosion resistance of materials to be used as evaporators, reactors, etc., was found to be (loss in g./sq. m./hr. on exposure to process conditions for 0-2 and 3-4 hrs., resp.): Gray cast iron (C 3.30, Si 2.04, Mn 0.55, P 0.217 and S 0.06%) 6.58 and 2.65; boiler plate of the Chusovo mills (C 0.172, Mn 0.34, P 0.032, S 0.042% and Si traces) 1.77 and 3.23; iron of the Armco type (C 0.025, Mn 0.035, S 0.025 and P 0.009%) 32.6 and 15.84; sheet aluminum 103.0 and 2.42. Rolled lead (Bi 0.004, Cu 0.005, Fe 0.003 and Sb 0.011%) in 3 hrs. lost 259.6. Ten references. A. A. Boehtlingk

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Determination of fluorine in tetrafluoborates. I. G. Ryss. *Zavodskaya Lab.* 12, 651-5(1946).—When an aq. soln. of KBF_4 is boiled with an excess of $CaCl_2$ soln., the reaction of $BF_4^- + 2Ca^{++} + 3H_2O = 2CaF_2 + H_3BO_3 + 3H^+$ will take place completely with a filterable ppt. of CaF_2 provided the liberated H^+ is slowly neutralized by adding suitable quantities of $KClO_3$ and KI together with a little KVO_3 as catalyst. The neutralization can also be accomplished by adding NaOAc to the boiling soln. For 0.2 g. of KBF_4 add 0.25 g. of $KClO_3$, 2 g. KI, 50 ml. of M $CaCl_2$ soln., and 0.15 ml. of 0.1 M KVO_3. Boil for at least an hr., filter, wash, dry, and weigh the CaF_2 ppt.

N. Thon

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2

Hydrolytic equilibria in solutions of sodium fluosilicate at 11°. I. G. Ryss (Dnepropetrovsk Metal Inst.). *J. Gen. Chem.* (U.S.S.R.) **16**, 331-40(1946).—The degree of hydrolysis of Na_2SiF_6 at 11° at concns. 0.02 *M* to 0.00048 *M* was detd. The following equil. consts. were calcd.: $SiF_6^{--} = SiF_4 + 2F^-$, $K_1 = 0.65 \times 10^{-4}$; $SiF_4 + 2H_2O = SiO_2 + 4HF$, $K_2 = 1.04 \times 10^{-9}$; $SiF_6^{--} + 2H_2O = SiO_2 + 4H^+ + 6F^-$, $K_3 = 5.4 \times 10^{-27}$. Generally speaking, the solns. of the hexafluoride reach hydrolytic equil. rapidly and further changes occur only very slowly.

G. M. Kosolapoff

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7

Determination of boron in tetrafluoroborates. I. G. Ryss. *J. Gen. Chem.* (U.S.S.R.) 16, 531-6(1946).—By boiling fluoroborates with an excess of $CaCl_2$ the BF_4^- anion is decompd.; use 25-30 cc. of 1-2 *M* $CaCl_2$ for 1 millimole of BF_4^- and boil for 1 hr. This procedure can be used for detg. B in fluorides, fluoroborates, and fluosilicates. Titration in the cold with methyl orange can be used to det. BF_3OH^-, and in this way BF_4^- can be distinguished from its hydrolysis products. G. M. K.

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RYSS,

PA 13T35

USSR/Chemistry - Tin Compounds **Sep 1946**
Crystallization

"The Crystallization Equilibrium of Tin Chloride Solutions," J. G. Ryss, E. J. Turchan, 7 pp

"Zhur Prik Khim" Vol XIX, No 9

Study of the solubility equilibrium in the system $SnCl_2$ - H_2O - HCl, leading to conclusions on the adequate conditions for the technological procedure of crystallization of a tin chloride solution.

13T35

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CO

PROCESSES AND PROPERTIES INDEX

2

The equilibrium of the hydrolysis of the tetrafluoborate ion. I. G. Ryss. *Compt. rend. acad. sci. U.R.S.S.* 52, 417-20(1946); cf. *C.A.* 41, [illegible].—Calcns. of equil. consts. were used to det. the extent of hydrolysis of the BF_4 ion. Solns. of $NaBF_4$ and KBF_4 were added to an excess of alkali, and the excess was titrated with 0.1 *N* HCl. Equil. consts. calcd. on the assumption that the hydrolysis reaction was $BF_4^- + H_2O \rightleftarrows BF_3OH^- + HF$ gave calcd. pH values in accord with measured values. In very dil. solns. further hydrolysis of the BF_3OH ion was observed. The following equil. consts. were calcd.: 20°, $2.4 \times 10^{[illegible]}$; 25°, $2.8 \times 10^{[illegible]}$; 80°, $5.5 \times 10^{[illegible]}$; 90°, $6.5 \times 10^{[illegible]}$; 100°, $7.3 \times 10^{[illegible]}$. I. K. Campbell

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RYSS, I. G.,

"The Properties and Synthesis of Trifluohydroxyborate of Potassium," Dokl. Ak. Nauk SSSR, 54, 325-7, 1946.

KBF_3OH was prepd. by dissolving 1.5-2.0 mols. KHF_2 and 1 mol. H_3BO_3 in 250-300 g. water, cooling with ice and filtering; yield 57%. Soly. of the product in water is 11% at 14°. The soln. is acid and, with methyl orange as the indicator 1 mol. reacts with 2.03 mols. NaOH. Prepns. according to Gasselin (Bull. soc. chim. France (3) 7, 654 (1892)) and Meerwein and Pannwitz (CA 29, 1060) gave mixts. of KBF_4 and KBF_3OH rather than pure KBF_3OH.

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Ca

2

Crystallization equilibrium of solutions of stannous chloride. I. O. Rys and K. Ya. Turkhan (Dnepropetrovsk Metallurg. Inst.). *J. Applied Chem.* (U.S.S.R.) 10, 958-65(1947)(in Russian).—In the system $SnCl_2-H_2O-HCl$, equil. is attained from both sides in 2-3 hrs. at 5°. At 0, 5, 15, 25°, with up to 10% HCl, the solid phase is $SnCl_2.2H_2O$. Isotherms at these temps., with % $SnCl_2.2H_2O$ in soln. plotted against % HCl, show a min. around 5.5-6% HCl, the flatter the higher the temp.; example of data, 5°, HCl 2.20, 3.31, 5.89, 6.31, 7.13%, $SnCl_2.2H_2O$ 55.5, 53.0, 48.8, 49.7, 50.5; 25°, HCl 1.87, 2.75, 3.53, 4.65, 6.56, 7.11%, $SnCl_2.2H_2O$ 75.5, 73.0, 71.8, 71.0, 71.5, 73.0, d. of satd. soln. 1.936, 1.884, 1.874, 1.850, 1.868, 1.912. Cryometric detns. without HCl (other than that due to hydrolysis of $SnCl_2$) gave: from a 34.7% $SnCl_2$ soln., the crystn. temp. of ice is −6.8°; $SnCl_2$ content of the soln. in equil. with the eutectic, 37.9%. From 36.8 and 37.3% $SnCl_2$, ice crystallizes at −6.25 and −6.45°, resp.; eutectic arrest at −6.8°. Slightly moist $SnCl_2.2H_2O$ (81.2% $SnCl_2$ instead of 84.2) showed on heating a temp. arrest at 41.4°; it could not be decided whether this corresponds to complete melting, nor could a second eutectic $SnCl_2.2H_2O-SnCl_2$ be established; it appears that $SnCl_2.2H_2O$ melts incongruently but with a compn. very close to it. On cooling 1 ton of an 80% $SnCl_2$ soln. to 20° the amt. of $SnCl_2.2H_2O$ pptd. is 308, 362, 410, 394, 305 kg., in the presence of 1, 2, 3, 4, 5% HCl, resp., corresponding to s = % HCl/% H_2O (*free* H_2O, not bound in $SnCl_2.2H_2O$) = 0.05, 0.11, 0.18, 0.25, 0.33, resp.; best crystn. yields are obtained at a definite optimum value of s, depending on the final crystn. temp., example: 0, 5, 10, 15, 20, 25°, optimum s = 0.11, 0.12, 0.14, 0.16, 0.19, 0.23; deviation from these s in either direction results in lowered yield in crystals. At a lower temp., at a given s, the same yield can be obtained from a more dil. soln., example: 600 kg. $SnCl_2.2H_2O$ are obtained, at s = 0.2, at 5, 12, 25°, from solns. contg. 76.3, 80.8, 85.4% $SnCl_2.2H_2O$, resp.; 300 kg. are obtained, under the same conditions, from 66.7, 73, 79.6% solns.

N. Thon

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RYSS, I. G. PA 18T100

USSR/Chemistry - Fluoborates May 1947
Chemistry - Kinetics

"Kinetics of the Decomposition of Tetrafluoroborates in Aqueous Solutions," I. G. Ryss, M. M. Slutskaya, Laboratory of General Chemistry, Dnepropetrovsk Metallurgical Institute, imeni Stalin, 12 pp

"Zhur Fiz Khim" Vol XXI, No 5

Discusses, with detailed tables, illustrations and formulae, the kinetics of decomposition with result that the constant of the rate k' = 0.4343k at temperature of 20 to 70-80 degrees. Rate of reaction was found to increase with rise in temperature. Published 26 Nov 1946.

18T100

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CA

Equilibrium of the hydrolysis of tetrafluoboric acid. I. G. Ryss and M. M. Slutskaya (Stalin Inst. Met., Dnepropetrovsk, Ukr.). *Doklady Akad. Nauk S.S.S.R.* 57, 689–91(1947); *Chem. Zentr.* (Russian Zone Ed.) 1949, I, 813; cf. *C.A.* 43, 2494b.—The basic soln. was prepd. by dissolving 8 mols. HF and 2 mols. H_3BO_3 in 1000 g. water. This soln. and various dilns. thereof (up to 0.06 mol./1000 g. water) were kept in paraffined flasks at room temp. for 72 and 504 hrs. for the establishment of equil. and then analyzed. The equil. const. $K = (M_0/4)(1 - \varphi)^2$, in which M_0 is the initial concn. of HF in mols. and φ is the amt. of BF_4^- formed. K = about (2.2–2.8) × 10^{-3}, although it increases at higher concns. The reaction equil. is represented only by $BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$. Only 1 mol. of HF is formed. $H(BF_3OH)$ is a strong acid which strongly represses the dissocn. of HF. At 60.7° equil. was attained in 100 min.; at 90° it was attained in 15 min. (M_0 = 0.08). The impossibility of titrating HBF_4 alkalimetrically is discussed briefly. M. G. Moore

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General properties of the transition elements. I. G. Ryss. *Uspekhi Khim.* 17, 372-88(1948).—Didactic.

N. Thon

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Ca

2

Thermal decomposition of tetrafluoborates. I. G. Ryss and E. M. Polyakova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, [illegible](in Russian).—(1) $Ba(BF_4)_2.2H_2O$ was prepd. by dissolving $BaCO_3$ in HBF_4 (made by soln. of the theoretical amt. of B_2O_3 in 20% HF) evapg. at 74-8° under 200 mm. Hg, filtering from BaF_2, crystg. the filtrate at 0° and drying over $CaCl_2$. On heating 1 hr. at 50, 70, 90, 150°, the loss of wt. is 2.88, 4.88, 10.26, 10.94%, i.e. dehydration is complete at 90° and no significant loss of BF_3 occurs at 150°. Protracted heating (up to 6 hrs.) at 100° fails to increase the loss of wt. any further. (2) In 1 hr., at 300, 400, 500, and 600°, anhyd. $Ba(BF_4)_2$ suffered dissocn. to the extent of 35.15, 85.02, 99.63, and 99.39%, resp. At 500°, in 5, 10, and 15 min., dissocn. attained 97.6, 98.2, and 99.5%, resp. Possibly, complete dissocn. can be attained even at 400° if heating is prolonged. (3) Decompn. of $Ba(BF_4)_2$ is recommended as a method of prepn. of pure dry BF_3. (4) KBF_4, in 1 hr. at 1130°, is dissocd. only to the extent of 90%. Addn. of $MgCl_2$, $CaCl_2$, $MgSO_4$, or $BaCl_2$ (1 mole per 2 moles KBF_4) facilitates dissocn. of KBF_4. E.g., $2KBF_4 + MgCl_2$, at 400°, 30 and 60 min., dissocn. 83.6 and 88.3%; at 450°, 74.6 and 86.5%; at 500°, 98.5 and 100.8%; $CaCl_2$, at 500°, 61.6 and 70.2%; $MgSO_4$, at 500°, 56.4 and 76.2%; $BaCl_2$, at 500°, 42.6 and 45.6%. The data relative to $MgCl_2$ are probably too high owing to a loss of wt. of about 15-18% suffered by $MgCl_2$ alone when heated 1 hr. at 500°.

N. Thon

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CA

2

Equilibrium of formation of tetrafluoboric acid in mixtures of hydrofluoric and boric acids. I. G. Ryss, M. M. Slutskaya, and S. D. Palevskaya. *Zhur. Fiz. Khim.* (J. Phys. Chem.) 22, 1322-30(1948); cf. *C.A.* 41, 6798*f*.—Mixts. of x mols. HF and y mols. H_3BO_3 were dissolved in water in waxed flasks. Some days later an excess of alkali was added, then inverted sugar, and the soln. was titrated (phenolphthalein). The decrease in acidity showed the amt. a of BF_4^- formed. When $x:y$ was 4, a was over 0.9 y, when x was 1.5 or greater, and was smaller the smaller x was (e.g. a = 0.75 y at x = 0.1). The equil. is represented by the reaction $BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$, and the const. $K = x(y - a)^2/4ay$ is at 11-18° about 3×10^{-3} mol./kg., i.e. agrees with that calcd. from hydrolysis of KBF_4 (*C.A.* 41, 1534*i*). When x was 1, a was 0.66 y at $x:y$ = 1 and 0.98 y at $x:y$ = 6. If HBF_4 were the sole reaction product of HF and H_3BO_3, a would have a min. at $x:y$ = 4; as a is smaller in the presence of an excess of H_3BO_3, hydroxyfluoboric acids must have formed. The yield a was even smaller when HF was dissolved in a satd. soln. of H_3BO_3. The method of prepg. HBF_4 solns. by satg. HF solns. with H_3BO_3 results in solns. contg. much BF_3OH^-. The *titration of HBF_4 solns.* according to Kern and Jones (*C.A.* 24, 5668) yields incorrect values. I. J. Bikerman

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

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The production of boron fluoride by acid methods. I. G. Ryss and K. M. Polyakova (Urals Sci. Research Chem. Inst., Sverdlovsk). *J. Gen. Chem. U.S.S.R.* 10, No. 9, a15-22(1940)(English translation).—See *C. A.* 44, 1235*i*.
E. J. C.

CA

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

The rate of formation of tetrafluoboric acid in mixtures of hydrofluoric and boric acids. I. I. G. Ryss and M. M. Slutskaya (Dnepropetrovsk Met. Inst.). *J. Gen. Chem. U.S.S.R.* 19, No. 10, a281-9(1949)(English translation).—See *C.A.* 44, 415c. II. I. G. Ryss. *Ibid.* a291-8.—See *C.A.* 44, 1311*d*. E. J. C.

CA

Preparation of boron trifluoride by acid methods. I. G. Ryss and E. M. Polyakova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1596-1603(1949).—In the production of BF_3 from KBF_4 and B_2O_3, according to $6KBF_4 + B_2O_3 + 6H_2SO_4 \rightarrow 8BF_3 + 6KHSO_4 + 3H_2O$, with a 50% excess of B_2O_3, use of oleum (105.9% H_2SO_4) gives markedly higher yields than concd. H_2SO_4; at 180°, with a 200% excess of 95.5 and 99.5% H_2SO_4, the total yield, after 3 hrs., was 9.5 and 42.6% (of the theoretical yield), and at 180°, with H_2SO_4 95.5, 99.5, and 105.9% (in 200% excess), the yield was 47.7, 64.0, and 79.1%, resp. With oleum, the ratio F/B in the absorbed gas is only slightly greater than 3, indicating a low proportion of SiF_4. At 180°, with a const. 50% excess of B_2O_3, and a 100, 200, and 300% excess of 105.9% H_2SO_4, the yield was 61.4, 79.1, and 80.2%, and the ratio F/B = 2.96, 3.19, and 3.0; there is, consequently, no point in raising the excess of oleum above 200%. With that amt. of oleum, at 180°, a 0, 10, 20, 50, and 200% excess of B_2O_3 gave a yield of 81, 80.1, 81.4, 75.6, and 58.1%, resp., with the ratio F/B closest to 3 with a 50% excess; consequently, an increase of the excess of B_2O_3 is unfavorable on all counts. Preliminary fusion of KBF_4 and B_2O_3 does not improve the yield or purity of the gas, but entails a loss of BF_3 in the course of the fusion. As compared with the KBF_4 + B_2O_3 method, the cryolite process based on the reaction $3CaF_2 + 3H_2SO_4 + B_2O_3 \rightarrow 2BF_3 + 3CaSO_4 + 3H_2O$ gives lower yields, e.g. 66.6% at 180°, with a 50% excess of B_2O_3 and a 200% of 105.9% H_2SO_4, and a low F/B ratio (~2.7), indicating contamination of the product with $(BOF)_x$, and presents no advantage. N. Thon

RYSS, I. G., SLOTSKAYA, M. M.

"Velocity of Formation of Tetrafluoboric Acid in Mixtures of Hydroflhoric and Boric Acids. I. Zhur. Obshchey Khim., 19, 1827-35 1949.

That the reaction $4HF + H_3BO_2 \rightarrow H^+ + BF_4^- + 3H_2O$ is not instantaneous is demonstrated by the fact that, directly on mixing, titration gives the total acidity of the left-hand member of the equation, and that the acidity decreases with time at a measurable rate. This change of acidity was used to det. the velocity of the reaction, expressed in the increase of the yield φ of HBF_4, in fractions of the stoichiometrically possible max. yield, which is equal to the amt. of H_3BO_3 in the presence of excess HF, and to $\frac{1}{4}$ of the amt. of HF in the presence of excess H_2BO_2. At 30.05°, at const. initial (HF), the rate increases with decreasing mol. ratio $q = HF/H_3BO_3$, for q = 8,4, and 2; the initial $d\varphi/dt$ varies very little with q. At equal q, the rate increases very rapidly with the total concn. The following are the exptl. data for the times t_c', in min., necessary to complete 10% of the reaction (formal order of the reaction in parentheses): for q = 2, 4, and 8, at the initial concn. M= 0.268, $t_c' = 4.5$ (2.43), 3.0 (2.66), and 2.5 (2.66); 0.1388 M, —, 9 (2.66), 7.5; 0.0783 M, 2.6 (2.79), 23, — ; 0.0394 M, ~90, —, —; the corresponding times of completion of 25% of the reaction are, at 0.2681 M, 12 (2.64), 9 (2.82), and 6.5 (3.04); 0.1388 M, —, 30 (2.84), 25; 0.0788 M, 90 (2.58), 85, ; 0.0394 M, 270, —, —, . In concd. soln. the reaction is very rapid; thus, if solid H_3BO_3 is added to 20% HF, cooled to 10°, equil. is reached in 2-3 min. Higher Temp. (60 and 90°) accelerates the reaction rate but lowers the equil. yield of HBF_4, evidently because of increased hydrolysis.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

v.

F 3091. ENERGY RESOURCES AND POWER DEVELOPMENTS IN AUSTRIA. Ruiss,
O. and Vas, O. (4th Wld Prw Conf., 1950, Sect. A, Pap. 24,
Prepr., 11 pp). Coal. Workable resources are estimated at
200 x 10^6 tons, comprising 1% bituminous coal, 10% high
quality and 89% low quality brown coal. Deposits are scattered
the most important coal findings are located on the eastern
border of the Alps in southern lower Austria; the main
brown coal fields are located in Styria (Koflach district)
and in the Hausruck district in Upper Austria (Wolfsegg-
Trauntal district). Gas. In twenty towns, total coal consumption
of the gas works accounts for about one sixth of imports. Five
sixth of the gas production is carried out at the gas works
of Vienna. For six years, natural gas from the oil fields
near by has been added to the town's gas. Electricity.
Ample raw hydro electric powers are available from the high
level of precipitation and great differncees of head in the
waters in the Austrian Alps. At present, about 40 x 10^9 kWh
(annual output) are worth developing, of which approximately
one eigth is already being utilised. The seasonal distribution

COMMON ELEMENTS

COMMON VARIABLES INDEX

MATERIALS INDEX

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

AUTHOR INDEX

1ST AND 2ND LETTER

6

CA

The equilibrium of the hydrolysis of silicon hexafluoride. I. G. Ryss (I. V. Stalin Inst. Met., Dnepropetrovsk). *Zhur. Fiz. Khim.* **25**, 654-61(1951).—The equil. of the hydrolysis $SiF_6^{--} + 2H_2O \rightleftarrows SiO_2$ aq. $+ 4 H^+ + 6 F^-$ has been studied before by colorimetric (I) (Kubelka and Pristoupil, *C.A.* **25**, 5073) and potentiometric (II) (*C.A.* 30. 7058^9) techniques. The values of the equil. const. $K = a_{H^+}^4(m_{NaF}\gamma_{NaF})^6/a_{Na_2SiF_6}a_{H_2O}^2$ are recalcd. from these data with the help of more recent values of γ_{NaF} (Karagunis, *et al.*, *C.A.* **25**, 2350; Robinson, *C.A.* **35**, 2056^3; Ivett and De Vries, *C.A.* **35**, 7805^6). $K_{20°} = 1.7 \times 10^{-27}$ from I and $K_{20°} = 4 \times 10^{-28}$ from II. Potentiometric data show that log K (av.) $= \overline{28}.02$ at 20° and $\overline{27}.96$ at 40° ($\Delta H = 17.6$ kcal./mol. from these data). Log K is 27.161, 27.397, 27.613, $\overline{27}.821$, and $\overline{28}.008$ at 15, 20, 25, 30, and 35°, resp. From these results, $\Delta H_{298}^{\circ} = 17.3$ kcal., $\Delta F_{298}^{\circ} = 35.97$ kcal. and $\Delta S_{298}^{\circ} = -62.6$ kcal./°C. for the hydrolysis.

Michel Boudart

RYSS, I. G.

PA 194T10

USSR/Chemistry - Crystal Solvates Oct 51

"Effect of the Formation of Crystal Solvates on the Stability of Complex Compounds," I. G. Ryss, Dnepropetrovsk Metallurgical Inst imeni Stalin

"Zhur Fiz Khim" Vol XXV, No 10, pp 1152-1159

Derived general thermodynamic dependence of stabilization of complex compds as a result of formation of crystal solvates on vapor tension of solvating addendum and number of latter's mols entering into compn of crystal solvate. Examd number of partial cases. Many salts with

194T10

USSR/Chemistry - Crystal Solvates Oct 51
(Contd)

complex anions and multicharged or small cations can exist stably only as crystal solvates. The derived dependence can be tied in with earlier found dependence between dissocn pressure of complex compds and their dissocn products' soly. Decrease in size or increase in charge of anion lowers cation's tendency toward solvation (i.e., lowers stability of complex cation). Examd tetrafluoroborates, hexafluorosilicates, and fluorides.

194T10

RYSS, I.G.; KULISH, N.F.

Equilibrium of the first step of hydrolysis of a hexafluogermanate ion. Zhur. neorg. khim. 9 no.5:1103-1108 My '64. (MIRA 17:9)

1. Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta i Dnepropetrovskiy khimiko-tekhnologicheskiy institut.

RISS, I. G., and SLUTSKAYA, M. M.

"Hydroxytrifluoroborates and new complexes of fluorine and boron.," Izv. Sektora Platiny i Drug. Blagorod. Metal.; Akad. Nauk SSR, Inst. Obshch. i Neorg. Khim., No. 26, 216-34 (1951)

The synthesis of KBF_3OH, $NaBF_3OH$, and $K_2B_2F_4O_3OH$ and their properties are discussed. The systems $NaF-H_3BO_3-H_2O$ and $NaF-Na_2B_4O_7-H_2O$ were studied at 25° Complexes are not formedeither in the solid phase or in soln. for the latter system but there is significant complex formation in the former. The general properties of the boron fluoride complexes are discussed.

RYSS, I. G.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Fluorine

Energy of dissociation and electron affinity of flourine. Usp. khim. 21 no. 7, 1952

Monthly List of Russian Accessions, Library of Congress, November 1952. Unclassified.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I. G.

USSR/Chemistry - **Fluorine and Boron** **Jan 52**
Compounds

"Hydroxytrifluoroborates," I. G. Ryss, M. M. Slutskaya, Chair of Gen Chem, Dnepropetrovsk Metallurgical Inst

"Zhur Obshch Khim" Vol XXII, No 1, pp 41-48

Synthesized KBF_3OH (I) by new method (interaction of mixt of KF_2 and HF with H_3BO_3. Described synthesis of $NaBF_3OH$ (II), quite sol in H_2O, whose chem properties are similar to those of I. In solns of I and II formation of tetrafluoroborate (III) is observed, proceeding to equil state little

207T13

USSR/Chemistry - Fluorine and Boron Jan 52
Compounds (Contd)

dependent on temp and concn of soln. Rate of formation of III falls slightly with increase in initial concn of I or II and rises sharply with increased temp. Soly of I at 0° and 45.1°C is 6.4% and 35.3%, resp.

207T13

RYSS, I. G. PA 240T6
APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

USSR/Chemistry - Boron Trifluoride Dec 52

"The Hydrolysis of Borontrifluoride Ammonate," I. G. Ryss and N. P. Pisarzhevskaya, Dnepropetrovsk Metallurgical Inst imeni I. V. Stalin

"DAN SSSR" Vol 87, No 6, pp 995-998

NH_3BF_3 was obtained by satg an ether soln of the etherate of boron trifluoride with gaseous ammonia. The degree of hydrolysis of NH_3BF_3 was plotted against time for both aqueous hydrolysis and hydrolysis in a 0.5 M soln of NaF. The degree of hydrolysis was determined by alkalimetric titration. Presented by Acad A. V. Topchiyev 8 Oct 52.

240T6

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

(1)

USSR

The thermochemistry of the boron fluoride complexes. I. G. Ryss and A. G. El'kenbard (I. V. Stalin Met. Inst., Dnepropetrovsk). *Doklady Akad. Nauk S.S.S.R.* 91, 805-8 62 (1953).—The thermochem. consts. were detd. for KBF_3OH (preceding abstr.). (cf. *C.A.* 41, 5046c) and $K_2B_2F_4O_2OH$. The heats of soln. were measured for 0.05 mole KBF_3OH and 0.025 mole $K_2B_2F_4O_2OH$ in 20 moles H_2O (Q_1 (25.5°) = −7.25 and Q_1 (23.6°) = −10.0 kcal./mole, resp.) and in 0.8*M* NaF (Q_1 (25.5°) = −7.18 kcal./mole and Q_1 (22.5°) = −16.9 kcal./mole, resp.). The heats of decompn. of these compds. in NaOH were also detd. From the measured values, the heats of formation are calcd. to be KBF_3OH (+419.3 kcal./mole) and $K_2B_2F_4O_2OH$ (+857.7 kcal./mole). I. Roytar Leach

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1

Ryss

27 21

4

4E4j

4E3d

Cosolution of sodium chromate and sulfate in water. I. G. Ryss and A. I. Zhukov. *Trudy Ural. Nauch.-Issledovatel. Khim. Inst.* 1954, No. 1, 23-8; *Referat. Zhur. Khim.* 1956, Abstr. No. 6393.—Study of cosoly. of Na_2SO_4 (I) and Na_2CrO_4 (II) at 55.7 ± 0.05° shows that the basic phases of the investigated systems are I and $Na_2CrO_4.4H_2O$ (III). Solns. satd. with I and contg. 0, 10.17, 19.79, 30.40, and 40.89% of II contain 31.40, 22.01, 15.60, 8.669, and 3.308% of I. A satd. soln. of I and III contains 1.448% of I and 47.40% of II. The soly. of III in water is equiv. to 51.83% of II. Juxtaposition of these data with the known data for 25.28 and 33° shows that the soly. curves of I in solns. of II at different temps. intersect. The soly. of I in dil. solns. of II decreases with increase in temp. The effect of temp. between 33 and 55° is negligible. Calcd. and given as curves for 33 and 55° are the limiting concns. of II to which solns. with different concns. of I and II can be evapd. without pptg. I.

N. Vasilieff

MT

RYSS, I. G

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

USSR/Chemistry

Card : 1/1

Authors : Ryss, I. G. and Vitukhnovskaya, B. S.

Title : Potassium and ammonium hexafluoromanganiates

Periodical : Dokl. AN SSSR, 97, Ed. 3, 471 - 473, July 21, 1954

Abstract : Experiments, for the purpose of obtaining K-and Am-hexafluoromanganiates by the introduction of a Mn-trifluoride solution into the concentrated fluoride solutions with consequent filtration and washing of residues, are described. Formation of hexafluoromanganiates was observed during continuous agitation of pentafluoromanganiates with concentrated fluoride solutions. The change in composition of the solid phase was determined by the change in color and crystal forms, and the composition of the crystals was established by the radicals method. Five references: 4-USA since 1887 and 1-USSR. Table, graphs.

Institution : The I. V. Stalin Metallurgical Institute, Dnepropetrovsk

Presented by : Academician, I. I. Chernyaev, March 26, 1954

RYSS, I.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

USSR/Chemistry - Synthesis

Card 1/1 **:** Pub. 22 - 31/46

Authors : Ryss, I. G.

Title : Trimeric Na and K- difluoro-orthoborates

Periodical : Dok. AN SSSR 97/4, 691-693, Aug 1, 1954

Abstract : The synthesis of trimeric Na and K-difluoro-orthoborates and their chemical structures, are described. The determination of the Na and F contents of the trimer, is explained. The products, derived after blending $NaHF_2$ with H_3BO_3 in equal ratios, are listed. The analysis results of such trimers, are shown in table. Four references: 2-USSR and 2-German (1932-1951).

Institution : The V. I. Stalin Metallurgical Institute, Dniepropetrovsk

Presented by : Academician I. I. Chernyaev, March 26, 1954

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.

USSR/Chemistry - General chemistry

Card 1/2 Pub. 116 - 2/25

Authors : Ryss, I. G., and Ustyanova, P. V.

Title : The chemical properties of potassium hydroxotrifluoroborate and tetrafluoro borate

Periodical : Ukr. khim. zhur. 21/1, 6-15, 1955

Abstract : New data are presented about the chemical properties of dissolved BF_3-OH' and $B_3F_4O_3OH$" ions. The data were obtained during potentiometric study of the hydrolysis of the ions. The existence of $BF_2(OH)_2$' ions in aqueous solutions was established by measurements. The data show that the hydrogen indicator of KBF_3OH solutions does not depend upon the salt concentration, it increases slightly during introduction of boric acid into the solution but increases sharply during the introduction of dissolved fluoride.

Institution : The I.V. Stalin Metalurgical Institute, Faculty of Gen. Chem. Dniepropetrovsk

Submitted : June 30, 1953

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Periodical : Ukr. khim. zhur. 21/1, 6-15, 1955

Card 2/2 : Pub. 116 - 2/25

Abstract : It is also pointed out that the introduction of glycerin which binds one of the hydrolysis products - boric acid - increases the acidity of the solution. Nine references : 4 USSR, 3 USA, 1 French and 1 German (1894-1952). Tables; graphs.

RYSS,I.G.; NILUS,E.L.

Solubility of calcium sulfate in hydrochloric acid solutions at 25°C.
Zhur.ob.khim.25 no.6:1076-1081 Je '55. (MLRA 8:12)

1. Dnepropetrovskiy metallurgicheskiy institut
(Calcium sulfate)

RYSS, I. G. and PLIT, V. A.

"The Rate of Decomposition of Sodium Fluoborate in Alcohol-water Mixtures."

Zhur. Obshchei Khim. 25, 19-27, 1955

The rate of decompn. of the fluoborate ion in the presence of base $(BF_4^- + 4OH^- \rightarrow BO_2^- + 4F^- + 2H_2O)$ was followed titrimetrically. The rate of decompn. of $NaBf_4$ (I) in a 1:1 (by wt.) H_2O-C_2H_5OH mixt. (II) is 0.096 as fast as in pure H_2O, both at 50° and 70°. The soly. of I in H_2O, CH_3OH, C_2H_5OH, and in H_2O-C_2H_5OH mixts. was measured at various temps. In H_2O, a eutectic m. -10.69° was found to contain 37.12% I. There was no evidence of cryst. hydrates of I. To obtain chemically pure I, slightly less than the calcd. amt. of HBF_4 required for complete neutralization was added to Na_2CO_3. After most of the CO_2 evolved, the rest of the HBF_4 plus a slight excess was added with immediately neutrdlized with NaOH to a pink color with phenolphthalein. After small amts. of NaF were filtered off, the soln. was concd. under a vacuum and I was recrystd. from II between 50° and 0°.

Met. Inst. Dnepropetrovsk.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Ryss I.G.

Chem 5

USSR.

✓The hydration and solubility of manganese fluoride. I. G. Ryss and B. S. Vitukhnovskaya (Met. Inst., Dnepropetrovsk). *Zhur. Obshchei Khim.* 25, 643-7(1955).—A method is described for the direct synthesis of manganese fluoride tetrahydrate ($MnF_2.4H_2O$) by dissolving the carbonate in dil. HF at 0°. The soly. polytherms are given for MnF_2 and $MnF_2.4H_2O$. These have a common point at 23.5°. The transition from one form to the other occurs very slowly. The heats of soln. of MnF_2 and of $MnF_2.4H_2O$ were found to be equal to 5.22 and −3.75 kcal./mole, resp. The heat of hydration of MnF_2 was calcd. to be 8.97 kcal./mole and the heat of dissocn. of the tetrahydrate was calcd. as −51.01 kcal./mole. J. Rovtar Leach

①

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1

Ryss, I. G.

Chem

The structure of copper monofluoride. I. G. Ryss (L. M. Kaganovich Inst. Railroad Transport. Engrs., Dnepropetrovsk). *Zhur. Fiz. Khim.* 29, 936-7(1955).—The CuF studied by Ebert and Woitinek (*C.A.* 27, 2078) is shown to be thermodynamically unstable at room temp. (Wartenberg, *C.A.* 33, 6741^{6}), and the possible compn. of the sample studied by E. and W. is suggested.

W. M. Sternberg

PM

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.

USSR/ Chemistry - Physical chemistry

Card 1/1 Pub. 147 - 10/21

Authors : Ryss, I. G., and Gribanova, T. A.

Title : The kinetics of fluorosulfonate ion decomposition in aqueous solutions

Periodical : Zhur. fiz. khim. 29/10, 1822-1826, Oct 1955

Abstract : Experiments showed that the decomposition of a fluorosulfonate ion in weak alkali solutions follows a hydrolysis stage and is described by a kinetic reaction equation of the first order. The thermal and activation entropy values of the decomposition process were established. The hydrolysis of fluorosulfonate had the same rate as in a diluted alkali medium and is followed by hydrogen ion catalysis. An approximate value was established for the constant of the hydrogen ion catalysis rate at 80.28°. Eight references: 5 Germ., 2 USSR and 1 USA (1913-1948). Table; graph.

Institution : Dnepropetrovsk Inst. of Railroad Transport Engineers and Dnepropetrovsk Metallurgical Inst.

Submitted : January 12, 1955

Ryss, I. G.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Khimiya Ftora i Yego Neorganicheskikh Soyedineniy (The Chemistry of Fluorine and of Its Inorganic Compounds), by Prof I. G. Ryss, Doctor of Chemical Sciences, Moscow, Goskhimizdat, 1956, 718 pp

In a brief publishers' annotation, the book is described as follows:

"This book represents a monograph on the chemistry of fluorine and of its inorganic compounds with elements of all groups of the periodic system. The chemical and physical properties of the substance in question, methods for their preparation, applications of the substances described, and the principal physicochemical and molecular constants of fluorine and of its compounds are described and listed in the book.

"The monograph contains an exhaustive bibliography of work published up to October 1953 and in part data published at the end of 1953 and during 1954. Additional references to the most important work done after 1954 are given in small print.

"The book will serve the needs of scientific workers and engineers. It may also be of use to aspirants and students working for a degree." (p 2)

1SUM.1345

RYSS, I.G.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

"The compounds of fluorine with different elements are discussed in the monograph in the order in which these elements appear in the periodic system. In naming individual substances, the author used both the Russian and the international terminology, because unfortunately there is as yet no generally accepted Russian system of nomenclature.

"The author hopes that because of the manifold nature of fluorides and of their characteristics the data compiled in the monograph will be of interest not only to persons who specialize in the chemistry of fluorine and of complex compounds, but also to wide circles of inorganic chemists in general." (pp 9-10)

According to the table of contents, the text of the book deals with the following subjects: Chapter 1, distribution of fluorine in nature (p 11); Chapter 2, [Elemental] fluorine (p 15); Chapter 3, hydrogen fluoride (p 49); Chapter 4, hydrofluoric acid (p 91); Chapter 5, preparation of hydrogen fluoride and of hydrofluoric acid (p 101); Chapter 6, acidic salts of hydrofluoric acid (p 111); Chapter 7, the fluorides of halogens (p 125); Chapter 8, fluorides of the elements of the sixth group (main subgroup: O, S, Se, Te) (p 147); Chapter 9, General review of complex fluorides (p 193); Chapter 10, fluorides of elements of the fifth group (main subgroup: N, P, As, Sb, Bi) (p 224); Chapter 11, fluorides of elements of the fourth group (main subgroup: C, Si, Ge, Sn, Pb) (p 287); Chapter 12, fluorosilieie acid and its salts (p 331); Chapter 13, boron fluoride and boron-fluorine complexes (p 411); Chapter 14, fluorides of aluminum and fluorolaluminates (p 509); Chapter 15, fluorides of elements

Sum. 1345

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Ryss, I.G.

of the gallium subgroup (Ga, In, Tl) (p 542); Chapter 16, fluorides of elements of the zinc subgroup (Zn, Cd, Hg) (p 551); Chapter 17, fluorides of elements of the copper subgroup (Cu, Ag, Au) (p 559); Chapter 18, fluorides of elements of the eighth group (Ni, Co, Fe, Pd, Rh, Ru, Pt, Ir, Os) (p 571); Chapter 19, fluorides of elements of the manganese subgroup (Mn, Re) (p 615); Chapter 20, fluorides of elements of the chromium subgroup (Cr, Mo, W) (p 629); Chapter 21, fluorides of elements of the vanadium subgroup (V, Nd, Ta) (p 650); Chapter 22, fluorides of elements of the titanium subgroup (Ti, Zr, Hf,) and of the scandium subgroup (the lower fluorides of titanium, p 665; fluorides of quadrivalent titanium and fluorititanates, p 666; the fluorides of zirconium and hafnium, p 672; brief review of fluorides of the subgroup of scandium, lanthanides, and actinides, p 678); Chapter 23, beryllium fluoride and fluoroberyllates (p 686); Chapter 24, fluorides of alkaline earth metals, alkali metals, and ammonium (p 698); and Chapter 24, thermodynamic properties of the fluorides of some metals (p 711). (pp 3-8)

The chemical properties of elemental fluorine, halogen fluorides, oxygen difluoride, and boron fluoride are discussed in considerable detail in the text of the book.

SUM.1345

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.

"In connection with the applications mentioned above, the number of scientific investigations on the chemistry of fluorine grows from year to year.

"In the present monograph an attempt has been made to give a comprehensive review of the literature on the chemistry of inorganic compounds of fluorine, giving information on the results of all important work which has been done in this field. Particular attention has been paid to the physicochemical properties of the substances discussed. The author attempted insofar as possible to give a critical evaluation of the results of the work discussed by him. In view of the profusion of data which are available, the material presented in the book had to be very succinct. To facilitate searches in the original literature, references are given in the text of the book.

"The monograph utilized work published in the USSR and in the most important non-USSR journals, including information given in Chemical Abstracts (US) during the time up to October 1953. Publications that appeared at the end of 1953 and in 1954 have also been partly utilized. References to the most important work done after 1954 are given in small print.

SUM. 1345

RYSS, I.G.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

In the section dealing with fluorides of elements of the scandium subgroup and those of lanthanides and actinides a considerable amount of information is given on the fluorides of rare earths, thorium, uranium, and transuranium elements. The following USSR work is described in this section:

According to D. I. Ryabchikov, the fluoride ion is the most effective precipitant of rare earths and of rare earth complexes. The lanthanum ion is a sensitive reagent for the detection of the fluoride ion.

V. G. Khlopin and M. S. Merkulova investigated the distribution of UX_1 between LaF_3 and ThF_4 and the distribution of radium between crystalline LaF_3 and a solution of LaF_3 in 3% nitric acid.

Complex compounds of the types $MeXF_4$ and Me_3XF_6 are known, while the existence of compounds of the type Me_2XF_5 is doubtful (Me = an alkali metal or ammonium). By investigating the melting point diagrams of systems composed of lanthanum fluoride or lanthanide fluorides and alkali metal fluorides, Ye. P. Dergunov and A. G. Bergman established the existence of a considerable number of compounds belonging to the first two types.

The properties of uranium tetrafluoride were investigated in detail by Khlopin and M. L. Yashchenko. They established that the solubility of this salt at 25° amounts to 0.00017 mol per liter and that its hemi-, di-, and 2.5-hydrates are transformed in solution into $H_2\,[UF_4\,(OH)_2]$.

SUM.1345

Many compounds of thorium fluoride with fluorides of alkali metals were discovered by Dergunov and Bergman, who applied the method of thermal analysis in their work on the double fluorides of thorium.

In Chapter 13 (p 438) the statement is made that because of the high neutron capture cross section exhibited by the isotope B^{10}, pure boron trifluoride is suitable for filling ionization chambers and proportional counters and is actually used for this purpose. It is furthermore pointed out that the B^{10} content can be increased by thermal diffusion.

The book constitutes a survey of the world literature on inorganic fluorine compounds rather than a compilation of USSR work: references to USSR work represent a minor part of the titles listed. For instance, the bibliography of Chapter 13, which consists of 274 items, lists 48 references to USSR work, and that of Chapter 22, which consists of 117 items, lists 12 USSR references. (C)

54M. 1345

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1

4

1-4E3d

The properties of dihydroxyfluoroboric acid. L. G. Ryss and L. P. Bogdanova (L. M. Kaganovich Inst. Engineers and Railroad Transportation, Dnepropetrovsk). *Zhur. Neorg. Khim.* 1, 2264-71(1956).—Methods for the analysis of $H_3BO_2F_2$ (I) and the reaction of I with a no. of solid Na salts were studied. I cannot be titrated directly with an alkali because of the rapid formation of BF_4^-. A method is described for the analysis of I based on the decompn. of BF_4^- by boiling with a soln. of $CaCl_2$. It was established that I does not contain a significant quantity of BF_4^-. The reaction of I with $NaHF_2$ and KHF_2 leads to the formation of the tetrafluoroborates. I reacts with $Na_2B_2O_2F_4$ to form $NaBF_4$ and H_3BO_3. I reacts with NaCl or Na_2CO_3 to form $Na_2B_2O_2F_4$ and with NaF to form the same salt plus $NaBF_4$. The chem. properties of I support the assumption that it corresponds to the formula $[H_3O]_2[B_2O_2F_4]$. J. R. L.

RM adz

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.; IDEL'S, S.L.

Pyridinium tetrafluoborate. Zhur.neorg.khim. 2 no.9:2270-2272 S '57. (MIRA 10:12)

(Pyridinium compounds)

RYSS, I.G.; IDEL'S, S.L.

[redacted]

Studying the properties of pyridine boron trifluoride $C_5H_5N \cdot BF_3$.
Zhur. neorg. khim. 2 no.12:2716-2722 D '57. (MIRA 11:2)

1. Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta, Kafedra khimii.

(Boron fluoride)

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1

Ryss, I. G.

7

7122

4E3d

4E4j

USE OF TETRAFLUOBORIC ACID IN QUANTITATIVE ANALYSIS. I. WEIGHT DETERMINATION OF ALKALI METALS IN BORATES, HALIDES, NITRATES, AND NITRITES. I. G. Ryss and E. L. Nilus (Dnepropetrovsk Metallurgical Inst.). Zhur. Analit. Khim. 12, 64-9(1957) Jan.-Feb. (In Russian)

The possibility of quantitative conversion of fluorides, chlorates, bromides, iodides, nitrates, nitrites, borates, and mixtures of borates and fluorides of alkali metals (with the exclusion of Li) into tetrafluorborates has been shown. Also, it was found that mixtures of HF and H_3BO_3 completely evaporate when the molar ratio HF/H_3BO_3 exceeds 2.5, and $LiBF_4$ decomposes very slowly at 110 to 150° while $NaBF_4$ remains quite stable at 200° and decomposes slowly at 250°. (tr-auth)

pm

"APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Ryss

78-3-5-21/39

AUTHORS: Ryss, I. G., Vitukhnovskaya, B. S.

TITLE: Cesium-and Chromium Manganic Fluoride (Ftoromanganiaty tseziya i khroma)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol 3, Nr 5, pp 1185 - 1187 (USSR)

ABSTRACT: The syntheses of $Cs_2MnF_5 \cdot H_2O$ and $MnF_3 \cdot CrF_3 \cdot 6\,H_2O$ were carried out.
$Cs_2MnF_5 \cdot H_2O$ has light rose-colored crystals and is very easily decomposable with water. $MnF_3 \cdot CrF_3 \cdot 6\,H_2O$ forms difficultly soluble lilac crystals. Their composition was determined by means of chemical analyses. The gradual formation constant of the above-mentioned complexes was calculated. In aqueous solution, the following complexes can simultaneously exist:

Card 1/2

$\left[CrF_2(H_2O)_4\right]^+$ and $\left[MnF_4(H_2O)_2\right]^-$.

Cesium-and Chromium Manganic Fluoride

The probable composition of $MnF_3.CrF_3.6\ H_2O$ is the following:

$[CrF_2(H_2O)_4][MnF_4(H_2O)_2]$ or $[CrF_2(H_2O)_5][MnF_5H_2O]$.

There are 9 references, 4 of which are Soviet.

SUBMITTED: May 15, 1957

AVAILABLE: Library of Congress

1. Complex compounds--Synthesis 2. Complex compounds--Chemical analysis 3. Cesium--Chemical reactions 4. Chromium manganic fluoride--Chemical reactions

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

78-3-6-20/30

AUTHORS: Ryss, I. G., Khordas, I. S.

TITLE: The Solubility-Polytherms of Potassium- and Cesium-Tetrafluorborates (Politermy rastvorimosti tetraftoroboratov kaliya i tseziya)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 6, pp. 1410-1415 (USSR)

ABSTRACT: The solubility of potassium- and cesium-tetrafluorborates was determined and compared with the values given in publications. A method for the determination of the solubility of the complexcompounds was given, in which a partial hydrolysis of the complex ions takes place. The activity coefficients of KBF_4 and $CsBF_4$ were also determined. Dependence of the logarithms of the activity in saturated solutions on temperature, was determined. The solubility of KBF_4 and $CsBF_4$ was determined at temperatures of from 0 to 70°C. The dependence of the activity of saturated solutions of KBF_4 and $CsBF_4$ on temperature is expressed by the following equation:

Card 1/3

$$\lg a_{KBF_4} = 7470-3080/T$$

$$\lg a_{CsBF_4} = 8236-3146/T$$

The heat of solubility for KBF_4 is expressed by ΔH^o = 14,1 k cal/mol, ΔF^o_{298} = 3,90 k cal/mol and ΔS^o_{298} = 34 k cal/mol/degree.

The heat of solubility of $CsBF_4$ is expressed by ΔH^o = 14,5 k cal/mol, ΔF^o_{298} = 3,24 k cal/mol and ΔS^o_{298} = 38 k cal/mol/degree. The great similarity of the ΔH^o of the two above-mentioned salts shows that the lattice energy differs very little and that also the hydration-energy of K^+ and Cs^+ is very similar. The entropy of solubility of KBF_4 is lower than that of $CsBF_4$. This leads to the

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

The Solubility-Polytherms of Potassium- and Cesium Tetrafluorborates 78-3-6-20/30

conclusion that the solubility of $CsBF_4$ is more endothermic.
There are 1 figure, 3 tables, and 11 references, 4 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute for Railroad Engineering)

SUBMITTED: April 22, 1957

AVAILABLE: Library of Congress

1. Potassium tetrafluorborates--Solubility. 2. Cesium tetrafluorborates--Solubility

Card 3/3

AUTHORS: Ryss, I.G., Gribanova, T.A. SOV/78-3-7-35/44

TITLE: The Solubility Polytherm of Potassium Fluorine Sulfonate (Politerma rastvorimosti ftorsul'fonata kaliya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 7, pp 1665-1668 (USSR)

ABSTRACT: Investigations of the solubility of potassium fluorine sulfonate (KSO_3F) were carried out at 0° C and 50° C. By taking the hydrolysis of the remaining anions into account, several modifications were effected. In the course of the analysis carried out the total content of SO_3F and HF was determined. On the strength of the results obtained the thermodynamic characteristic on the dissolution process of KSO_3F was calculated: for $\Delta NH^0 \sim 10.5$ kcal/mol; for $\Delta S^0 \sim 30.5$ enthropy units. For the gaseous SO_3F hydration heat was calculated as amounting to ~ 50 kcal/mol. The thermodynamic characteristic of the dissolution processes of KBF_4, $KClO_4$ $KMnO_4$ and KSO_3F were compared. There are 1 figure, 1 table, and 13 references, 9 of which are Soviet.

Card 1/2

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta i Dnepropetrovskiy metallurgicheskiy institut (Dnepropetrovsk Institute of Railroad Transport Engineers and Dnepropetrovsk Metallurgical Institute)

SUBMITTED: May 15, 1957

1. Potassium fluorine sulfonate--Solubility 2. Potassium fluorine sulfonate--Thermodynamic properties 3. Ions--Hydrolysis

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

AUTHORS: Ryss, I.G., Bogdanova, L.P. SOV/ 78-3-7-36/44

TITLE: The Solubility Polytherm of $Na_3B_3O_3F_6$. Equilibrium of the System $Na_3B_3O_3F_6$-NaI-H_2O at 25° (Politerma rastvorimosti $Na_3B_3O_3F_6$. Ravnovesiye sistemy $Na_3B_3O_3F_6$-NaJ-H_2O pri 25°)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 7, pp 1669-1674 (USSR)

ABSTRACT: The velocity of the formation of BF_4^- in solutions of $Na_3B_3O_3F_6$ at 70-90° C was determined. At 30° C the forming of BF_4^- from solutions of $Na_3B_3O_3F_6$ develops comparatively slowly, and therefore it is possible to determine the solubility of $Na_3B_3O_3F_6$. The velocity of the formation of NF_4^- increases with rising temperature and decreases with an increase of the concentration of $Na_3B_3O_3F_6$. The heat of solution in water is -7.5 kcal/mol. The equilibrium in the system $Na_3B_3O_3F_6$-NaI-H_2O at 25° was investigated. The results obtained confirm the chemical formula of these compounds. At a higher concentration of $B_3O_3F_6^{3-}$ in the solution and in the domain of a lower concentration of Na^+ no considerable depolimerization of $B_3O_3F_6^{3-}$ occurs. There are

Card 1/2

The Solubility Polytherm of $Na_3B_3O_3F_6$. SOV/78-3-7-36/44
Equilibrium of the System $Na_3B_3O_3F_6$-NaF-H_2O
at 25°

4 figures, 2 tables, and 9 references, 7 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Transport Engineers)

SUBMITTED: May 28, 1957

1. Complex compounds--Solubility 2. Chemical equilibrium --Determination 3. Complex compounds--Chemical analysis

Card 2/2

SOV/32-24-7-61/65

AUTHOR: Ryss, I. G., Doctor of Chemical Sciences

TITLE: On the Problem of the Volumetric Determination of Fluorine in Tetrafluoro Borates(K voprosu ob ob"yemnom opredelenii ftora v tetraftoroboratakh)Concerning the Article by Z.T. Maksimycheva, Sh.T.Talipov and A.M.Koginova, Zavodskaya Laboratoriya, 1956, Vol. 22, Nr 7, pp. 791 (O stat'ye Z.T. Maksimychevoy, Sh.T.Talipova i A.M.Koginovoy, Zavodskaya laboratoriya, XXII, 7, 791, 1956)

PERIODICAL: Zavodskaya Laboratoriya, 1958, Vol. 24, Nr 7, pp. 905 - 906 (USSR)

ABSTRACT: In the article mentioned above the experimental conditions were insufficiently characterized and the physical and chemical foundations of the analytical method investigated were not explained in spite of the data known. The statement that the introduction of acid into the solution of tetrafluoro borate shifts the equilibrium in the hydrolysis in the desired direction is not correct; also the statement that a complete hydrolysis of BF_4^- in acid medium is obtained by the dissociation of the hydrofluoric acid is incorrect. It is generally known that the addition of catalysts does not change the position

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On the Problem of the Volumetric Determination of Fluorine in Tetrafluoro Borates. Concerning the Article by Z.T.Maksimycheva, Sh.T.Talipov and A.M.Koginova, Zavodskaya Laboratoriya, 1956, Vol. 22, Nr 7, pp. 791

of the equilibrium. According to the data mentioned the pure tetrafluoro boric acid can not be hydrolysed completely as the contact with glass is lacking, however, an excess in boric acid highly effects the degree of hydrolysis. The paper mentioned above does, however, not give any data on this. It is therefore recommended to perfect the method suggested. The given degree of the hydrolysis of tetrafluoro boric acid at room temperature is of no use as the concentration of the solution is not given. The attempt to achieve a decomposition BF_4^- in an alkaline medium by boiling for several hours could not be successful; this is explained and a corresponding diagram is given. On the other hand it is a fact generally known that the hydrolysis of BF_4^- in alkaline medium increases with the duration of heating. There are 1 figure and 7 references, which are Soviet.

Card 2/3

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

On the Problem of the Volumetric Determination SOV/32-24-7-61/65
of Fluorine in Tetrafluoro Borates. Concerning the Article by Z.T.Maksimycheva, Sh.T.Talipov and A.M.Koginova, Zavodskaya Laboratoriya, 1956, Vol. 22, Nr 7, pp. 791

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad-Transport Engineers)

Card 3/3

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

5(2) SOV/32-24-11-11/37

AUTHORS: Ryss, I. G., Nilus, E. L.

TITLE: Use of Tetrafluoro Boric Acid in Quantitative Analysis (Primeneniye tetraftorobornoy kisloty v kolichestvennom analize) Determination of Potassium and Sodium in Mixtures of Chlorides (Opredeleniye kaliya i natriya v smesi khloridov)

PERIODICAL: Zavodskaya Laboratoriya, 1958, Vol 24, Nr 11, pp 1349 - 1352 (USSR)

ABSTRACT: It has already been shown (Ref 1) that in the evaporation of the chlorides of alkali metals with tetrafluoro boric acid tetrafluoro borates are quantitatively produced. The content of potassium and sodium chlorides in the mixture can be calculated from the weight of the chloride mixture $\Sigma_{(Chl)}$ and the weight of the tetrafluoro borate $\Sigma_{(Tfb)}$ using the equations:

$m_{NaCl} = 5.2741 \Sigma_{(Tfb)} - 8.908 \Sigma_{(Chl)}$ and

$m_{KCL} = 9.9085 \Sigma_{(Chl)} - 5.2741 \Sigma_{Tfb)}$; The sodium tetra-

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APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Use of Tetrafluoro Boric Acid in Quantitative Analysis. SOV/32-24-11-11/37
Determination of Potassium and Sodium in Mixtures of Chlorides

fluoro borate is separated from the potassium salt by a rapid leaching out with a 10% NH_4BF_4 solution. NH_4BF_4 is separated from $NaBF_4$ by volatilization at 300° and from KBF_4 by washing out with 96% ethanol. In the extraction of the $NaBF_4$ from the mixture of tetrafluoro borates treating with 2.5 ml. NH_4BF_4 for 5 minutes was sufficient. It was found that the use of alcohol (instead of water) considerably decreased the solubility of KBF_4, the value of which was somewhat higher than that found by Fadeyev (Ref 8). The analytical results on mixtures ranging in composition from 5% KCL and 95% NaCl to 95% KCL and 5% NaCl were completely satisfactory. The relative analytical error is greater for those components which were present in smaller amounts. There are 3 tables and 9 references, 5 of which are Soviet.

Card 2/3

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta i Dnepropetrovskiy metallurgicheskiy institut (Dnepropetrovsk Institute of Railroad Transport Engineers and the Dnepropetrovsk Metallurgical Institute)

AUTHOR: Ryss, I. G. SOV/2o-12o-4-3o/67

TITLE: Kinetics of Hydrolysis of Boron Trifluoride Coordination Compounds (Kinetika gidroliza koordinatsionnykh soyedineniy ftoristogo bora)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 12o, Nr 4, pp. 797-800 (USSR)

ABSTRACT: The author proved that the kinetics of hydrolysis of F_3B:Am with Am denoting an amine does not only depend on the nature of the amine with respect to quality but also with respect to quantity. The first stage of hydrolysis which can be determined by analysis is apparently irreversible. In a neutral and acidous medium the reaction becomes more complicated, in an alkaline medium BF_3OH^- undergoes a rapid quantitative decomposition to borate and fluoride. An earlier attempt to investigate the hydrolysis of $F_3B : NH_3$ did not bring about any quantitative results. In this paper a new method is investigated. It is based upon the determination of concentration of $F_3B : NH_3$ which was not hydrolized at a given time. The same method was applied in the case of $F_3B:NH_2CH_3$. The velocity of hydrolysis of this compound is small. The hydrolysis

Card 1/4

SOV/2o-12o-4-3o/67

Kinetics of Hydrolysis of Boron Trifluoride Coordination Compounds

proceeds according to an equation of the first order and is neither catalysed nor inhibited by H^+-ions; at the same time the formation of BF_4^- is inhibited. The latter velocity is proportional to its concentration in the presence of F^--ions. The acidification of the NaF-solution to pH 5,2 did not eliminate the catalytic effect of F^-. Since the velocity of hydrolysis of $F_3B:NC_5H_5$ and of BF_4 does not depend on the alkalinity of the solution, it is determined by the solvolytic dissociation of the complexes. The high electronegativity of fluorine and the structure of the electron shell of boron justify the statement that these processes are a nucleophilic replacement of S_N1. The same refers to the hydrolysis of the complexes BF_3 with NH_3 and NH_2CH_3. In a highly alkaline medium they decompose very quickly; the velocity of their hydrolysis, however, is not determined by the OH^--ions which form in connection with the water dissociation. The acceleration of the mentioned hydrolysis in the presence of F^--ions is not due to the course of reaction which is usually assumed for S_N-2-processes(attacks on the complexes by F^- which replaces the amine).

Card 2/4

The catalytic effect of F^- can be

explained by the following hypothesis: the coordination of ammonia by boron fluoride is accompanied by the withdrawal of the electron pair of N to B. It increases the acidous properties of the ammonia hydrogen and its capability of forming hydrogen bindings. A quickly established equilibrium in the solution is related to this phenomenon:

$$F_3B : NH_3 + F^- \rightleftarrows F_3B : NH_3 \ldots F^- \quad (6)$$

The addition of a negative ion is bound to weaken $B \leftarrow \dot{N}$ in its complex and facilitate its solvolytic dissociation. The acceleration of decomposition of $F_3B : NH_3$ and NH_2CH_3 in the presence of ions HCO_3^-, CO_3^{2-} and OH^- is apparently started by analogous processes. Figure 1 shows that the activation energy E of the hydrolysis of boron fluoride complexes increases with increased alkaline properties of the addition products. A relationship exists between the thermodynamical properties of the addition product and those of the state of transition. H^+-catalyses the hydrolysis of BF_4^-, SO_3F^-, PF_6^- and probably also of other complex fluorine ions in consequence of an association outside the shell (vneshnesfernaya assostiatsiya)

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SOV/20-120-4-30/67

Kinetics of Hydrolysis of Boron Trifluoride Coordination Compounds

caused by the attraction of ion charges. This association facilitates an HF-separation. A rapid decomposition of BF_3OH^- in an alkaline medium is apparently connected with an intraspherical transition (vnutrisfernyy perenos) of a proton and the following processes of HF-separation and of the water addition. There are 1 figure, 1 table, and 9 references, 7 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovskiy Institute of Railway-Transport-Engineers)

PRESENTED: February 5, 1958, by A. V. Topchiyev, Member, Academy of Sciences, USSR

SUBMITTED: February 5, 1958

1. Boron fluorides--Hydrolysis 2. Ions--Chemical effects
3. Chemical equilibrium

Card 4/4

5(3),5(2)

AUTHORS: Ryss, I. G., Trakhtenberg, F. I. SOV/78-4-6-36/44

TITLE: The Hydrofluorides of Aniline (Gidroftoridy anilina)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 6, pp 1431 - 1436 (USSR)

ABSTRACT: The solubility of the hydrofluorides of aniline was investigated in hydrofluoric acid at 0° and 20° and the results are given in table 1. The phases $[C_6H_5NH_3]F.H_2O$ and $[C_6H_5NH_3]HF_2$ were determined. The "eutonic" solution contains at 0° 12.11% $[C_6H_5NH_3]F$ and 43.89% $[C_6H_5NH_3]HF_2$. The compound does not pass over into polyhydrofluoride at -18° in the case of an increase of the HF-concentration up to 52%. The dissociation degree of aniline fluoride was calculated at 0°. The compounds $C_6H_5NH_2.3HF.0.5H_2O$ (Ref 1) and $C_6H_5NH_2.4HF$ (Ref 3) described in the publications are probably hexafluoro-silicates of aniline. There are 1 figure, 1 table, and 7 references, 4 of which are Soviet.

SUBMITTED: March 25, 1958

Card 1/1

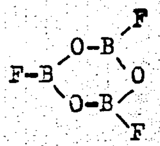
5(2) SOV/78-4-8-22/43

AUTHORS: Ryss, I. G., Bogdanova, L. P.

TITLE: Potassium-hexafluoroboroxolate $K_3[B_3O_3F_6]$ and Potassium Hydroxopentafluoroboron-oxolate $K_3[B_3O_3F_5OH]$ (Geksaftorobor-oksolat kaliya $K_3[B_3O_3F_6]$ i gidroksopentaftorobor-oksolat kaliya $K_3[B_3O_3F_5OH]$)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 8, pp 1839-1843 (USSR)

ABSTRACT: Boron fluoride complexes were synthesized for the first time by the author mentioned first (Refs 1,2). They are ascribed a cyclic structure. They may be regarded as addition products of F- and OH-ions to trifluoroboroxol



which is unstable in free state (Ref 3). Besides the hydroxotetrafluoroboroxolic salt of potassium $K_2[B_3O_3F_4OH]$ which was

Potassium-hexafluoroboroxolate $K_3[B_3O_3F_6]$ and Potassium Hydroxopentafluoroboron-oxolate $K_3[B_3O_3F_5OH]$

produced already earlier the compounds mentioned in the title were obtained and the denotation mentioned in the title was suggested because of the genetic connection with boroxol $H_3B_3O_3$ and trifluoroboroxol. $K_2[B_3O_3F_4OH]$ is transformed into $K_3[B_3O_3F_5OH]$ in weakly alkali. 40% KF-solution. In the absence of alkali a partial substitution of the hydroxyl by fluorine takes place. In the case of an excess of KHF_2 in concentrated potassium fluoride solution the hydroxotetrafluoride compound reacts under the formation of $K_3[B_3O_3F_6]$. It is stable at room temperature in a potassium fluoride concentration of more than 35%. The hexafluoride compound and the hydroxopentafluoride compound are decomposed under the action of water or diluted KF-solutions and $K_2[B_3O_3F_4OH]$ is precipitated. The synthesized substances are new derivatives of trifluoroboroxol. There are 2 tables and 9 references, 8 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railway Transport Engineers)

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

5(2) SOV/78-4-8-43/43

AUTHOR: I. G. Ryss

TITLE: Ya. A. Fialkov: Interhalogen Compounds (Ya. A. Fialkov: Mezhgaloidnyye soyedineniya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 8, pp 1941-1942 (USSR)

ABSTRACT: The revised paper mentioned in the title was published only after the death of the author, who was Corresponding Member of the AS UkrSSR. The monograph includes the entire publications dealing with this subject which were issued until the middle of 1956 and some papers published later. After having pointed to some wrong data in a table, the reviewer emphasizes the value of this edition and regrets that only 2000 copies were issued.

Card 1/1

USCOMM-DC-61,538

PROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

SOV/78-4-9-10/44

5(2)

AUTHORS: Ryss, I. G., Idel's, S. L.

TITLE: The Anilinium Tetrafluoroborate, Aniline Trifluoroboron and Anilinium Hydroxotrifluoroborate

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 9, pp 1990-1994 (USSR)

ABSTRACT: I. G. Ryss in his investigation on the coordination compounds of boron fluorides with amines made assumptions concerning a relationship between hydrolysis and the properties of the amine (Ref 1). In order to verify these assumptions, $AnHBF_4$ (An = aniline), which had not been described in publications, was synthesized. Its solutions are acid owing to hydrolysis, and oxidize on standing for some time. Its crystals are monoclinic. Furthermore, the synthesis of $F_3B{:}An$ is described, which hydrolyzes to give the compound $AnH[BF_3OH]$. This hydrolysis was investigated by titration. It proceeds according to the equation

$$\log \frac{x}{x_0} = -0.4343\, k\vartheta ,$$

Card 1/2

where x_o denotes the initial concentration of the complex compound, x the concentration at the time ϑ, and k the reaction constant. This equation confirms the dependence of the hydrolysis on the type of amine. $F_3B:An$ is very soluble in ethanol and methanol. Distillation with absolute methanol leads to a reaction described by the following equation: $4F_3B:An + 3CH_3OH = 3AnHBF_4 + B(OCH_3)_3 + An$. There are 9 references, 5 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute for Railroad Transport Engineers)

SUBMITTED: June 7, 1958

5(2)

AUTHORS: Ryss, I. G., Vitukhnovskaya, B. S. SOV/75-14-3-11/29

TITLE: Titrimetric Determination of Manganese After Its Oxidation to Trivalent State (Titrimetricheskoye opredeleniye margantsa posle okisleniya do trekhvalentnogo sostoyaniya)

PERIODICAL: Zhurnal analiticheskoy khimii, 1959, Vol 14, Nr 3, pp 318-321 (USSR)

ABSTRACT: A simple method is described for the determination of Mn^{2+} ions, which is based on the formation of fluoro manganate. The first experiments with KNO_3 as oxidizing agent in the presence of HF indicated that the oxidation of Mn^{2+} does not proceed quantitatively. With ammonium nitrate however exact results were obtained (Table 1). The determination of the fluoro manganate formed can be carried out iodometrically or by means of titration with Mohr's salt. Fe^{3+}-ions do not disturb. In the presence of Cr^{3+} the dissolution and reduction of the precipitate of $CrF_3.MnF_3.6H_2O$ is accelerated by addition of boric and hydrochloric acid and the titration thus proceeds undisturbed. If Fe^{3+} and Cr^{3+} occur together, only the titration with Mohr's salt is possible (Table 3). The presence of Co^{2+} (up to 250 mg) or Ni^{2+} (up to 70 mg) does

Card 1/2

SOV/75-14-3-11/29

Titrimetric Determination of Manganese After Its Oxidation to Trivalent State

not disturb the iodometric determination of manganese (Table 4). The analysis was tried with ferromanganese alloys and yielded satisfactory results (Table 5). There are 5 tables and 9 references, 5 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railway Engineers). Dnepropetrovskiy metallurgicheskiy institut (Dnepropetrovsk Metallurgical Institute)

SUBMITTED: May 13, 1957

5(4) SOV/76-33-1-18/45

AUTHORS: Ryss, I. G., Donskaya, D. B.

TITLE: The Over-All Equilibrium Constant of Hydrolysis of Tetrafluoroborate Ion BF_4^- (Obshchaya konstanta ravnovesiya gidroliza iona tetraftoroborata, BF_4^-)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 1, pp 1o7 - 111 (USSR)

ABSTRACT: I. G. Ryss and N. P. Bakina (Ref 1) determined the hydrolysis constant of the BF_4^--ions without considering the fact that boric acid reacts with F^--ions (as was found out later on (Ref 2)). Since the value of the equilibrium constant c ((Ref 1) in the paper) was therefore not reliable the determinations were repeated and the sources of the errors mentioned above were taken into account. The presence of the solid phases KBF_4 and H_3BO_3 in all mixtures were microscopically checked during the investigations. The pH values were measured by hydrogen or quinhydrone electrodes. The electric circuit was in a thermostat chamber at 25.0 ± 0.03° and was measured by a potentiometer PPTV-1 with a mirror galvano-

Card 1/2

meter M-25 as balancing apparatus. The results, shown in tables, prove that a strong reaction of H_3BO_3 with F^--ions takes place. In the reaction

$KBF_{4(cryst.)} + 3H_2O \rightleftarrows H_3BO_{3(cryst.)} + 3H^+ + 4F^- + K^+$ (4)

lgK' = 23.15± 0.1; and in the reaction

$BF_4^- + 3H_2O \rightleftarrows H_3BO_{3(cryst.)} + 3H^+ + 4F^-$ (1) lgK=20.01±0.1 and

ΔF_{298^0} = 27.27± 0.14 kcal. Instead of the value (-343 kcal) found by Latimer (Ref 12), for BF_4^- the value of about -352 kcal is given for free formation energy. There are 1 figure, 1 table, and 12 references, 10 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Engineers)

SUBMITTED: June 21, 1957

5(4) SOV/76-33-2-21/45

AUTHORS: Ryss, I. G., Idel's, S. L.

TITLE: Kinetics of the Hydrolysis of Boron Ammine Trifluoride, $H_3N:BF_3$ (Kinetika gidroliza triftor-ammin-bora, $H_3N:BF_3$)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 2, pp 374 - 380 (USSR)

ABSTRACT: A method is described which (as it differs from previous experiments in reference 1) makes possible a determination of boron ammine trifluoride (I) in the presence of its hydrolysis products. A study of the hydrolysis kinetics of (I) could be carried out by determining the concentration of (I) as a function of the time without the BF_4^- ions produced in the reaction affecting the experimental results. The $H_3N:BF_3$ was obtained by reacting ammonia and boron fluoride in benzene in a reaction vessel (Fig 1), and its fine crystalline powder was found to be readily soluble in water. The hydrolysis kinetics of (I) were titrimetrically determined in a solution neutral to methyl orange using an excess of $CaCl_2$ and applying a TS-15 thermostat.

Card 1/3

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Kinetics of the Hydrolysis of Boron Ammine Trifluoride, $H_3N:BF_3$ SOV/76-33-2-21/45

The experimental results obtained showed (Fig 2) that the hydrolysis of (I) is a reaction of the first order and is not catalyzed by hydrogen ions (Table 1), since the molecule $H_3N:BF_3$ possesses no charge. The function of the rate constant in dependence upon the temperature can be represented by a straight line

$\lg k' = 14.70 - \frac{5945}{T}$ (2). This equation corresponds to an activation energy E = 27.2 kcal/mol and an activation entropy $\Delta S^{\neq}$ = 3.2 cal/degree. The mechanism of the hydrolysis of the various double salts of boron fluoride will be treated in detail in a later paper. Preliminary experiments showed that the hydrolysis of the $H_3N:BF_3$ is markedly accelerated in the presence of F^- and especially by OH^- ions. A hydrolysis mechanism for (I) is given, and it is mentioned that the hydrolysis of (I) in a NaF solution occurs in two parallel processes (in three including the effect of the OH^- ions). There are 4 figures, 3 tables, and 6 references, 4 of which are Soviet.

Card 2/3

, APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Kinetics of the Hydrolysis of Boron Ammine Trifluoride, $H_3N:BF_3$ SOV/76-33-2-21/45

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute for Railroad Transportation Engineering)

SUBMITTED: July 15, 1957

69533

S/078/60/005/05/08/037
B004/B016

5.2400(B)

AUTHORS: Ryss, I. G., Bogdanova, L. P.

TITLE: Ammonium Salts of Fluoboric Acids

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 5, pp. 1028-1035

TEXT: The authors describe the synthesis of $(NH_4)_2[B_3O_3F_4OH]$ (I) and NH_4BF_3OH (II). Salt (I) was obtained by triturating anhydrous ammonium bifluoride with boric acid: $2NH_4HF_2 + 3H_3BO_3 = (NH_4)_2[B_3O_3F_4OH] + 5H_2O$. Analyses of the products of syntheses repeatedly carried out under different conditions (triturating of the anhydrous initial products, synthesis in water-alcohol mixtures at 0° or -7°, addition of small quantities of HF) are represented in table 1. Complete elimination of impurities (H_2O, NH_4F) was not possible. The solubility of salt (I) was investigated by the isothermal method. Table 2 gives the results. Fig. 1 shows the solubility at

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B004/B016

Ammonium Salts of Fluoboric Acids

25° in the presence of NH_4F (Abstracter's Note: This figure is missing). Reactions between (I) and NH_4F were found to occur. The reaction products could not be isolated owing to their considerable (and obviously incongruent) solubility. The results of thermal decomposition of (I) are listed in table 3. H_2O and NH_3 are split off. After heating for two hours up to 150° 38% of (I) was decomposed under the formation of NH_4BF_4; the remaining 62% had lost its water. At 200° and 250° the weight loss continued with NH_3 and a boron fluoride compound being released. Compound (II) was prepared according to the equation: $(NH_4)_2[B_3O_3F_4OH] + 4NH_4HF_2 = 3NH_4[BF_3OH] + + 3NH_4F + H_2O$. Analyses of the reaction products are represented in table 4. Owing to the very high solubility of (II) in water, complete elimination of the NH_4F impurity was not possible. The authors further attempted to prepare the compound $B_2O_3.NH_4F.HF$ which was described by G. I. Petrenko (Ref. 3). However, they obtained only a mixture consisting of (I), boric acid, and presumably ammonium borates (Table 5). Nor was it possible to prepare the compound $(NH_4)_2[O(BF_3)_4]$, described by Svaynkhert, and patented

4

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Ammonium Salts of Fluoboric Acids

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B004/B016

for him. The syntheses performed according to the patent yielded an inhomogeneous mixture mainly consisting of NH_4BF_4 (Table 6). There are 6 tables and 13 Soviet references.

ASSOCIATION: Dnepropetrovskiy institut zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Transportation)

SUBMITTED: February 7, 1959

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

86491
S/078/60/005/008/026/031/XX
B023/B066

5.3700 2209 1236 1273

AUTHORS: Ryss, I. G., Idel's, S. L.

TITLE: Kinetics of Hydrolysis of Dimethyl-amino Boron Trifluoride

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 8, pp. 1756-1760

TEXT: Following their previous papers (Refs. 1-5) the authors studied the kinetics of hydrolysis of dimethyl-amino boron trifluoride, $F_3B:NH(CH_3)_2$. The compound was obtained by reaction of the carefully dried components in the presence of a benzene-ether mixture. Dimethyl-amino boron trifluoride is a colorless substance. When slowly heated in a closed capillary it melts at 50-51°C. It is sparingly soluble in benzene and easily soluble in ether, methanol, and water. Hydrolysis of $F_3B:NH(CH_3)_2$ is a first-order reaction which proceeds according to the mechanism S_N1. Its rate constant (in min^{-1}) as a function of temperature is expressed by the following equation: $\log(0.4343\ k) = 16.21 - \frac{6972}{T}$. Its activation energy E

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86491

Kinetics of Hydrolysis of Dimethyl-amino Boron Trifluoride

S/078/60/005/008/026/031/XX
B023/B066

equals 31.9 kcal; the activation entropy $\Delta S^{\neq} = 7.2$ entropy units. The values of E and $\Delta S^{\neq}$ are in good agreement with the data of Ref. 2 where E and $\Delta S^{\neq}$ were found to depend on the pK of the amine for the coordination compounds of BF_3 with amines. The hydrolysis of $F_3B : NH(CH_3)_2$ is accelerated by the presence of F^- ions. In a strongly alkaline medium $F_3B:NH(CH_3)_2$ is decomposed rapidly. The mechanism of the action of OH^- and F^- ions is analogous to that of the hydrolysis of BF_3 compounds with ammonia and methylenamine (Refs. 3,4). There are 4 figures, 2 tables, and 7 references: 5 Soviet, 1 US, and 1 British.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Engineers)

SUBMITTED: February 7, 1959

Card 2/2

RYSS, I.G.; IDEL'S, S.L.

Kinetics of the hydroloysis of boron trifluoride trimethlamine. Zhur. neorg. khim. 5 no.8:1761-1767 Ag '60. (MIRA 13:9)

1. Dnepropetrovskiy transportnyy institut.
(Boron trifluoride)

11.2223
5.3700 also 2209

84214
S/078/60/005/010/007/021
B004/B067

AUTHORS: Ryss, I. G., Donskaya, D. B.

TITLE: Diethylaminoboron Trifluoride. Diethylammonium Tetrafluoroborate

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 10, pp. 2251-2257

TEXT: In reacting anhydrous diethylamine with BF_3 or $F_3B:O(C_2H_5)_2$ the authors did not obtain the substance designated in Ref. 1 as diethylaminoboron trifluoride but diethylammonium tetrafluoroborate $\left[(C_2H_5)_2NH_2\right]BF_4$. They obtained the same compound when neutralizing tetrafluoroboric acid with diethylamine. This is a colorless crystalline substance with the melting point at about 168°C. Diethylaminoboron trifluoride $F_3B:NH(C_2H_5)_2$ could be synthesized by passing BF_3 and N_2 (obtained by thermal decomposition of $C_6H_5N_2BF_4$) through anhydrous

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Card 1/4

diethylamine cooled to -25±5°C. Fig. 4 shows the scheme of the apparatus used for this purpose. This compound is a neutrally reacting, rather unstable liquid which gradually turns yellow at -20°C and rapidly decomposes in alkaline media. Its melting point is found at approximately -25°C. It could not be exactly determined due to the tendency of the substance toward undercooling and decomposition. Table 1 gives the analytical data. Their deviation from the theoretical composition, especially in samples stored for longer periods is explained by the following reactions: $2F_3B{:}NH(C_2H_5)_2 = F_3B{-}N(C_2H_5)_2 + [(C_2H_5)_2NH_2]BF_4$; $F_3B{:}NH(C_2H_5)_2 = C_2H_5F\uparrow + F_2B{-}NHC_2H_5$; $F_3B{:}NH(C_2H_5)_2 = HF\uparrow + F_2B{-}N(C_2H_5)_2$. Purer preparations could be obtained at -25°C by passing BF_3 through $NH(C_2H_5)_2$ dissolved in CCl_4. In this case the liquid was separated into two layers, the upper one of which contained the $F_3B{:}NH(C_2H_5)_2$ dissolved in CCl_4. CCl_4 was evaporated in vacuum. The best results, however, were obtained by saturating a mixture of diethylamine and toluene with BF_3 at -78°C. Diethylaminoboron trifluoride was separated as a white powder.

84214
S/078/60/005/010/007/021
B004/B067

Diethylaminoboron Trifluoride.
Diethylammonium Tetrafluoroborate

By means of this preparation the rate of hydrolysis of the compound was studied. x = n_ϑ/n_0 was determined, where n_0 denotes the content of diethylaminoboron trifluoride at the beginning of the experiment, and n_ϑ the content after the period ϑ. Fig. 1 shows the function log x = f(ϑ). Its linear course corresponds to a first-order reaction. Table 2 gives the data found at 60, 70, 80, and 90°C for calculating the rate constant k, and Fig. 2 represents the function log k = f(1/T). The dependence log(0.4343k) = 17.29 - 7016/T was found. The activation energy of hydrolysis is 22.1kcal/mole, and the activation entropy is 12 e.u. . The value of the activation energy corresponds to the expected value pK for the dissociation of diethylamine. Fig. 3 shows E = f(pK) for coordination compounds of BF_3 with pyridine, ammonia, trimethylamine, methylamine, dimethylamine, and diethylamine. In the apparatus used for the synthesis the air humidity was kept out either by means of tubes filled with P_2O_5, partly by means of a Tishchenko flask filled with H_2SO_4. There are 4 figures, 2 tables, and 12 references: 11 Soviet and 1 US.

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84214

Diethylaminoboron Trifluoride.
Diethylammonium Tetrafluoroborate

S/078/60/005/010/007/021
B004/B067

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Engineers)

SUBMITTED: March 27, 1959

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

29162 R
S/073/60/026/004/001/008
B103/B220

5. 2420

AUTHORS: Ryss, I. G. and Bogdanova, L. P.

TITLE: Hydroxy tetrafluoro-boroxolates of rubidium and cesium

PERIODICAL: Ukrainskiy khimicheskiy zhurnal, v. 25, no. 4, 1960, 403-408

TEXT: Synthesis, properties, and analysis of rubidium and cesium hydroxy tetrafluoro-boroxolates are described. The Ru and Cs content of the compounds was determined gravimetrically as tetrafluoroborate. The complex anion was determined by double titration: 1) titration in the presence of methyl orange and excess of 1 mole of $CaCl_2$ to boric acid and CaF_2; 2) titration of the boric acid (after addition to mannite and phenolphthalein). The consumption of alkali in titrations 1) and 2) is indicated by n_1 and n_2. The portions were weighed by the microbalance BM-20 (VM-20). A) Synthesis of $Rb_2[B_3O_3F_4OH]$. $RbNO_3$ is dissolved in a saturated solution of $(NH_4)_2[B_3O_3F_4OH]$. The precipitate is not yet a pure final product. By slight amounts of HF before the addition of $RbNO_3$, the purity could be improved (optimum molar ratio $HF / (NH_4)_2 [B_3O_3F_4OH] = 2.04$). The crystals of $Rb_2 [B_3O_3F_4OH]$ are similar to those of the potassium salt. They may belong to the planar type of the rhombic syngony. Their solubility in water amounts to 16% at 17°C. B) Synthesis of $Cs_2 [B_3O_3F_4OH]$. Boric acid and $CsHF_2$ are dissolved completely at 30°C in the ratio $2CsHF_2 + 3H_3BO_3 \longrightarrow Cs_2 [B_3O_3F_4OH] + 5H_2O$. When this solution is cooled, crystallization does not occur. Only after the addition of 3.5 times as much alcohol two layers are forming, the lower of which crystallizes slowly. Also in this case, F is substituted partly by OH. An addition of 0.10 mole of HF improves the composition of the final product slightly. A crystal hydrate is formed which gives off its water only after 4 hr at 110°C and reaches the theoretical composition approximately. The water solubility of the water-free cesium salt amounts to 77.7% at 18°C. The equilibrium constants of the substitution of F by OH in dissolved boron complexes are calculated by the authors for the first and second stage of the hydrolysis: $K_1 \cong 2.2 \cdot 10^8$ and $K_2 \cong 2 \cdot 10^7$. From the total equilibrium constant of hydrolysis, from the solubility and the dissociation constant of boric acid the equilibrium constant of the process was calculated $BF_4^- - 4OH^- \rightleftarrows B(OH)_4^- + 4F^- : K_3 \simeq 6\cdot 10^{26}$. Based on the comparison of the values K_1, K_2, and K_3 the authors conclude that the equilibrium constant of the substitution of the fluorine atom by OH decreases in every stage of substitution. A substitution of OH by F is possible for low pH values only. An increasing number of F atoms in the complex reduces the pH value required for the substitution. The different stability of the triple-charged trimer fluoro-hydroxy complexes is explained by the authors as follows: in solutions, equilibrium may exist between the cyclic and the linear form of the trimer anions as well as between the trimer form and its depolarization products. The addition of any further OH or F anion entails an increase of the repulsive powers between the anions having charges of equal sign, the stability of the cyclic forms decreases. The following general conditions are mentioned for the stability of fluoro and hydroxy complexes in solutions: for low values of pH and excess of fluorine, the prevailing form is BF_4^-. When the pH is increased and the ratio F/B reduced, first of all BF_3OH^- forms and then $B_3O_3F_6^{3-}$, $B_3O_3F_5OH^{3-}$, and $B_3O_3F_4OH^{2-}$ being in the solution probably in equilibrium with the linear forms which have been formed by addition of water molecules. In case of a further slight increase of the pH, polymer boron hydroxy complexes are formed and finally $B(OH)_4^-$. Since all these boron complexes (except BF_4^-) form very quickly, they are heavy and can be separated only in a relatively narrow range of pH values and of volumetric proportion of the reagents. For the coordination of any donor by a boron atom, the plane sp^2 bonds are replaced by tetrahedral sp^3 bonds. Therefore, the plane $B_3O_3F_3$ ring will curve when liganda are added. Thus, the accommodation of large cations may be rendered difficult. Therefore, the complexes of type $M_3[B_3O_3F_6]$ are separated most easily when M = Na, whereas this is more difficult for M = K, and impossible for $M = NH_4$. It may be possible that the above-mentioned crystal hydrate of the cesium complex actually does not contain cyclic but linear anions and has an empirical

X

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RYSS4I8G8

600

1. RYSS, I.G.

2. USSR (600)

"The Thermodynamic Relation Between the Elasticity of Dissociation and the Solubility of Complex Strong Electrolytes," 13, no.4, 1939. Metallurgical Insti., Chair of Gen'l Chem. Dnepropetrovsk. Received 17 June 1938.

9. [redacted] Report U-1613, 2 Jan 1951.

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1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

Ca

2

Virtual entropy of silicon tetrafluoride, calculated from the molecular constants. I. G. Ryss. *Compt. rend. acad. sci. U. R. S. S.* **24**, 568-9(1939)(in German).—Using the available electron diffraction, Raman and infrared data, the entropy (translational, rotational and vibrational) of gaseous SiF_4 was calcd. as follows (°K., entropy in cal./degree mol.): 298.2°, 67.439; 373.2°, 71.560; 400°, 72.870; 473.2°, 76.347; 500°, 77.476; and 573.2°, 80.404. In the above calcns., the Si-F distance was taken as 1.56 A. (cf. Braune and Pinnow, *C. A.* 31, 4177⁹); if the distance is taken as 1.54 A. (cf. Brockway and Wall, *C. A.* 29, 996¹), the above entropy values must each be diminished by 0.089 cal./degree mol. The error in the calcd. entropy values is probably less than ±0.5 cal./degree mol.

George Ayers

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

18

Cr

Continuous process for the preparation of chromium oxide. J. G. Ryss and R. Mandel. *Novosti Tekhniki* **1938**, No. 21, 37-8.—Na_2CrO_4 is rapidly reduced by producer gas at 600° and higher. An addn. of soda or NaOH sharply increased the velocity of reaction. The product, after washing with alkali, is calcined at 800° for a short period.

A. A. Podgorny

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

Ca

2

Viscosity of solutions of alkali chromates. I. G. Ryss, V. M. Shutova and A. I. Zelyanskaya. *J. Applied Chem.* (U. S. S. R.) 12, 1787-9(1939).—The viscosities were detd. in Ostwald viscometers and the calcns. were made with the formula: $\eta = \eta_0 Pt/P_0t_0$, where η_0 is the viscosity, P_0 the sp. gr., t_0 duration of discharge of water at the given temp., and η the viscosity, P the sp. gr. and t the duration of discharge of the soln. at the same temp. The closeness of the properties of the hydrated SO_4^{--} and CrO_4^{--} ions justifies the assumption that the viscosity of concd. solns. contg. Na_2CrO_4 and Na_2SO_4 is also given basically by the total molarity of the soln. Partial conversion of Na_2CrO_4 to $Na_2Cr_2O_7$ lowers the viscosity.

A. A. Bochtlingk

COMMON ELEMENTS

OPEN

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1ST AND 2ND LETTER

3RD LETTER

3RD AND 4TH ORDERS

GROUPS

RYSS, I. G.

"The Velocity of formation of tetrafluoboric acid in mixtures of hydrofluerie and boric acids. H. I. Zhur, Obshch. Khim. 10, 1936-42, (1940) cf. C. A. 44, 415c--The exptl. kinetic data for the over-all reaction 4HF +3H20 in soln. contradict both the assumption of a rate law $k(HF]^{\lambda}[H2B03]2$. A rate law in agreement with the expts. can be derived on the assumption of a mechanism involoing the rapid initial step $H3B03 + 3HF \rightarrow [BF3OH]^{-} + H^{+}$, a maintained equil. $[BF3OH]^{-} + H^{+} \rightleftarrows$ BF 3H02 with the equil. const. $K = [BF3\overline{O}H]- + [H^{+}]/[BF3H20],^{+}$ and the rate-detg. step $Bf3H20 + HF \rightarrow Bf3-H^{-} + H20$; the over-all rate is then detd. by e the bimol, fate dx/dt - k [HF3H20] [HF], which leads for the rate of increase of the yield φ of $Hf4^{-}$ (in fractions of the therotically possible max. yeild), to $d\varphi/dt = (k/K)- M^{2}(q-^{3}-\varphi)\ (1-\varphi)q^{2}$, where M = initial concn. of HF (inmoles/l.), and q = mol. ratio Hf/H2B03 in the mist. This equation is verified in 2 ways. In the initial stages, it simplifies to $d\varphi/dt = (k/K)M2(q-3/q2$, calling for rapid increase with increasing, q, in conformity with the expt. in the integrated form, the rate equation calls for linearity between t and $\log)(5-\varphi)/(1-\varphi)[$for q - 8, and with $\log[\varphi/(1-\varphi)$ for q - 4, verified except for deviations at high φ, owing no doubt to the reverse reaction. For q - 4, M3 - 0,2681 and 0,1388, at 30.058, k//K - 7.3 (const.) and for q = 8, k/K - 9.3 and 8.0 (1 4 Mole 2 Minl), The exptl. data of Wamser (C. A. 42, 4430) at 25 yield the somewhat lower values k/K - 6.34, 4.35, and 3.55, for Mo 0.052, 0.2244, and 0.4422, showing the same trend with the concn. The fore-

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going reaction scheme is applicable only for $q > 3$. Formation of the hydrate $BF_3.2H_2O$, tantamount to the hydrated acid $H[BF_2OH]$.-_ H_2O, accounts for the old finding of Thomsen that, on mixing dil. solns. of HF and H_3BO_3, the heat of reaction increases with q only up to q - 3 and then remains const; this indicates that, whereas formation of $Bf_2.2H_2O$ is rapid and stronly exothermal, further addn. of HF to form HFB_4 is only weakly exothermal, and slow. The observation of Abegg, et al. (Z. anorg. allgem. Chem. 35, 129(1903) that the elec. cond. of a mixt. of HF with H_3BO_3 is established momentarily and does not change with time despite the decrease of acidity, is explained by the closeness of the mobilities of the ions $[BF_2OH]^-$ and $[BF]^-$, high dissocn. of BF_3H_2O, and suppression of the dissocn. of HF; owing to these factors, progress of the rate-detg. reaction $BF_3H_2O + HF \rightarrow BF_4^- + H^+ + H_2O$ witll not significantly affect the elec. cond. N. T.

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Ca

2

Thermodynamic constants of silicon tetrafluoride. The hydrolysis equilibrium of silicon tetrafluoride. I. G. Ryss. *J. Phys. Chem.* (U. S. S. R.) 14, 571-81(1940).—The thermodynamic functions C_p, translational, rotational and vibrational entropies and free energies of SiF_4 were calcd. from known mol. (spectroscopic, etc.) consts. From various thermochem. data in the literature the heat of hydrolysis of SiF_4 to yield β-quartz is found to be 22.5 cal. and values of the hydrolysis const. are calcd. that differ considerably from the exptl. results of Baur (*Z. Physik. Chem.* 48, 483(1904)) which are considered subject to considerable exptl. errors. F. H. Rathmann

Dnepropetrovsk Metallurgical Inst. im. Stalin

Inst. Phys. Chem. im. Pisarzhevskii AS UkrSSR

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CA

2

Kinetics of the decomposition of fluosilicate ions under the action of alkali. I. G. Ryss and M. M. Slutskaya. *J. Phys. Chem.* (U. S. S. R.) 14, 701-7(1940).—The decompn. of SiF_6 ions in alk. solns. for concns. of fluosilicate from 0.010 to 0.087 *M*, NaOH from 0.000 to 0.028 *M* and at temps. from 10 to 50°, as measured by the time till the reaction $2H_2O + SiF_6^{--} \rightarrow 4H^+ + 6F^- + SiO_2$ neutralizes the base added, as indicated by decoloration of phenolphthalein indicator present, obeys the equation for a unimol. reaction. The values of *k* are given by $\log k = (4248/T) + 13.083$, and $E = 19.44$ Cal.

F. H. Rathmann

Lab. Gen. Chemistry, Metallurgical Inst.

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Cr

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Preparation of crystallized chromic anhydride from calcium chromate. I. G. Ryss, A. E. Zayarnyi and A. I. Zelyanskaya. *J. Applied Chem.* (U. S. S. R.) 14, 46-61 (in German, 62) (1941).—A boiling mixt. of 456 g./l. Na_2CrO_4, 29.6 g./l. Na_2SO_4 and traces of free alkali was treated with an equiv. quantity of a soln. contg. $CaCl_2$ 33, KCl 2.04, and $KClO_3$ 0.75%. The filtered and washed $CaCrO_4$ was decompd. with H_2SO_4 and the soln. of CrO_3 obtained was filtered and concd. to about 60%. Yield of CrO_3 was 97-98%. The corrosion resistance of materials to be used as evaporators, reactors, etc., was found to be (loss in g./sq. m./hr. on exposure to process conditions for 0-2 and 3-4 hrs., resp.): Gray cast iron (C 3.30, Si 2.04, Mn 0.55, P 0.217 and S 0.06%) 6.58 and 2.65; boiler plate of the Chusovo mills (C 0.172, Mn 0.34, P 0.032, S 0.042% and Si traces) 1.77 and 3.23; iron of the Armco type (C 0.025, Mn 0.035, S 0.025 and P 0.009%) 32.6 and 15.84; sheet aluminum 103.0 and 2.42. Rolled lead (Bi 0.004, Cu 0.005, Fe 0.003 and Sb 0.011%) in 3 hrs. lost 259.0. Ten references. A. A. Boehtlingk

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Determination of fluorine in tetrafluoborates. I. G. Ryss. *Zavodskaya Lab.* 12, 651-5(1946).—When an aq. soln. of KBF_4 is boiled with an excess of $CaCl_2$ soln., the reaction of $BF_4^- + 2Ca^{++} + 3H_2O = 2CaF_2 + H_3BO_3 + 3H^+$ will take place completely with a filterable ppt. of CaF_2 provided the liberated H^+ is slowly neutralized by adding suitable quantities of $KClO_3$ and KI together with a little KVO_3 as catalyst. The neutralization can also be accomplished by adding NaOAc to the boiling soln. For 0.2 g. of KBF_4 add 0.25 g. of $KClO_3$, 2 g. KI, 50 ml. of *M* $CaCl_2$ soln., and 0.15 ml. of 0.1 *M* KVO_3. Boil for at least an hr., filter, wash, dry, and weigh the CaF_2 ppt.

N. Thon

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2

Hydrolytic equilibria in solutions of sodium fluosilicate at 11°. I. G. Ryss (Dnepropetrovsk Metal Inst.). *J. Gen. Chem.* (U.S.S.R.) **16**, 331-40(1946).—The degree of hydrolysis of Na_2SiF_6 at 11° at concns. 0.02 *M* to 0.00048 *M* was detd. The following equil. consts. were calcd.: $SiF_6^{--} = SiF_4 + 2F^-$, $K_1 = 0.65 \times 10^{-4}$; $SiF_4 + 2H_2O = SiO_2 + 4HF$, $K_2 = 1.04 \times 10^{-9}$; $SiF_6^{--} + 2H_2O = SiO_2 + 4H^+ + 6F^-$, $K_3 = 5.4 \times 10^{-27}$. Generally speaking, the solns. of the hexafluoride reach hydrolytic equil. rapidly and further changes occur only very slowly.

G. M. Kosolapoff

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7

Determination of boron in tetrafluoroborates. I. G. Ryss. *J. Gen. Chem.* (U.S.S.R.) 16, 531-6(1946).—By boiling fluoroborates with an excess of $CaCl_2$ the BF_4^- anion is decompd.; use 25-30 cc. of 1-2 *M* $CaCl_2$ for 1 millimole of BF_4^- and boil for 1 hr. This procedure can be used for detg. B in fluorides, fluoroborates, and fluosilicates. Titration in the cold with methyl orange can be used to det. BF_3OH^-, and in this way BF_4^- can be distinguished from its hydrolysis products. G. M. K.

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RYSS, J. G.

PA 13T35

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USSR/Chemistry - Tin Compounds **Sep 1946**
Crystallization

"The Crystallization Equilibrium of Tin Chloride Solutions," J. G. Ryss, E. J. Turchan, 7 pp

"Zhur Prik Khim" Vol XIX, No 9

Study of the solubility equilibrium in the system $SnCl_2 - H_2O - HCl$, leading to conclusions on the adequate conditions for the technological procedure of crystallization of a tin chloride solution.

13T35

"APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

CA

2

The equilibrium of the hydrolysis of the tetrafluoborate ion. I. G. Ryss. *Compt. rend. acad. sci. U.R.S.S.* 52, 417-20(1946); cf. *C.A.* 41, 6816e.—Calcns. of equil. consts. were used to det. the extent of hydrolysis of the BF_4 ion. Solns. of $NaBF_4$ and KBF_4 were added to an excess of alkali, and the excess was titrated with 0.1 *N* HCl. Equil. consts. calcd. on the assumption that the hydrolysis reaction was $BF_4^- + H_2O \rightleftarrows BF_3OH^- + HF$ gave calcd. pH values in accord with measured values. In very dil. solns. further hydrolysis of the BF_3OH ion was observed. The following equil. consts. were calcd.: 20°, 2.4×10^{-3}; 25°, 2.8×10^{-3}; 80°, 5.5×10^{-3}; 90°, 6.5×10^{-3}; 100°, 7.3×10^{-3}. L. E. Campbell

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RYSS, I. G.,

"The Properties and Synthesis of Trifluohydroxyborate of Potassium," Dokl. Ak. Nauk SSSR, 54, 325-7, 1946.

KBF_3OH was prepd. by dissolving 1.5-2.0 mols. KHF_2 and 1 mol. H_3BO_3 in 250-300 g. water, cooling with ice and filtering; yield 57%. Soly. of the product in water is 11% at 14°. The soln. is acid and, with methyl orange as the indicator 1 mol. reacts with 2.03 mols. NaOH. Prepns. according to Gasselin (Bull. soc. chim. France (3) 7, 654 (1892)) and Meerwein and Pannwitz (CA 29, 1060) gave mixts. of KBF_4 and KBF_3OH rather than pure KBF_3OH.

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Ca

2

Crystallization equilibrium of solutions of stannous chloride. I. G. Ryss and K. Ya. Turkhan (Dnepropetrovsk Metallurg. Inst.). *J. Applied Chem.* (U.S.S.R.) 10, 958-65(1947)(in Russian).—In the system $SnCl_2$-H_2O-HCl, equil. is attained from both sides in 2-3 hrs. at 5°. At 0, 5, 15, 25°, with up to 10% HCl, the solid phase is $SnCl_2.2H_2O$. Isotherms at these temps., with % $SnCl_2.2H_2O$ in soln. plotted against % HCl, show a min. around 5.5-6% HCl, the flatter the higher the temp.; example of data, 5°, HCl 2.20, 3.31, 5.89, 6.31, 7.13%, $SnCl_2.2H_2O$ 55.5, 53.0, 48.8, 49.7, 50.5; 25°, HCl 1.87, 2.75, 3.53, 4.65, 6.56, 7.11%, $SnCl_2.2H_2O$ 75.5, 73.0, 71.8, 71.0, 71.5, 73.0, d. of satd. soln. 1.936, 1.894, 1.874, 1.850, 1.868, 1.912. Cryometric detns. without HCl (other than that due to hydrolysis of $SnCl_2$) gave: from a 34.7% $SnCl_2$ soln., the crystn. temp. of ice is −6.8°; $SnCl_2$ content of the soln. in equil. with the eutectic, 37.9%. From 36.8 and 37.3% $SnCl_2$, ice crystallizes at −6.25 and −6.45°, resp.; eutectic arrest at −6.8°. Slightly moist $SnCl_2.2H_2O$ (81.2% $SnCl_2$ instead of 84.2) showed on heating a temp. arrest at 41.4°; it could not be decided whether this corresponds to complete melting, nor could a second eutectic $SnCl_2.2H_2O$-$SnCl_2$ be established; it appears that $SnCl_2.2H_2O$ melts incongruently but with a compn. very close to it. On cooling 1 ton of an 80% $SnCl_2$ soln. to 20° the amt. of $SnCl_2.2H_2O$ pptd. is 308, 362, 410, 394, 305 kg., in the presence of 1, 2, 3, 4, 5% HCl, resp., corresponding to s = % HCl/% H_2O (*free* H_2O, not bound in $SnCl_2.2H_2O$) = 0.05, 0.11, 0.18, 0.25, 0.33, resp.; best crystn. yields are obtained at a definite optimum value of s, depending on the final crystn. temp., example: 0, 5, 10, 15, 20, 25°, optimum s = 0.11, 0.12, 0.14, 0.16, 0.19, 0.23; deviation from these s in either direction results in lowered yield in crystals. At a lower temp., at a given s, the same yield can be obtained from a more dil. soln., example: 500 kg. $SnCl_2.2H_2O$ are obtained, at s = 0.2, at 5, 12, 25°, from solns. contg. 76.3, 80.8, 85.4% $SnCl_2.2H_2O$, resp.; 300 kg. are obtained, under the same conditions, from 68.7, 73, 79.6% solns.

N. Thon

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RYSS, I. G. PA 18T100

USSR/Chemistry - Fluoborates **May 1947**
Chemistry - Kinetics

"Kinetics of the Decomposition of Tetrafluoroborates in Aqueous Solutions," I. G. Ryss, M. M. Slutskaya, Laboratory of General Chemistry, Dnepropetrovsk Metallurgical Institute, imeni Stalin, 12 pp

"Zhur Fiz Khim" Vol XXI, No 5

Discusses, with detailed tables, illustrations and formulae, the kinetics of decomposition with result that the constant of the rate $k' = 0.4343k$ at temperature of 20 to 70-80 degrees. Rate of reaction was found to increase with rise in temperature. Published 26 Nov 1946.

18T100

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CA

Equilibrium of the hydrolysis of tetrafluoboric acid. I. G. Ryss and M. M. Slutskaya (Stalin Inst. Met., Dnepropetrovsk, Ukr.). *Doklady Akad. Nauk S.S.S.R.* 57, 689–91(1947); *Chem. Zentr.* (Russian Zone Ed.) 1949, I, 813; cf. *C.A.* 43, 2404b.—The basic soln. was prepd. by dissolving 8 mols. HF and 2 mols. H_3BO_3 in 1000 g. water. This soln. and various dilns. thereof (up to 0.08 mol./1000 g. water) were kept in paraffined flasks at room temp. for 72 and 504 hrs. for the establishment of equil. and then analyzed. The equil. const. $K = (M_0/4)(1 - \varphi)^2$, in which M_0 is the initial concn. of HF in mols. and φ is the amt. of BF_4^- formed. K = about $(2.2\text{-}2.8) \times 10^{-3}$, although it increases at higher concns. The reaction equil. is represented only by $BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$. Only 1 mol. of HF is formed. $H(BF_3OH)$ is a strong acid which strongly represses the dissocn. of HF. At 60.7° equil. was attained in 100 min.; at 90° it was attained in 15 min. ($M_0 = 0.08$). The impossibility of titrating HBF_4 alkalimetrically is discussed briefly. M. G. Moore

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2

General properties of the transition elements. I. G. Ryss. *Uspekhi Khim.* 17, 372-88(1948).—Didactic.

N. Thon

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CA

2

Thermal decomposition of tetrafluoborates. I. G. Ryss and E. M. Polyakova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 2[illegible]-8(1948)(in Russian).—(1) $Ba(BF_4)_2.2H_2O$ was prepd. by dissolving $BaCO_3$ in HBF_4 (made by soln. of the theoretical amt. of B_2O_3 in 20% HF) evapg. at 74-8° under 200 mm. Hg, filtering from BaF_2, crystg. the filtrate at 0° and drying over $CaCl_2$. On heating 1 hr. at 50, 70, 90, 150°, the loss of wt. is 2.88, 4.88, 10.26, 10.94%, i.e. dehydration is complete at 90° and no significant loss of BF_3 occurs at 150°. Protracted heating (up to 6 hrs.) at 100° fails to increase the loss of wt. any further. (2) In 1 hr., at 300, 400, 500, and 600°, anhyd. $Ba(BF_4)_2$ suffered dissocn. to the extent of 35.15, 85.02, 99.63, and 99.39%, resp. At 500°, in 5, 10, and 15 min., dissocn. attained 97.6, 98.2, and 99.5%, resp. Possibly, complete dissocn. can be attained even at 400° if heating is prolonged. (3) Decompn. of $Ba(BF_4)_2$ is recommended as a method of prepn. of pure dry BF_3. (4) KBF_4, in 1 hr. at 1130°, is dissocd. only to the extent of 90%. Addn. of $MgCl_2$, $CaCl_2$, $MgSO_4$, or $BaCl_2$ (1 mole per 2 moles KBF_4) facilitates dissocn. of KBF_4. E.g., $2KBF_4 + MgCl_2$, at 400°, 30 and 60 min., dissocn. 83.6 and 86.3%; at 450°, 74.6 and 86.5%; at 500°, 98.5 and 100.8%; $CaCl_2$, at 500°, 61.6 and 70.2%; $MgSO_4$, at 500°, 56.4 and 76.2%; $BaCl_2$, at 500°, 42.6 and 45.6%. The data relative to $MgCl_2$ are probably too high owing to a loss of wt. of about 15-18% suffered by $MgCl_2$ alone when heated 1 hr. at 500°. N. Thon

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CA

2

Equilibrium of formation of tetrafluoboric acid in mixtures of hydrofluoric and boric acids. I. G. Ryss, M. M. Shutskaya, and S. D. Palevskaya. *Zhur. Fiz. Khim.* (J. Phys. Chem.) 22, 1322-30(1948); cf. *C.A.* 41, 6798f. —Mixts. of *x* mols. HF and *y* mols. H_3BO_3 were dissolved in water in waxed flasks. Some days later an excess of alkali was added, then inverted sugar, and the soln. was titrated (phenolphthalein). The decrease in acidity showed the amt. *a* of BF_4^- formed. When *x:y* was 4, *a* was over 0.9 *y*, when *x* was 1.5 or greater, and was smaller the smaller *x* was (e.g. $a = 0.75\ y$ at $x = 0.1$). The equil. is represented by the reaction $BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$, and the const. $K = x(y - a)^2/4ay$ is at 11-18° about 3×10^{-3} mol./kg., i.e. agrees with that calcd. from hydrolysis of KBF_4 (*C.A.* 41, 1534i). When *x* was 1, *a* was 0.66 *y* at $x:y = 1$ and 0.98 *y* at $x:y = 6$. If HBF_4 were the sole reaction product of HF and H_3BO_3, *a* would have a min. at $x:y = 4$; as *a* is smaller in the presence of an excess of H_3BO_3, hydroxyfluoboric acids must have formed. The yield *a* was even smaller when HF was dissolved in a satd. soln. of H_3BO_3. The method of prepg. HBF_4 solns. by satg. HF solns. with H_3BO_3 results in solns. contg. much BF_3OH^-. The *titration of HBF_4 solns.* according to Kern and Jones (*C.A.* 24, 5668) yields incorrect values.

I. J. Bikerman

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CA

The production of boron fluoride by acid methods. I. G. Ryss and K. M. Polyakova (Urals Sci. Research Chem. Inst., Sverdlovsk). *J. Gen. Chem. U.S.S.R.* 10, No. 9, a15-22(1940)(English translation).—See C. A. 44, 1235*i*.

E. J. C.

CA

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The rate of formation of tetrafluoboric acid in mixtures of hydrofluoric and boric acids. I. I. G. Ryss and M. M. Slutskaya (Dnepropetrovsk Met. Inst.). *J. Gen. Chem. U.S.S.R.* 19, No. 10, a281-9(1949)(English translation).—See *C.A.* 44, 415c. II. I. G. Ryss. *Ibid.* a291-8.—See *C.A.* 44, 1311*d*. E. J. C.

CA

18

Preparation of boron trifluoride by acid methods. I. G. Ryss and E. M. Polyakova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1506-1603(1949).—In the production of BF_3 from KBF_4 and B_2O_3, according to $6KBF_4 + B_2O_3 + 6H_2SO_4 \rightarrow 8BF_3 + 6KHSO_4 + 3H_2O$, with a 50% excess of B_2O_3, use of oleum (105.9% H_2SO_4) gives markedly higher yields than concd. H_2SO_4; at 180°, with a 200% excess of 95.5 and 99.5% H_2SO_4, the total yield, after 3 hrs., was 9.5 and 42.6% (of the theoretical yield), and at 180°, with H_2SO_4 95.5, 99.5, and 105.9% (in 200% excess), the yield was 47.7, 64.0, and 79.1%, resp. With oleum, the ratio F/B in the absorbed gas is only slightly greater than 3, indicating a low proportion of SiF_4. At 180°, with a const. 50% excess of B_2O_3, and a 100, 200, and 300% excess of 105.9% H_2SO_4, the yield was 61.4, 79.1, and 80.2%, and the ratio F/B = 2.96, 3.19, and 3.0; there is, consequently, no point in raising the excess of oleum above 200%. With that amt. of oleum, at 180°, a 0, 10, 20, 50, and 200% excess of B_2O_3 gave a yield of 81, 80.1, 81.4, 75.6, and 58.1%, resp., with the ratio F/B closest to 3 with a 50% excess; consequently, an increase of the excess of B_2O_3 is unfavorable on all counts. Preliminary fusion of KBF_4 and B_2O_3 does not improve the yield or purity of the gas, but entails a loss of BF_3 in the course of the fusion. As compared with the KBF_4 + B_2O_3 method, the cryolite process based on the reaction $3CaF_2 + 3H_2SO_4 + B_2O_3 \rightarrow 2BF_3 + 3CaSO_4 + 3H_2O$ gives lower yields, e.g. 66.6% at 180°, with a 50% excess of B_2O_3 and a 200% of 105.9% H_2SO_4, and a low F/B ratio (~2.7), indicating contamination of the product with $(BOF)_3$, and presents no advantage. N. Thon

RYSS, I. G., SLOTSKAYA, [illegible]

"Velocity of Formation of Tetrafluoboric Acid in Mixtures of Hydroflhoric and Boric Acids. I. Zhur. Obshchey Khim., 19, 1827-35 1949.

That the reaction $4HF + H_3BO_2 \rightarrow H^+ + BF_4^- + 3H_2O$ is not instantaneous is demonstrated by the fact that, directly on mixing, titration gives the total acidity of the left-hand member of the equation, and that the acidity decreases with time at a measurable rate. This change of acidity was used to det. the velocity of the reaction, expressed in the increase of the yield φ of HBF_4, in fractions of the stoichiometrically possible max. yield, which is equal to the amt. of H_3BO_3 in the presence of excess HF, and to $\frac{1}{4}$ of the amt. of HF in the presence of excess H_2BO_2. At 30.05°, at const. initial (HF), the rate increases with decreasing mol. ratio $q = HF/H_3BO_3$, for q = 8,4, and 2; the initial $d\varphi/dt$ varies very little with q. At equal q, the rate increases very rapidly with the total concn. The following are the exptl. data for the times t_{c}.', in min., necessary to complete 10% of the reaction (formal order of the reaction in parentheses): for q = 2, 4, and 8, at the initial concn. M= 0.268, t_c.'=4.5 (2.43), 3.0 (2.66), and 2.5 (2.66); 0.1388 M,—, 9 (2.66), 7.5; 0.0788 M, 2.6 (2.79), 23, — ; 0.0394 M,~90, — ,—; the corresponding times of completion of 25% of the reaction are, at 0.2681 M, 12 (2.64), 9 (2.82), and 6.5 (3.04); 0.1388 M, — , 30 (2.84), 25; 0.0788 M, 90 (2.58), 85, ; 0.0394 M, 270, — , —, . In concd. soln. the reaction is very rapid; thus, if solid H_3BO_3 is added to 20% HF, cooled to 10°, equil. is reached in 2-3 min. Higher Temp. (60 and 90°) accelerates the reaction rate but lowers the equil. yield of HBF_4, evidently because of increased hydrolysis.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

v.

F 3091. ENERGY RESOURCES AND POWER DEVELOPMENTS IN AUSTRIA. Ruiss,
O. and Vas, O. (4th Wld Pr Conf., 1950, Sect. A, Pap. 24,
Prepr., 11 pp). Coal. Workable resources are estimated at
200 x 10^6 tons, comprising 1% bituminous coal, 10% high
quality and 89% low quality brown coal. Deposits are scattered
the most important coal findings are located on the eastern
border of the Alps in southern lower Austria; the main
brown coal fields are located in Styria (Koflach district)
and in the Hausruck district in Upper Austria (Wolfsegg-
Trauntal district). Gas. In twenty towns, total coal consumption
of the gas works accounts for about one sixth of imports. Five
sixth of the gas production is carried out at the gas works
of Vienna. For six years, natural gas from the oil fields
near by has been added to the town's gas. Electricity.
Ample raw hydro electric powers are available from the high
level of precipitation and great differncees of head in the
waters in the Austrian Alps. At present, about 40 x 10^9 kWh
(annual output) are worth developing, of which approximately
one eigth is already being utilised. The seasonal distribution

COMMON ELEMENTS

COMMON VARIABLES INDEX

MATERIALS INDEX

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

AUTHOR INDEX

6

CA

The equilibrium of the hydrolysis of silicon hexafluoride. I. G. Ryss (I. V. Stalin Inst. Met., Dnepropetrovsk). *Zhur. Fiz. Khim.* 25, 654-61(1951).—The equil. of the hydrolysis $SiF_6^{--} + 2H_2O \rightleftarrows SiO_2$ aq. $+ 4H^+ + 6F^-$ has been studied before by colorimetric (I) (Kubelka and Pristoupil, *C.A.* 25, 5073) and potentiometric (II) (*C.A.* 30, 7058⁹) techniques. The values of the equil. const. $K = a_{H^+}^4(m_{NaF}\gamma_{NaF})^6/a_{Na_2SiF_6}a_{H_2O}^2$ are recalcd. from these data with the help of more recent values of γ_{NaF} (Karagunis, *et al.*, *C.A.* 25, 2350; Robinson, *C.A.* 35, 2050³; Ivett and De Vries, *C.A.* 35, 7805⁹). $K_{25°} = 1.7 \times 10^{-27}$ from I and $K_{25°} = 4 \times 10^{-28}$ from II. Potentiometric data show that log K (av.) = $\bar{28}.02$ at 20° and $\bar{27}.96$ at 40° (ΔH = 17.6 kcal./mol. from these data). Log K is $\bar{27}.161$, $\bar{27}.397$, $\bar{27}.613$, $\bar{27}.821$, and $\bar{26}.008$ at 15, 20, 25, 30, and 35°, resp. From these results, ΔH°_{298} = 17.3 kcal., ΔF°_{298} = 35.97 kcal. and ΔS°_{298} = −62.6 kcal./°C. for the hydrolysis.

Michel Boudart

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I. G.

PA 194T10

USSR/Chemistry - Crystal Solvates Oct 51

"Effect of the Formation of Crystal Solvates on the Stability of Complex Compounds," I. G. Ryss, Dnepropetrovsk Metallurgical Inst imeni Stalin

"Zhur Fiz Khim" Vol XXV, No 10, pp 1152-1159

Derived general thermodynamic dependence of stabilization of complex compds as a result of formation of crystal solvates on vapor tension of solvating addendum and number of latter's mols entering into compn of crystal solvate. Examd number of partial cases. Many salts with

194T10

USSR/Chemistry - Crystal Solvates Oct 51
(Contd)

complex anions and multicharged or small cations can exist stably only as crystal solvates. The derived dependence can be tied in with earlier found dependence between dissocn pressure of complex compds and their dissocn products' soly. Decrease in size or increase in charge of anion lowers cation's tendency toward solvation (i.e., lowers stability of complex cation). Examd tetrafluoroborates, hexafluorosilicates, and fluorides.

194T10

RYSS, I.G.; KULISH, N.F.

Equilibrium of the first step of hydrolysis of a hexafluogermanate ion. Zhur. neorg. khim. 9 no.5:1103-1108 My '64. (MIRA 17:9)

1. Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta i Dnepropetrovskiy khimiko-tekhnologicheskiy institut.

RISS, I. G., and SLUTSKAYA, M. M.

"Hydroxytrifluoroborates and new complexes of fluorine and boron.," Izv. Sektora Platiny i Drug. Blagorod. Metal.; Akad. Nauk SSR, Inst. Obshch. i Neorg. Khim., No. 26, 216-34 (1951)

The synthesis of KBF_3OH, $NaBF_3OH$, and $K_2B_3F_4O_3OH$ and their properties are discussed. The systems $NaF-H_3BO_3-H_2O$ and $NaF-Na_2B_4O_7-H_2O$ were studied at 25° Complexes are not formedeither in the solid phase or in soln. for the latter system but there is significant complex formation in the former. The general properties of the boron fluoride complexes are discussed.

RYSS, I. G.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Fluorine

Energy of dissociation and electron affinity of flourine. Usp. khim. 21 no. 7, 1952

<u>Monthly List of Russian Accessions</u>, Library of Congress, November 1952. Unclassified.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I. G.

USSR/Chemistry - **Fluorine and Boron** Compounds Jan 52

"Hydroxytrifluoroborates," I. G. Ryss, M. M. Slutskaya, Chair of Gen Chem, Dnepropetrovsk Metallurgical Inst

"Zhur Obshch Khim" Vol XXII, No 1, pp 41-48

Synthesized KBF_3OH (I) by new method (interaction of mixt of KF_2 and HF with H_3BO_3. Described synthesis of $NaBF_3OH$ (II), quite sol in H_2O, whose chem properties are similar to those of I. In solns of I and II formation of tetrafluoroborate (III) is observed, proceeding to equil state little

207T13

USSR/Chemistry - Fluorine and Boron Compounds (Contd) Jan 52

dependent on temp and concn of soln. Rate of formation of III falls slightly with increase in initial concn of I or II and rises sharply with increased temp. Soly of I at 0° and 45.1°C is 6.4% and 35.3%, resp.

207T13

RYSS, I. G. PA 240T6

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

USSR/Chemistry - Boron Trifluoride Dec 52

"The Hydrolysis of Borontrifluoride Ammonate," I. G. Ryss and N. P. Pisarzhevskaya, Dnepropetrovsk Metallurgical Inst imeni I. V. Stalin

"DAN SSSR" Vol 87, No 6, pp 995-998

NH_3BF_3 was obtained by satg an ether soln of the etherate of boron trifluoride with gaseous ammonia. The degree of hydrolysis of NH_3BF_3 was plotted against time for both aqueous hydrolysis and hydrolysis in a 0.5 M soln of NaF. The degree of hydrolysis was determined by alkalimetric titration. Presented by Acad A. V. Topchiyev 8 Oct 52.

240T6

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

USSR

①

The thermochemistry of the boron fluoride complexes. I. G. Ryss and A. G. El'kenbard (I. V. Stalin Met. Inst., Dnepropetrovsk). *Doklady Akad. Nauk S.S.S.R.* 91, 805-8 (1953).—The thermochem. consts. were detd. for KBF_2OH (cf. *C.A.* 41, 5046c) and $K_2B_2F_4O_2OH$ (preceding abstr.). The heats of soln. were measured for 0.05 mole KBF_2OH and 0.025 mole $K_2B_2F_4O_2OH$ in 20 moles H_2O (Q_1 (25.5°) = −7.25 and Q_1 (23.6°) = −10.0 kcal./mole, resp.) and in 0.8*M* NaF (Q_1 (25.5°) = −7.18 kcal./mole and Q_1 (22.5°) = −16.9 kcal./mole, resp.). The heats of decompn. of these compds. in NaOH were also detd. From the measured values, the heats of formation are calcd. to be KBF_2OH (+419.3 kcal./mole) and $K_2B_2F_4O_2OH$ (+857.7 kcal./mole). J. Roytar Leach

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APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1

Ryss

21 21

4
4E4j
4E3d

V Cosolution of sodium chromate and sulfate in water.
I. G. Ryss and A. I. Zhukov. *Trudy Ural. Nauch.-Issle-*
dovatel. Khim. Inst. 1954, No. 1, 23-8; *Referat. Zhur.*
Khim. 1956, Abstr. No. 6393.—Study of cosoly. of Na_2SO_4
(I) and Na_2CrO_4 (II) at 55.7 ± 0.05° shows that the basic
phases of the investigated systems are I and $Na_2CrO_4.4H_2O$
(III). Solns. satd. with I and contg. 0, 10.17, 19.79,
30.40, and 40.89% of II contain 31.40, 22.01, 15.60, 8.669,
and 3.308% of I. A satd. soln. of I and III contains 1.448%
of I and 47.49% of II. The soly. of III in water is equiv. to
51.83% of II. Juxtaposition of these data with the known
data for 25.28 and 33° shows that the soly. curves of I in
solns. of II at different temps. intersect. The soly. of I in
dil. solns. of II decreases with increase in temp. The
effect of temp. between 33 and 55° is negligible. Calcd.
and given as curves for 33 and 55° are the limiting concns. of
II to which solns. with different concns. of I and II can be
evapd. without pptg. I. N. Vasileff

MT

RYSS, I. G

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

USSR/Chemistry

Card : 1/1

Authors : Ryss, I. G. and Vitukhnovskaya, B. S.

Title : Potassium and ammonium hexafluoromanganiates

Periodical : Dokl. AN SSSR, 97, Ed. 3, 471 - 473, July 21, 1954

Abstract : Experiments, for the purpose of obtaining K-and Am-hexafluoromanganiates by the introduction of a Mn-trifluoride solution into the concentrated fluoride solutions with consequent filtration and washing of residues, are described. Formation of hexafluoromanganiates was observed during continuous agitation of pentafluoromanganiates with concentrated fluoride solutions. The change in composition of the solid phase was determined by the change in color and crystal forms, and the composition of the crystals was established by the radicals method. Five references: 4-USA since 1887 and 1-USSR. Table, graphs.

Institution : The I. V. Stalin Metallurgical Institute, Dnepropetrovsk

Presented by : Academician, I. I. Chernyaev, March 26, 1954

RYSS, I.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

USSR/ Chemistry - Synthesis

Card 1/1 **:** Pub. 22 - 31/46

Authors : Ryss, I. G.

Title : Trimeric Na and K- difluoro-orthoborates

Periodical : Dok. AN SSSR 97/4, 691-693, Aug 1, 1954

Abstract : The synthesis of trimeric Na and K-difluoro-orthoborates and their chemical structures, are described. The determination of the Na and F contents of the trimer, is explained. The products, derived after blending $NaHF_2$ with H_3BO_3 in equal ratios, are listed. The analysis results of such trimers, are shown in table. Four references: 2-USSR and 2-German (1932-1951).

Institution : The V. I. Stalin Metallurgical Institute, Dniepropetrovsk

Presented by : Academician I. I. Chernyaev, March 26, 1954

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.

USSR/Chemistry - General chemistry

Card 1/2 Pub. 116 - 2/25

Authors : Ryss, I. G., and Ustyanova, P. V.

Title : The chemical properties of potassium hydroxotrifluoroborate and tetrafluoro borate

Periodical : Ukr. khim. zhur. 21/1, 6-15, 1955

Abstract : New data are presented about the chemical properties of dissolved BF_3-OH' and $B_3F_4O_3OH''$ ions. The data were obtained during potentiometric study of the hydrolysis of the ions. The existence of $BF_2(OH)_2'$ ions in aqueous solutions was established by measurements. The data show that the hydrogen indicator of KBF_3OH solutions does not depend upon the salt concentration, it increases slightly during introduction of the boric acid into the solution but increases sharply during the introduction of dissolved fluoride.

Institution : The I.V. Stalin Metalurgical Institute, Faculty of Gen. Chem. Dniepropetrovsk

Submitted : June 30, 1953

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Periodical : Ukr. khim. zhur. 21/1, 6-15, 1955

Card 2/2 : Pub. 116 - 2/25

Abstract : It is also pointed out that the introduction of glycerin which binds one of the hydrolysis products - boric acid - increases the acidity of the solution. Nine references : 4 USSR, 3 USA, 1 French and 1 German (1894-1952). Tables; graphs.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.; NILUS, E.L.

Solubility of calcium sulfate in hydrochloric acid solutions at 25°C.
Zhur.ob.khim.25 no.6:1076-1081 Je '55. (MLRA 8:12)

1. Dnepropetrovskiy metallurgicheskiy institut
(Calcium sulfate)

RYSS, I. G. and PILT, V. A.

"The Rate of Decomposition of Sodium Fluoborate in Alcohol-water Mixtures."
Zhur. Obshchei Khim. 25, 19-27, 1955

The rate of decompn. of the fluoborate ion in the presence of base ($BF_4^- + 4OH^- \rightarrow BO_2^- + 4F^- + 2H_2O$) was followed titrimetrically. The rate of decompn. of $NaBf_4$ (I) in a 1:1 (by wt.) H_2O-C_2H_5OH mixt. (II) is 0.096 as fast as in pure H_2O, both at 50° and 70°. The soly. of I in H_2O, CH_3OH, C_2H_5OH, and in H_2O-C_2H_5OH mixts. was measured at various temps. In H_2O, a eutectic m. -10.69° was found to contain 37.12% I. There was no evidence of cryst. hydrates of I. To obtain chemically pure I, slightly less than the calcd. amt. of HBF_4 required for complete neutralization was added to Na_2CO_3. After most of the CO_2 evolved, the rest of the HBF_4 plus a slight excess was added with immediately neutralized with NaOH to a pink color with phenolphthalein. After small amts. of NaF were filtered off, the soln. was concd. under a vacuum and I was recrystd. from II between 50° and 0°.

Met. Inst. Dnepropetrovsk.

Ryss I.G.

Chem 5

USSR.

✓**The hydration and solubility of manganese fluoride.** L. G. Ryss and B. S. Vitukhnovskaya (Met. Inst., Dnepropetrovsk). *Zhur. Obshchei Khim.* 25, 643-7(1955).—A method is described for the direct synthesis of manganese fluoride tetrahydrate ($MnF_2.4H_2O$) by dissolving the carbonate in dil. HF at 0°. The soly. polytherms are given for MnF_2 and $MnF_2.4H_2O$. These have a common point at 23.5°. The transition from one form to the other occurs very slowly. The heats of soln. of MnF_2 and of $MnF_2.4H_2O$ were found to be equal to 5.22 and -3.75 kcal./mole, resp. The heat of hydration of MnF_2 was calcd. to be 8.97 kcal./mole and the heat of dissocn. of the tetrahydrate was calcd. as -51.01 kcal./mole. J. Rovtar Leach

①

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1

Ryss, I. G.

chem

The structure of copper monofluoride. I. G. Ryss (L. M. Kaganovich Inst. Railroad Transport, Engrs., Dnepropetrovsk). *Zhur. Fiz. Khim.* 29, 936-7(1955).—The CuF studied by Ebert and Woitinek (*C.A.* 27, 2078) is shown to be thermodynamically unstable at room temp. (Wartenberg, *C.A.* 33, 6741^9), and the possible compn. of the sample studied by E. and W. is suggested.

W. M. Sternberg

pm

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.

USSR/ Chemistry - Physical chemistry

Card 1/1 Pub. 147 - 10/21

Authors : Ryss, I. G., and Gribanova, T. A.

Title : The kinetics of fluorosulfonate ion decomposition in aqueous solutions

Periodical : Zhur. fiz. khim. 29/10, 1822-1826, Oct 1955

Abstract : Experiments showed that the decomposition of a fluorosulfonate ion in weak alkali solutions follows a hydrolysis stage and is described by a kinetic reaction equation of the first order. The thermal and activation entropy values of the decomposition process were established. The hydrolysis of fluorosulfonate had the same rate as in a diluted alkali medium and is followed by hydrogen ion catalysis. An approximate value was established for the constant of the hydrogen ion catalysis rate at 80.28°. Eight references: 5 Germ., 2 USSR and 1 USA (1913-1948). Table; graph.

Institution : Dnepropetrovsk Inst. of Railroad Transport Engineers and Dnepropetrovsk Metallurgical Inst.

Submitted : January 12, 1955

RYSS, I. G.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Khimiya Ftora i Yego Neorganicheskikh Soyedineniy (The Chemistry of Fluorine and of Its Inorganic Compounds), by Prof I. G. Ryss, Doctor of Chemical Sciences, Moscow, Goskhimizdat, 1956, 718 pp

In a brief publishers' annotation, the book is described as follows:

"This book represents a monograph on the chemistry of fluorine and of its inorganic compounds with elements of all groups of the periodic system. The chemical and physical properties of the substance in question, methods for their preparation, applications of the substances described, and the principal physicochemical and molecular constants of fluorine and of its compounds are described and listed in the book.

"The monograph contains an exhaustive bibliography of work published up to October 1953 and in part data published at the end of 1953 and during 1954. Additional references to the most important work done after 1954 are given in small print.

"The book will serve the needs of scientific workers and engineers. It may also be of use to aspirants and students working for a degree." (p 2)

1SUM.1345

KYSS, I.G.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

"The compounds of fluorine with different elements are discussed in the monograph in the order in which these elements appear in the periodic system. In naming individual substances, the author used both the Russian and the international terminology, because unfortunately there is as yet no generally accepted Russian system of nomenclature.

"The author hopes that because of the manifold nature of fluorides and of their characteristics the data compiled in the monograph will be of interest not only to persons who specialize in the chemistry of fluorine and of complex compounds, but also to wide circles of inorganic chemists in general." (pp 9-10)

According to the table of contents, the text of the book deals with the following subjects: Chapter 1, distribution of fluorine in nature (p 11); Chapter 2, [Elemental] fluorine (p 15); Chapter 3, hydrogen fluoride (p 49); Chapter 4, hydrofluoric acid (p 91); Chapter 5, preparation of hydrogen fluoride and of hydrofluoric acid (p 101); Chapter 6, acidic salts of hydrofluoric acid (p 111); Chapter 7, the fluorides of halogens (p 125); Chapter 8, fluorides of the elements of the sixth group (main subgroup: O, S, Se, Te) (p 147); Chapter 9, General review of complex fluorides (p 193); Chapter 10, fluorides of elements of the fifth group (main subgroup: N, P, As, Sb, Bi) (p 224); Chapter 11, fluorides of elements of the fourth group (main subgroup: C, Si, Ge, Sn, Pb) (p 287); Chapter 12, fluorosilicic acid and its salts (p 331); Chapter 13, boron fluoride and boron-fluorine complexes (p 411); Chapter 14, fluorides of aluminum and fluorolaluminates (p 509); Chapter 15, fluorides of elements

Sum. 1345

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.

of the gallium subgroup (Ga, In, Tl) (p 542); Chapter 16, fluorides of elements of the zinc subgroup (Zn, Cd, Hg) (p 551); Chapter 17, fluorides of elements of the copper subgroup (Cu, Ag, Au) (p 559); Chapter 18, fluorides of elements of the eighth group (Ni, Co, Fe, Pd, Rh, Ru, Pt, Ir, Os) (p 571); Chapter 19, fluorides of elements of the manganese subgroup (Mn, Re) (p 615); Chapter 20, fluorides of elements of the chromium subgroup (Cr, Mo, W) (p 629); Chapter 21, fluorides of elements of the vanadium subgroup (V, Nd, Ta) (p 650); Chapter 22, fluorides of elements of the titanium subgroup (Ti, Zr, Hf,) and of the scandium subgroup (the lower fluorides of titanium, p 665; fluorides of quadrivalent titanium and fluorititanates, p 666; the fluorides of zirconium and hafnium, p 672; brief review of fluorides of the subgroup of scandium, lanthanides, and actinides, p 678); Chapter 23, beryllium fluoride and fluoroberyllates (p 686); Chapter 24, fluorides of alkaline earth metals, alkali metals, and ammonium (p 698); and Chapter 24, thermodynamic properties of the fluorides of some metals (p 711). (pp 3-8)

The chemical properties of elemental fluorine, halogen fluorides, oxygen difluoride, and boron fluoride are discussed in considerable detail in the text of the book.

SUM.1345

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.

"In connection with the applications mentioned above, the number of scientific investigations on the chemistry of fluorine grows from year to year.

"In the present monograph an attempt has been made to give a comprehensive review of the literature on the chemistry of inorganic compounds of fluorine, giving information on the results of all important work which has been done in this field. Particular attention has been paid to the physicochemical properties of the substances discussed. The author attempted insofar as possible to give a critical evaluation of the results of the work discussed by him. In view of the profusion of data which are available, the material presented in the book had to be very succinct. To facilitate searches in the original literature, references are given in the text of the book.

"The monograph utilized work published in the USSR and in the most important non-USSR journals, including information given in Chemical Abstracts (US) during the time up to October 1953. Publications that appeared at the end of 1953 and in 1954 have also been partly utilized. References to the most important work done after 1954 are given in small print.

SUM. 1345

RYSS, I. G.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

In the section dealing with fluorides of elements of the scandium subgroup and those of lanthanides and actinides a considerable amount of information is given on the fluorides of rare earths, thorium, uranium, and transuranium elements. The following USSR work is described in this section:

According to D. I. Ryabchikov, the fluoride ion is the most effective precipitant of rare earths and of rare earth complexes. The lanthanum ion is a sensitive reagent for the detection of the fluoride ion.

V. G. Khlopin and M. S. Merkulova investigated the distribution of UX_1 between LaF_3 and ThF_4 and the distribution of radium between crystalline LaF_3 and a solution of LaF_3 in 3% nitric acid.

Complex compounds of the types $MeXF_4$ and Me_3XF_6 are known, while the existence of compounds of the type Me_2XF_5 is doubtful (Me = an alkali metal or ammonium). By investigating the melting point diagrams of systems composed of lanthanum fluoride or lanthanide fluorides and alkali metal fluorides, Ye. P. Dergunov and A. G. Bergman established the existence of a considerable number of compounds belonging to the first two types.

The properties of uranium tetrafluoride were investigated in detail by Khlopin and M. L. Yashchenko. They established that the solubility of this salt at 25° amounts to 0.00017 mol per liter and that its hemi-, di-, and 2.5-hydrates are transformed in solution into $H_2 [UF_4 (OH)_2]$.

SUM.1345

Many compounds of thorium fluoride with fluorides of alkali metals were discovered by Dergunov and Bergman, who applied the method of thermal analysis in their work on the double fluorides of thorium.

In Chapter 13 (p 438) the statement is made that because of the high neutron capture cross section exhibited by the isotope B^{10}, pure boron trifluoride is suitable for filling ionization chambers and proportional counters and is actually used for this purpose. It is furthermore pointed out that the B^{10} content can be increased by thermal diffusion.

The book constitutes a survey of the world literature on inorganic fluorine compounds rather than a compilation of USSR work: references to USSR work represent a minor part of the titles listed. For instance, the bibliography of Chapter 13, which consists of 274 items, lists 48 references to USSR work, and that of Chapter 22, which consists of 117 items, lists 12 USSR references. (C)

54M. 1345

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1

1-4E3d

The properties of dihydroxyfluoroboric acid. L. G. Ryss and L. P. Bogdanova (L. M. Kaganovich Inst. Engineers and Railroad Transportation, Dnepropetrovsk). *Zhur. Neorg. Khim.* 1, 2284-71(1956).—Methods for the analysis of $H_3BO_2F_2$ (I) and the reaction of I with a no. of solid Na salts were studied. I cannot be titrated directly with an alkali because of the rapid formation of BF_4^-. A method is described for the analysis of I based on the decompn. of BF_4^- by boiling with a soln. of $CaCl_2$. It was established that I does not contain a significant quantity of BF_4^-. The reaction of I with $NaHF_2$ and KHF_2 leads to the formation of the tetrafluoroborates. I reacts with $Na_2B_2O_2F_4$ to form $NaBF_4$ and H_3BO_3. I reacts with NaCl or Na_2CO_3 to form $Na_2B_2O_2F_4$ and with NaF to form the same salt plus $NaBF_4$. The chem. properties of I support the assumption that it corresponds to the formula $[H_3O]_2[B_2O_2F_4]$. J. R. L.

RM aag

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Ry

RYSS, I.G.; IDEL'S, S.L.

[redacted]

Pyridinium tetrafluoborate. Zhur.neorg.khim. 2 no.9:2270-2272
S '57. (MIRA 10:12)

(Pyridinium compounds)

RYSS, I.G.; IDEL'S, S.L.

Studying the properties of pyridine boron trifluoride $C_5H_5N \cdot BF_3$.
Zhur. neorg. khim. 2 no.12:2716-2722 D '57. (MIRA 11:2)

1. Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta, Kafedra khimii.

(Boron fluoride)

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1

Ryss, I. G.

7

4E3d
4E4j

7122

USE OF TETRAFLUOBORIC ACID IN QUANTITATIVE ANALYSIS. I. WEIGHT DETERMINATION OF ALKALI METALS IN BORATES, HALIDES, NITRATES, AND NITRITES. I. G. Ryss and E. L. Nilus (Dnepropetrovsk Metallurgical Inst.). Zhur. Analit. Khim. 12, 64-9(1957) Jan.-Feb. (In Russian)

The possibility of quantitative conversion of fluorides, chlorates, bromides, iodides, nitrates, nitrites, borates, and mixtures of borates and fluorides of alkali metals (with the exclusion of Li) into tetrafluorborates has been shown. Also, it was found that mixtures of HF and H_3BO_3 completely evaporate when the molar ratio HF/H_3BO_3 exceeds 2.5, and $LiBF_4$ decomposes very slowly at 110 to 150° while $NaBF_4$ remains quite stable at 200° and decomposes slowly at 250°. (tr-auth)

PM

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Ryss

78-3-5-21/39

AUTHORS: Ryss, I. G., Vitukhnovskaya, B. S.

TITLE: Cesium-and Chromium Manganic Fluoride (Ftoromanganiaty tseziya i khroma)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol 3, Nr 5, pp 1185 - 1187 (USSR)

ABSTRACT: The syntheses of $Cs_2MnF_5 \cdot H_2O$ and $MnF_3 \cdot CrF_3 \cdot 6\,H_2O$ were carried out.
$Cs_2MnF_5 \cdot H_2O$ has light rose-colored crystals and is very easily decomposable with water. $MnF_3 \cdot CrF_3 \cdot 6\,H_2O$ forms difficultly soluble lilac crystals. Their composition was determined by means of chemical analyses. The gradual formation constant of the above-mentioned complexes was calculated. In aqueous solution, the following complexes can simultaneously exist:

Card 1/2

$[CrF_2(H_2O)_4]^+$ and $[MnF_4(H_2O)_2]^-$.

78-3-5-21/39

Cesium-and Chromium Manganic Fluoride

The probable composition of $MnF_3 \cdot CrF_3 \cdot 6\ H_2O$ is the following:

$$[CrF_2(H_2O)_4][MnF_4(H_2O)_2] \text{ or } [CrF_2(H_2O)_5][MnF_5H_2O].$$

There are 9 references, 4 of which are Soviet.

SUBMITTED: May 15, 1957

AVAILABLE: Library of Congress

1. Complex compounds--Synthesis 2. Complex compounds--Chemical analysis 3. Cesium--Chemical reactions 4. Chromium manganic fluoride--Chemical reactions

Card 2/2

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

78-3-6-20/30

AUTHORS: Ryss, I. G., Khordas, I. S.

TITLE: The Solubility-Polytherms of Potassium- and Cesium-Tetrafluorborates (Politermy rastvorimosti tetraftoroboratov kaliya i tseziya)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 6, pp. 1410-1415 (USSR)

ABSTRACT: The solubility of potassium- and cesium-tetrafluorborates was determined and compared with the values given in publications. A method for the determination of the solubility of the complexcompounds was given, in which a partial hydrolysis of the complex ions takes place. The activity coefficients of KBF_4 and $CsBF_4$ were also determined. Dependence of the logarithms of the activity in saturated solutions on temperature, was determined. The solubility of KBF_4 and $CsBF_4$ was determined at temperatures of from 0 to 70°C. The dependence of the activity of saturated solutions of KBF_4 and $CsBF_4$ on temperature is expressed by the following equation:

Card 1/3

$$\lg a_{KBF_4} = 7470-3080/T$$

$$\lg a_{CsBF_4} = 8236-3146/T$$

The heat of solubility for KBF_4 is expressed by $\Delta H^o = 14,1$ k cal/mol, $\Delta F^o_{298} = 3,90$ k cal/mol and $\Delta S^o_{298} = 34$ k cal/mol/degree.

The heat of solubility of $CsBF_4$ is expressed by $\Delta H^o = 14,5$ k cal/mol, $\Delta F^o_{298} = 3,24$ k cal/mol and $\Delta S^o_{298} = 38$ k cal/mol/degree. The great similarity of the ΔH^o of the two above-mentioned salts shows that the lattice energy differs very little and that also the hydration-energy of K^+ and Cs^+ is very similar. The entropy of solubility of KBF_4 is lower than that of $CsBF_4$. This leads to the

The Solubility-Polytherms of Potassium- and Cesium Tetrafluorborates

78-3-6-20/30

conclusion that the solubility of $CsBF_4$ is more endothermic.
There are 1 figure, 3 tables, and 11 references, 4 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute for Railroad Engineering)

SUBMITTED: April 22, 1957

AVAILABLE: Library of Congress

1. Potassium tetrafluorborates--Solubility. 2. Cesium tetrafluorborates--Solubility

Card 3/3

AUTHORS: Ryss, I.G., Gribanova, T.A. SOV/78-3-7-35/44

TITLE: The Solubility Polytherm of Potassium Fluorine Sulfonate (Politerma rastvorimosti ftorsul'fonata kaliya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 7, pp 1665-1668 (USSR)

ABSTRACT: Investigations of the solubility of potassium fluorine sulfonate (KSO_3F) were carried out at 0° C and 50° C. By taking the hydrolysis of the remaining anions into account, several modifications were effected. In the course of the analysis carried out the total content of SO_3F and HF was determined. On the strength of the results obtained the thermodynamic characteristic on the dissolution process of KSO_3F was calculated: for $\Delta NH^{o} \sim 10.5$ kcal/mol; for $\Delta S^{o} \sim 30.5$ enthropy units. For the gaseous SO_3F hydration heat was calculated as amounting to ~ 50 kcal/mol. The thermodynamic characteristic of the dissolution processes of KBF_4, $KClO_4$ $KMnO_4$ and KSO_3F were compared. There are 1 figure, 1 table, and 13 references, 9 of which are Soviet.

Card 1/2

The Solubility Polytherm of Potassium Fluorine Sulfonate SOV/78-3-7-35/44

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta i Dnepropetrovskiy metallurgicheskiy institut (Dnepropetrovsk Institute of Railroad Transport Engineers and Dnepropetrovsk Metallurgical Institute)

SUBMITTED: May 15, 1957

1. Potassium fluorine sulfonate--Solubility 2. Potassium fluorine sulfonate--Thermodynamic properties 3. Ions--Hydrolysis

Card 2/2

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

AUTHORS: Ryss, I.G., Bogdanova, L.P. SOV/ 78-3-7-36/44

TITLE: The Solubility Polytherm of $Na_3B_3O_3F_6$. Equilibrium of the System $Na_3B_3O_3F_6$-NaI-H_2O at 25° (Politerma rastvorimosti $Na_3B_3O_3F_6$. Ravnovesiye sistemy $Na_3B_3O_3F_6$-NaJ-H_2O pri 25°)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 7, pp 1669-1674 (USSR)

ABSTRACT: The velocity of the formation of BF_4^- in solutions of $Na_3B_3O_3F_6$ at 70-90° C was determined. At 30° C the forming of BF_4^- from solutions of $Na_3B_3O_3F_6$ develops comparatively slowly, and therefore it is possible to determine the solubility of $Na_3B_3O_3F_6$. The velocity of the formation of NF_4^- increases with rising temperature and decreases with an increase of the concentration of $Na_3B_3O_3F_6$. The heat of solution in water is -7.5 kcal/mol. The equilibrium in the system $Na_3B_3O_3F_6$-NaI-H_2O at 25° was investigated. The results obtained confirm the chemical formula of these compounds. At a higher concentration of $B_3O_3F_6^{3-}$ in the solution and in the domain of a lower concentration of NaI no considerable depolimerization of $B_3O_3F_6^{3-}$ occurs. There are

Card 1/2

The Solubility Polytherm of $Na_3B_3O_3F_6$. SOV/78-3-7-36/44
Equilibrium of the System $Na_3B_3O_3F_6$-NaF-H_2O
at 25°

4 figures, 2 tables, and 9 references, 7 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Transport Engineers)

SUBMITTED: May 28, 1957

1. Complex compounds--Solubility 2. Chemical equilibrium --Determination 3. Complex compounds--Chemical analysis

Card 2/2

SOV/32-24-7-61/65

AUTHOR: Ryss, I. G., Doctor of Chemical Sciences

TITLE: On the Problem of the Volumetric Determination of Fluorine in Tetrafluoro Borates(K voprosu ob ob"yemnom opredelenii ftora v tetraftoroboratakh)Concerning the Article by Z.T. Maksimycheva, Sh.T.Talipov and A.M.Koginova, Zavodskaya Laboratoriya, 1956, Vol. 22, Nr 7, pp. 791 (O stat'ye Z.T. Maksimychevoy, Sh.T.Talipova i A.M.Koginovoy, Zavodskaya laboratoriya, XXII, 7, 791, 1956)

PERIODICAL: Zavodskaya Laboratoriya, 1958, Vol. 24, Nr 7, pp. 905 - 906 (USSR)

ABSTRACT: In the article mentioned above the experimental conditions were insufficiently characterized and the physical and chemical foundations of the analytical method investigated were not explained in spite of the data known. The statement that the introduction of acid into the solution of tetrafluoro borate shifts the equilibrium in the hydrolysis in the desired direction is not correct; also the statement that a complete hydrolysis of BF_4^- in acid medium is obtained by the dissociation of the hydrofluoric acid is incorrect. It is generally known that the addition of catalysts does not change the position

Card 1/3

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

SOV/32-24-7-61/65

On the Problem of the Volumetric Determination of Fluorine in Tetrafluoro Borates. Concerning the Article by Z.T.Maksimycheva, Sh.T.Talipov and A.M.Koginova, Zavodskaya Laboratoriya, 1956, Vol. 22, Nr 7, pp. 791

of the equilibrium. According to the data mentioned the pure tetrafluoro boric acid can not be hydrolysed completely as the contact with glass is lacking, however, an excess in boric acid highly effects the degree of hydrolysis. The paper mentioned above does, however, not give any data on this. It is therefore recommended to perfect the method suggested. The given degree of the hydrolysis of tetrafluoro boric acid at room temperature is of no use as the concentration of the solution is not given. The attempt to achieve a decomposition BF_4^- in an alkaline medium by boiling for several hours could not be successful; this is explained and a corresponding diagram is given. On the other hand it is a fact generally known that the hydrolysis of BF_4^- in alkaline medium increases with the duration of heating. There are 1 figure and 7 references, which are Soviet.

Card 2/3

On the Problem of the Volumetric Determination SOV/32-24-7-61/65
of Fluorine in Tetrafluoro Borates. Concerning the Article by Z.T.Maksimycheva, Sh.T.Talipov and A.M.Koginova, Zavodskaya Laboratoriya, 1956, Vol. 22, Nr 7, pp. 791

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad-Transport Engineers)

Card 3/3

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

5(2) SOV/32-24-11-11/37

AUTHORS: Ryss, I. G., Nilus, E. L.

TITLE: Use of Tetrafluoro Boric Acid in Quantitative Analysis (Primeneniye tetraftorobornoy kisloty v kolichestvennom analize) Determination of Potassium and Sodium in Mixtures of Chlorides (Opredeleniye kaliya i natriya v smesi khloridov)

PERIODICAL: Zavodskaya Laboratoriya, 1958, Vol 24, Nr 11, pp 1349 - 1352 (USSR)

ABSTRACT: It has already been shown (Ref 1) that in the evaporation of the chlorides of alkali metals with tetrafluoro boric acid tetrafluoro borates are quantitatively produced. The content of potassium and sodium chlorides in the mixture can be calculated from the weight of the chloride mixture $\Sigma_{(Chl)}$ and the weight of the tetrafluoro borate $\Sigma_{(Tfb)}$ using the equations:

$m_{NaCl} = 5.2741\,\Sigma_{(Tfb)} - 8.908\,\Sigma_{(Chl)}$ and

$m_{KCL} = 9.9085\,\Sigma_{(Chl)} - 5.2741\,\Sigma_{Tfb)}$; The sodium tetra-

Card 1/3

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Use of Tetrafluoro Boric Acid in Quantitative Analysis. SOV/32-24-11-11/37
Determination of Potassium and Sodium in Mixtures of Chlorides

fluoro borate is separated from the potassium salt by a rapid leaching out with a 10% NH_4BF_4 solution. NH_4BF_4 is separated from $NaBF_4$ by volatilization at 300° and from KBF_4 by washing out with 96% ethanol. In the extraction of the $NaBF_4$ from the mixture of tetrafluoro borates treating with 2.5 ml. NH_4BF_4 for 5 minutes was sufficient. It was found that the use of alcohol (instead of water) considerably decreased the solubility of KBF_4, the value of which was somewhat higher than that found by Fadeyev (Ref 8). The analytical results on mixtures ranging in composition from 5% KCL and 95% NaCl to 95% KCL and 5% NaCl were completely satisfactory. The relative analytical error is greater for those components which were present in smaller amounts. There are 3 tables and 9 references, 5 of which are Soviet.

Card 2/3

Use of Tetrafluoro Boric Acid in Quantitative Analysis. SOV/32-24-11-11/37
Determination of Potassium and Sodium in Mixtures of Chlorides

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta i Dnepropetrovskiy metallurgicheskiy institut (Dnepropetrovsk Institute of Railroad Transport Engineers and the Dnepropetrovsk Metallurgical Institute)

AUTHOR: Ryss, I. G. SOV/20-120-4-30/67

TITLE: Kinetics of Hydrolysis of Boron Trifluoride Coordination Compounds (Kinetika gidroliza koordinatsionnykh soyedineniy ftoristogo bora)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 4, pp. 797-800 (USSR)

ABSTRACT: The author proved that the kinetics of hydrolysis of F_3B:Am with Am denoting an amine does not only depend on the nature of the amine with respect to quality but also with respect to quantity. The first stage of hydrolysis which can be determined by analysis is apparently irreversible. In a neutral and acidous medium the reaction becomes more complicated, in an alkaline medium BF_3OH^- undergoes a rapid quantitative decomposition to borate and fluoride. An earlier attempt to investigate the hydrolysis of $F_3B : NH_3$ did not bring about any quantitative results. In this paper a new method is investigated. It is based upon the determination of concentration of $F_3B : NH_3$ which was not hydrolized at a given time. The same method was applied in the case of $F_3B:NH_2CH_3$. The velocity of hydrolysis of this compound is small. The hydrolysis

Card 1/4

Kinetics of Hydrolysis of Boron Trifluoride Coordination Compounds

proceeds according to an equation of the first order and is neither catalysed nor inhibited by H^+-ions; at the same time the formation of BF_4^- is inhibited. The latter velocity is proportional to its concentration in the presence of F^--ions. The acidification of the NaF-solution to pH 5,2 did not eliminate the catalytic effect of F^-. Since the velocity of hydrolysis of $F_3B:NC_5H_5$ and of BF_4 does not depend on the alkalinity of the solution, it is determined by the solvolytic dissociation of the complexes. The high electronegativity of fluorine and the structure of the electron shell of boron justify the statement that these processes are a nucleophilic replacement of S_N1. The same refers to the hydrolysis of the complexes BF_3 with NH_3 and NH_2CH_3. In a highly alkaline medium they decompose very quickly; the velocity of their hydrolysis, however, is not determined by the OH^--ions which form in connection with the water dissociation. The acceleration of the mentioned hydrolysis in the presence of F^--ions is not due to the course of reaction which is usually assumed for S_N-2-processes(attacks on the complexes by F^- which replaces the amine).

Card 2/4

The catalytic effect of F^- can be

explained by the following hypothesis: the coordination of ammonia by boron fluoride is accompanied by the withdrawal of the electron pair of N to B. It increases the acidous properties of the ammonia hydrogen and its capability of forming hydrogen bindings. A quickly established equilibrium in the solution is related to this phenomenon:

$$F_3B : NH_3 + F^- \rightleftarrows F_3B : NH_3 \dots F^- \quad (6)$$

The addition of a negative ion is bound to weaken B ⟵ N in its complex and facilitate its solvolytic dissociation. The acceleration of decomposition of $F_3B : NH_3$ and NH_2CH_3 in the presence of ions HCO_3^-, CO_3^{2-} and OH^- is apparently started by analogous processes. Figure 1 shows that the activation energy E of the hydrolysis of boron fluoride complexes increases with increased alkaline properties of the addition products. A relationship exists between the thermodynamical properties of the addition product and those of the state of transition. H^+-catalyses the hydrolysis of BF_4^-, SO_3F^-, PF_6^- and probably also of other complex fluorine ions in consequence of an association outside the shell (vneshnesfernaya assostiatsiya) caused by the attraction of ion charges. This association facilitates an HF-separation. A rapid decomposition of BF_3OH^- in an alkaline medium is apparently connected with an intraspherical transition (vnutrisfernyy perenos) of a proton and the following processes of HF-separation and of the water addition. There are 1 figure, 1 table, and 9 references, 7 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovskiy Institute of Railway-Transport-Engineers)

PRESENTED: February 5, 1958, by A. V. Topchiyev, Member, Academy of Sciences, USSR

SUBMITTED: February 5, 1958

1. Boron fluorides--Hydrolysis 2. Ions--Chemical effects
3. Chemical equilibrium

Card 4/4

5(3),5(2)

AUTHORS: Ryss, I. G., Trakhtenberg, F. I. SOV/78-4-6-36/44

TITLE: The Hydrofluorides of Aniline (Gidroftoridy anilina)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 6, pp 1431 - 1436 (USSR)

ABSTRACT: The solubility of the hydrofluorides of aniline was investigated in hydrofluoric acid at 0° and 20° and the results are given in table 1. The phases $[C_6H_5NH_3]F.H_2O$ and $[C_6H_5NH_3]HF_2$ were determined. The "eutonic" solution contains at 0° 12.11% $[C_6H_5NH_3]F$ and 43.89% $[C_6H_5NH_3]HF_2$. The compound does not pass over into polyhydrofluoride at -18° in the case of an increase of the HF-concentration up to 52%. The dissociation degree of aniline fluoride was calculated at 0°. The compounds $C_6H_5NH_2.3HF.0.5H_2O$ (Ref 1) and $C_6H_5NH_2.4HF$ (Ref 3) described in the publications are probably hexafluoro-silicates of aniline. There are 1 figure, 1 table, and 7 references, 4 of which are Soviet.

SUBMITTED: March 25, 1958

Card 1/1

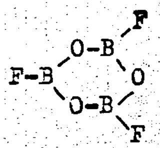
5(2) SOV/78-4-8-22/43

AUTHORS: Ryss, I. G., Bogdanova, L. P.

TITLE: Potassium-hexafluoroboroxolate $K_3[B_3O_3F_6]$ and Potassium Hydroxopentafluoroborон-oxolate $K_3[B_3O_3F_5OH]$ (Geksaftorobor-oksolat kaliya $K_3[B_3O_3F_6]$ i gidroksopentaftorobor-oksolat kaliya $K_3[B_3O_3F_5OH]$)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 8, pp 1839-1843 (USSR)

ABSTRACT: Boron fluoride complexes were synthesized for the first time by the author mentioned first (Refs 1,2). They are ascribed a cyclic structure. They may be regarded as addition products of F- and OH-ions to trifluoroboroxol



which is unstable in free state (Ref 3). Besides the hydroxotetrafluoroboroxolic salt of potassium $K_2[B_3O_3F_4OH]$ which was

Card 1/3

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

Potassium-hexafluoroboroxolate $K_3[B_3O_3F_6]$ and Potassium Hydroxopentafluoroboron-oxolate $K_3[B_3O_3F_5OH]$

produced already earlier the compounds mentioned in the title were obtained and the denotation mentioned in the title was suggested because of the genetic connection with boroxol $H_3B_3O_3$ and trifluoroboroxol. $K_2[B_3O_3F_4OH]$ is transformed into $K_3[B_3O_3F_5OH]$ in weakly alkali 40% KF-solution. In the absence of alkali a partial substitution of the hydroxyl by fluorine takes place. In the case of an excess of KHF_2 in concentrated potassium fluoride solution the hydroxotetrafluoride compound reacts under the formation of $K_3[B_3O_3F_6]$ It is stable at room temperature in a potassium fluoride concentration of more than 35%. The hexafluoride compound and the hydroxopentafluoride compound are decomposed under the action of water or diluted KF-solutions and $K_2[B_3O_3F_4OH]$ is precipitated. The synthesized substances are new derivatives of trifluoroboroxol. There are 2 tables and 9 references, 8 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railway Transport Engineers)

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

5(2) SOV/78-4-8-43/43

AUTHOR: I. G. Ryss

TITLE: Ya. A. Fialkov: Interhalogen Compounds (Ya. A. Fialkov: Mezhgaloidnyye soyedineniya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 8, pp 1941-1942 (USSR)

ABSTRACT: The revised paper mentioned in the title was published only after the death of the author, who was Corresponding Member of the AS UkrSSR. The monograph includes the entire publications dealing with this subject which were issued until the middle of 1956 and some papers published later. After having pointed to some wrong data in a table, the reviewer emphasizes the value of this edition and regrets that only 2000 copies were issued.

Card 1/1

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

SOV/78-4-9-10/44

5(2)

AUTHORS: Ryss, I. G., Idel's, S. L.

TITLE: The Anilinium Tetrafluoroborate, Aniline Trifluoroboron and Anilinium Hydroxotrifluoroborate

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 9, pp 1990-1994 (USSR)

ABSTRACT: I. G. Ryss in his investigation on the coordination compounds of boron fluorides with amines made assumptions concerning a relationship between hydrolysis and the properties of the amine (Ref 1). In order to verify these assumptions, $AnHBF_4$ (An = aniline), which had not been described in publications, was synthesized. Its solutions are acid owing to hydrolysis, and oxidize on standing for some time. Its crystals are monoclinic. Furthermore, the synthesis of $F_3B:An$ is described, which hydrolyzes to give the compound $AnH[BF_3OH]$. This hydrolysis was investigated by titration. It proceeds according to the equation

$$\log \frac{x}{x_0} = - 0.4343\ k\vartheta,$$

Card 1/2

where x_o denotes the initial concentration of the complex compound, x the concentration at the time ϑ, and k the reaction constant. This equation confirms the dependence of the hydrolysis on the type of amine. F_3B:An is very soluble in ethanol and methanol. Distillation with absolute methanol leads to a reaction described by the following equation: $4F_3B:An + 3CH_3OH = 3AnHBF_4 + B(OCH_3)_3 + An$. There are 9 references, 5 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute for Railroad Transport Engineers)

SUBMITTED: June 7, 1958

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

5(2)

AUTHORS: Ryss, I. G., Vitukhnovskaya, B. S. SOV/75-14-3-11/29

TITLE: Titrimetric Determination of Manganese After Its Oxidation to Trivalent State (Titrimetricheskoye opredeleniye margantsa posle okisleniya do trekhvalentnogo sostoyaniya)

PERIODICAL: Zhurnal analiticheskoy khimii, 1959, Vol 14, Nr 3, pp 318-321 (USSR)

ABSTRACT: A simple method is described for the determination of Mn^{2+} ions, which is based on the formation of fluoro manganate. The first experiments with KNO_3 as oxidizing agent in the presence of HF indicated that the oxidation of Mn^{2+} does not proceed quantitatively. With ammonium nitrate however exact results were obtained (Table 1). The determination of the fluoro manganate formed can be carried out iodometrically or by means of titration with Mohr's salt. Fe^{3+}-ions do not disturb. In the presence of Cr^{3+} the dissolution and reduction of the precipitate of $CrF_3.MnF_3.6H_2O$ is accelerated by addition of boric and hydrochloric acid and the titration thus proceeds undisturbed. If Fe^{3+} and Cr^{3+} occur together, only the titration with Mohr's salt is possible (Table 3). The presence of Co^{2+} (up to 250 mg) or Ni^{2+} (up to 70 mg) does

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SOV/75-14-3-11/29

Titrimetric Determination of Manganese After Its Oxidation to Trivalent State

not disturb the iodometric determination of manganese (Table 4). The analysis was tried with ferromanganese alloys and yielded satisfactory results (Table 5). There are 5 tables and 9 references, 5 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railway Engineers). Dnepropetrovskiy metallurgicheskiy institut (Dnepropetrovsk Metallurgical Institute)

SUBMITTED: May 13, 1957

5(4) SOV/76-33-1-18/45

AUTHORS: Ryss, I. G., Donskaya, D. B.

TITLE: The Over-All Equilibrium Constant of Hydrolysis of Tetrafluoroborate Ion BF_4^- (Obshchaya konstanta ravnovesiya gidroliza iona tetraftoroborata, BF_4^-)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 1, pp 1o7 - 111 (USSR)

ABSTRACT: I. G. Ryss and N. P. Bakina (Ref 1) determined the hydrolysis constant of the BF_4^--ions without considering the fact that boric acid reacts with F^--ions (as was found out later on (Ref 2)). Since the value of the equilibrium constant c ((Ref 1) in the paper) was therefore not reliable the determinations were repeated and the sources of the errors mentioned above were taken into account. The presence of the solid phases KBF_4 and H_3BO_3 in all mixtures were microscopically checked during the investigations. The pH values were measured by hydrogen or quinhydrone electrodes. The electric circuit was in a thermostat chamber at 25.0 ± 0.03° and was measured by a potentiometer PPTV-1 with a mirror galvano-

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The Over-All Equilibrium Constant of Hydrolysis of Tetrafluoroborate Ion BF_4^- SOV/76-33-1-18/45

meter M-25 as balancing apparatus. The results, shown in tables, prove that a strong reaction of H_3BO_3 with F^--ions takes place. In the reaction
$KBF_{4(cryst.)} + 3H_2O \rightleftarrows H_3BO_{3(cryst.)} + 3H^+ + 4F^- + K^+$ (4)
$\lg K' = 23.15 \pm 0.1$; and in the reaction
$BF_4^- + 3H_2O \rightleftarrows H_3BO_{3(cryst.)} + 3H^+ + 4F^-$ (1) $\lg K = 20.01 \pm 0.1$ and
$\Delta F_{298}^{o} = 27.27 \pm 0.14$ kcal. Instead of the value (-343 kcal) found by Latimer (Ref 12), for BF_4^- the value of about -352 kcal is given for free formation energy. There are 1 figure, 1 table, and 12 references, 10 of which are Soviet.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Engineers)

SUBMITTED: June 21, 1957

Card 2/2

5(4) SOV/76-33-2-21/45

AUTHORS: Ryss, I. G., Idel's, S. L.

TITLE: Kinetics of the Hydrolysis of Boron Ammine Trifluoride, $H_3N:BF_3$ (Kinetika gidroliza triftor-ammin-bora, $H_3N:BF_3$)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 2, pp 374 - 380 (USSR)

ABSTRACT: A method is described which (as it differs from previous experiments in reference 1) makes possible a determination of boron ammine trifluoride (I) in the presence of its hydrolysis products. A study of the hydrolysis kinetics of (I) could be carried out by determining the concentration of (I) as a function of the time without the BF_4^- ions produced in the reaction affecting the experimental results. The $H_3N:BF_3$ was obtained by reacting ammonia and boron fluoride in benzene in a reaction vessel (Fig 1), and its fine crystalline powder was found to be readily soluble in water. The hydrolysis kinetics of (I) were titrimetrically determined in a solution neutral to methyl orange using an excess of $CaCl_2$ and applying a TS-15 thermostat.

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The experimental results obtained showed (Fig 2) that the hydrolysis of (I) is a reaction of the first order and is not catalyzed by hydrogen ions (Table 1), since the molecule $H_3N:BF_3$ possesses no charge. The function of the rate constant in dependence upon the temperature can be represented by a straight line

$\lg k' = 14.70 - \frac{5945}{T}$ (2). This equation corresponds to an activation energy $E = 27.2$ kcal/mol and an activation entropy $\Delta S^{\neq} = 3.2$ cal/degree. The mechanism of the hydrolysis of the various double salts of boron fluoride will be treated in detail in a later paper. Preliminary experiments showed that the hydrolysis of the $H_3N:BF_3$ is markedly accelerated in the presence of F^- and especially by OH^- ions. A hydrolysis mechanism for (I) is given, and it is mentioned that the hydrolysis of (I) in a NaF solution occurs in two parallel processes (in three including the effect of the OH^- ions). There are 4 figures, 3 tables, and 6 references, 4 of which are Soviet.

Kinetics of the Hydrolysis of Boron Ammine Trifluoride, $H_3N:BF_3$ SOV/76-33-2-21/45

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute for Railroad Transportation Engineering)

SUBMITTED: July 15, 1957

Card 3/3

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S/078/60/005/05/08/037
B004/B016

5.2400(B)

AUTHORS: Ryss, I. G., Bogdanova, L. P.

TITLE: Ammonium Salts of Fluoboric Acids

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 5, pp. 1028-1035

TEXT: The authors describe the synthesis of $(NH_4)_2[B_3O_3F_4OH]$ (I) and NH_4BF_3OH (II). Salt (I) was obtained by triturating anhydrous ammonium bifluoride with boric acid: $2NH_4HF_2 + 3H_3BO_3 = (NH_4)_2[B_3O_3F_4OH] + 5H_2O$. Analyses of the products of syntheses repeatedly carried out under different conditions (triturating of the anhydrous initial products, synthesis in water-alcohol mixtures at 0° or -7°, addition of small quantities of HF) are represented in table 1. Complete elimination of impurities (H_2O, NH_4F) was not possible. The solubility of salt (I) was investigated by the isothermal method. Table 2 gives the results. Fig. 1 shows the solubility at

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B004/B016

Ammonium Salts of Fluoboric Acids

25° in the presence of NH_4F (Abstracter's Note: This figure is missing). Reactions between (I) and NH_4F were found to occur. The reaction products could not be isolated owing to their considerable (and obviously incongruent) solubility. The results of thermal decomposition of (I) are listed in table 3. H_2O and NH_3 are split off. After heating for two hours up to 150° 38% of (I) was decomposed under the formation of NH_4BF_4; the remaining 62% had lost its water. At 200° and 250° the weight loss continued with NH_3 and a boron fluoride compound being released. Compound (II) was prepared according to the equation: $(NH_4)_2[B_3O_3F_4OH] + 4NH_4HF_2 = 3NH_4[BF_3OH] + + 3NH_4F + H_2O$. Analyses of the reaction products are represented in table 4. Owing to the very high solubility of (II) in water, complete elimination of the NH_4F impurity was not possible. The authors further attempted to prepare the compound $B_2O_3.NH_4F.HF$ which was described by G. I. Petrenko (Ref. 3). However, they obtained only a mixture consisting of (I), boric acid, and presumably ammonium borates (Table 5). Nor was it possible to prepare the compound $(NH_4)_2[O(BF_3)_4]$, described by Svaynkhert, and patented

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Ammonium Salts of Fluoboric Acids S/078/60/005/05/08/037
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for him. The syntheses performed according to the patent yielded an inhomogeneous mixture mainly consisting of NH_4BF_4 (Table 6). There are 6 tables and 13 Soviet references.

ASSOCIATION: Dnepropetrovskiy institut zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Transportation)

SUBMITTED: February 7, 1959

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AUTHORS: Ryss, I. G., Idel's, S. L.

TITLE: Kinetics of Hydrolysis of Dimethyl-amino Boron Trifluoride

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 8, pp. 1756-1760

TEXT: Following their previous papers (Refs. 1-5) the authors studied the kinetics of hydrolysis of dimethyl-amino boron trifluoride, $F_3B:NH(CH_3)_2$. The compound was obtained by reaction of the carefully dried components in the presence of a benzene-ether mixture. Dimethyl-amino boron trifluoride is a colorless substance. When slowly heated in a closed capillary it melts at 50-51°C. It is sparingly soluble in benzene and easily soluble in ether, methanol, and water. Hydrolysis of $F_3B:NH(CH_3)_2$ is a first-order reaction which proceeds according to the mechanism S_N1. Its rate constant (in min^{-1}) as a function of temperature is expressed by the following equation: $\log(0.4343\ k) = 16.21 - \frac{6972}{T}$. Its activation energy E

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equals 31.9 kcal; the activation entropy $\Delta S^{\neq}$ = 7.2 entropy units. The values of E and $\Delta S^{\neq}$ are in good agreement with the data of Ref. 2 where E and $\Delta S^{\neq}$ were found to depend on the pK of the amine for the coordination compounds of BF_3 with amines. The hydrolysis of $F_3B : NH(CH_3)_2$ is accelerated by the presence of F^- ions. In a strongly alkaline medium $F_3B:NH(CH_3)_2$ is decomposed rapidly. The mechanism of the action of OH^- and F^- ions is analogous to that of the hydrolysis of BF_3 compounds with ammonia and methylenamine (Refs. 3,4). There are 4 figures, 2 tables, and 7 references: 5 Soviet, 1 US, and 1 British.

ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Engineers)

SUBMITTED: February 7, 1959

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R001446510009-1"

RYSS, I.G.; IDEL'S, S.L.

Kinetics of the hydroloysis of boron trifluoride trimethlamine. Zhur. neorg. khim. 5 no.8:1761-1767 Ag '60. (MIRA 13:9)

1. Dnepropetrovskiy transportnyy institut.
(Boron trifluoride)

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B004/B067

AUTHORS: Ryss, I. G., Donskaya, D. B.

TITLE: Diethylaminoboron Trifluoride. Diethylammonium Tetrafluoroborate

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 10, pp. 2251-2257

TEXT: In reacting anhydrous diethylamine with BF_3 or $F_3B:O(C_2H_5)_2$ the authors did not obtain the substance designated in Ref. 1 as diethylaminoboron trifluoride but diethylammonium tetrafluoroborate $[(C_2H_5)_2NH_2]BF_4$. They obtained the same compound when neutralizing tetrafluoroboric acid with diethylamine. This is a colorless crystalline substance with the melting point at about 168°C. Diethylaminoboron trifluoride $F_3B:NH(C_2H_5)_2$ could be synthesized by passing BF_3 and N_2 (obtained by thermal decomposition of $C_6H_5N_2BF_4$) through anhydrous

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diethylamine cooled to -25±5°C. Fig. 4 shows the scheme of the apparatus used for this purpose. This compound is a neutrally reacting, rather unstable liquid which gradually turns yellow at -20°C and rapidly decomposes in alkaline media. Its melting point is found at approximately -25°C. It could not be exactly determined due to the tendency of the substance toward undercooling and decomposition. Table 1 gives the analytical data. Their deviation from the theoretical composition, especially in samples stored for longer periods is explained by the following reactions: $2F_3B{:}NH(C_2H_5)_2 = F_3B{-}N(C_2H_5)_2 + [(C_2H_5)_2NH_2]BF_4$; $F_3B{:}NH(C_2H_5)_2 = C_2H_5F\uparrow + F_2B{-}NHC_2H_5$; $F_3B{:}NH(C_2H_5)_2 = HF\uparrow + F_2B{-}N(C_2H_5)_2$. Purer preparations could be obtained at -25°C by passing BF_3 through $NH(C_2H_5)_2$ dissolved in CCl_4. In this case the liquid was separated into two layers, the upper one of which contained the $F_3B{:}NH(C_2H_5)_2$ dissolved in CCl_4. CCl_4 was evaporated in vacuum. The best results, however, were obtained by saturating a mixture of diethylamine and toluene with BF_3 at -78°C. Diethylaminoboron trifluoride was separated as a white powder.

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Diethylaminoboron Trifluoride.
Diethylammonium Tetrafluoroborate

By means of this preparation the rate of hydrolysis of the compound was studied. $x = n_{\vartheta}/n_o$ was determined, where n_o denotes the content of diethylaminoboron trifluoride at the beginning of the experiment, and n_{ϑ} the content after the period ϑ. Fig. 1 shows the function $\log x = f(\vartheta)$. Its linear course corresponds to a first-order reaction. Table 2 gives the data found at 60, 70, 80, and 90°C for calculating the rate constant k, and Fig. 2 represents the function $\log k = f(1/T)$. The dependence $\log(0.4343k) = 17.29 - 7016/T$ was found. The activation energy of hydrolysis is 22.1kcal/mole, and the activation entropy is 12 e.u. . The value of the activation energy corresponds to the expected value pK for the dissociation of diethylamine. Fig. 3 shows $E = f(pK)$ for coordination compounds of BF_3 with pyridine, ammonia, trimethylamine, methylamine, dimethylamine, and diethylamine. In the apparatus used for the synthesis the air humidity was kept out either by means of tubes filled with P_2O_5, partly by means of a Tishchenko flask filled with H_2SO_4. There are 4 figures, 2 tables, and 12 references: 11 Soviet and 1 US.

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ASSOCIATION: Dnepropetrovskiy institut inzhenerov zheleznodorozhnogo transporta (Dnepropetrovsk Institute of Railroad Engineers)

SUBMITTED: March 27, 1959

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S/073/60/026/004/001/008
B103/B220

5. 2420

AUTHORS: Ryss, I. G. and Bogdanova, L. P.

TITLE: Hydroxy tetrafluoro-boroxolates of rubidium and cesium

PERIODICAL: Ukrainskiy khimicheskiy zhurnal, v. 25, no. 4, 1960, 403-408

TEXT: Synthesis, properties, and analysis of rubidium and cesium hydroxy tetrafluoro-boroxolates are described. The Ru and Cs content of the compounds was determined gravimetrically as tetrafluoroborate. The complex anion was determined by double titration: 1) titration in the presence of methyl orange and excess of 1 mole of $CaCl_2$ to boric acid and CaF_2; 2) titration of the boric acid (after addition to mannite and phenolphthalein). The consumption of alkali in titrations 1) and 2) is indicated by n_1 and n_2. The portions were weighed by the microbalance BM-20 (VM-20). A) Synthesis of $Rb_2[B_3O_3F_4OH]$. $RbNO_3$ is dissolved in a saturated solution of $(NH_4)_2[B_3O_3F_4OH]$. The precipitate is not yet a pure final product. By slight amounts of HF before the addition of $RbNO_3$, the purity could be

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improved (optimum molar ratio HF / $(NH_4)_2[B_3O_3F_4OH]$ = 2.04). The crystals of $Rb_2[B_3O_3F_4OH]$ are similar to those of the potassium salt. They may belong to the planar type of the rhombic syngony. Their solubility in water amounts to 16% at 17°C. B) Synthesis of $Cs_2[B_3O_3F_4OH]$. Boric acid and $CsHF_2$ are dissolved completely at 30°C in the ratio $2CsHF_2 + 3H_3BO_3 \longrightarrow Cs_2[B_3O_3F_4OH] + 5H_2O$. When this solution is cooled, crystallization does not occur. Only after the addition of 3.5 times as much alcohol two layers are forming, the lower of which crystallizes slowly. Also in this case, F is substituted partly by OH. An addition of 0.10 mole of HF improves the composition of the final product slightly. A crystal hydrate is formed which gives off its water only after 4 hr at 110°C and reaches the theoretical composition approximately. The water solubility of the water-free cesium salt amounts to 77.7% at 18°C. The equilibrium constants of the substitution of F by OH in dissolved boron complexes are calculated by the authors for the first and second stage of the hydrolysis: $K_1 \cong 2.2 \cdot 10^8$ and $K_2 \cong 2 \cdot 10^7$. From the total equilibrium constant of hydrolysis, from the solubility and the dissociation constant of boric acid the equilibrium constant of the process was calculated $BF_4^- - 4OH^- \rightleftarrows B(OH)_4^- + 4F^- : K_3 \simeq 6\cdot 10^{26}$. Based on the comparison of the values K_1, K_2, and K_3 the authors conclude that the equilibrium constant of the substitution of the fluorine atom by OH decreases in every stage of substitution. A substitution of OH by F is possible for low pH values only. An increasing number of F atoms in the complex reduces the pH value required for the substitution. The different stability of the triple-charged trimer fluoro-hydroxy complexes is explained by the authors as follows: in solutions, equilibrium may exist between the cyclic and the linear form of the trimer anions as well as between the trimer form and its depolarization products. The addition of any further OH or F anion entails an increase of the repulsive powers between the anions having charges of equal sign, the stability of the cyclic forms decreases. The following general conditions are mentioned for the stability of fluoro and hydroxy complexes in solutions: for low values of pH and excess of fluorine, the prevailing form is BF_4^-. When the pH is increased and the ratio F/B reduced, first of all BF_3OH^- forms and then $B_3O_3F_6^{3-}$, $B_3O_3F_5OH^{3-}$, and $B_3O_3F_4OH^{2-}$ being in the solution probably in equilibrium with the linear forms which have been formed by addition of water molecules. In case of a further slight increase of the pH, polymer boron hydroxy complexes are formed and finally $B(OH)_4^-$. Since all these boron complexes (except BF_4^-) form very quickly, they are heavy and can be separated only in a relatively narrow range of pH values and of volumetric proportion of the reagents. For the coordination of any donor by a boron atom, the plane sp^2 bonds are replaced by tetrahedral sp^3 bonds. Therefore, the plane $B_3O_3F_3$ ring will curve when liganda are added. Thus, the accommodation of large cations may be rendered difficult. Therefore, the complexes of type $M_3[B_3O_3F_6]$ are separated most easily when M = Na, whereas this is more difficult for M = K, and impossible for $M = NH_4$. It may be possible that the above-mentioned crystal hydrate of the cesium complex actually does not contain cyclic but linear anions and has an empirical

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