

ORNL
STER COPY

OAK RIDGE NATIONAL LABORATORY LIBRARIES



3 4456 0566292 1

ORNL 1490
Chemistry

GENERAL INFORMATION
CONCERNING FLUORIDES



OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION



POST OFFICE BOX P
OAK RIDGE, TENNESSEE

ORNL 1490

This document consists of 22 pages.
Copy 9 of 330 copies. Series A.

Contract No. W-7405-eng-26

AIRCRAFT NUCLEAR PROPULSION DIVISION

GENERAL INFORMATION CONCERNING FLUORIDES

Mary E. Lee

DATE ISSUED

FEB 27 1953

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

INTERNAL DISTRIBUTION

- | | |
|--|---------------------------|
| 1. C. E. Center | 33. D. W. Cardwell |
| 2. Biology Library | 34. E. M. King |
| 3. Health Physics Library | 35. A. J. Miller |
| 4-5. Central Research Library | 36. D. D. Cowen |
| 6. Reactor Experimental
Engineering Library | 37. M. E. Lee |
| 7-12. Central Files | 38. E. S. Bettis |
| 13. C. E. Larson | 39. A. P. Fraas |
| 14. W. B. Humes (K-25) | 40. L. A. Mann |
| 15. L. B. Emler (Y-12) | 41. H. F. Poppendiek |
| 16. A. M. Weinberg | 42. H. W. Savage |
| 17. E. H. Taylor | 43. W. K. Ergen |
| 18. E. D. Shipley | 44. P. M. Reyling |
| 19. R. C. Briant | 45. F. Kertesz |
| 20. F. C. VonderLage | 46. M. A. Bredig |
| 21. J. A. Swartout | 47. W. D. Manly |
| 22. S. C. Lind | 48. E. G. Bohlmann |
| 23. F. L. Steahly | 49. J. L. English |
| 24. A. H. Snell | 50. C. D. Susano |
| 25. A. Hollaender | 51. Frances Sachs |
| 26. M. T. Kelley | 52. Elizabeth Carter |
| 27. G. H. Clewett | 53. C. H. Secoy |
| 28. K. Z. Morgan | 54. E. Wischhusen |
| 29. J. S. Felton | 55. J. Courtney White |
| 30. A. S. Householder | 56. J. P. Blakely |
| 31. C. S. Harrill | 57. J. M. Adamson |
| 32. C. E. Winters | 58-67. ANP Reports Office |
| | 68-73. W. R. Grimes |

EXTERNAL DISTRIBUTION

74. B. W. O. Dickinson, Wright Air Development Center
 75-78. T. W. Laughlin, AEC, Oak Ridge
 79-330. Given distribution as shown in TID-4500 under Chemistry
 Category.

GENERAL INFORMATION CONCERNING FLUORIDES

Abstract

This report is an addition to ORNL-1252. It is a compilation of abstracts, taken from Chemical Abstracts (Sec. 4, 1952 through Sec. 22, 1952), containing general information concerning the fluorides of aluminum, barium, beryllium, calcium, cesium, lead, lithium, magnesium, potassium, rubidium, sodium, strontium and uranium.

CA 46, 405h

Coating Ferrous Metal with Aluminum or an Aluminum Alloy
Howard L. Grange and Dean K. Hanink (to General Motors Corp.)
U.S. 2,569,097, Sept. 25, 1951

Degrease the steel or ferrous material; if necessary, pickle in acid and dip in a flux soln. of $ZnCl_2$ 32, NH_4Cl 8, and H_2O 60 parts. Immerse in molten salt floating on top of a molten Al or Al alloy coating bath. Hold in a salt bath at 1300-1400°F until the metal reaches this temp. Then pass into the molten metal at between 1150° to 1600°F and hold there one second or longer. The satisfactory salt bath consisted of KCl 47, $NaCl$ 35, Na_3AlF_6 12, and AlF_3 6%, which is able to dissolve Al and Fe oxides. This salt mixt. melts at 1180°F. Addns. of about 20% $LiCl$ lowers the m.p. to 1075°F. Some control of the thickness of metal coating is obtained by holding the coated article in the molten salt and on emerging to drain excess coating material. Excess coating metal also may be removed by an air blast. The steel may be preheated in a nonoxidizing or reducing atm. before being immersed in the fused salt bath.

CA 46, 1341b

The Melting Point and Heat of Sublimation of Plutonium Trifluoride
Edgar F. Westrum, Jr., and James C. Wallmann (Univ. of Calif., Berkeley)
J. Am. Chem. Soc. 73, 3530-1 (1951)

In high vacuum and under 10^{-2} atm. A the fusion temp. of PuF_3 is $1426 \pm 2^\circ$, and the solidification temp. $1425 \pm 3^\circ$. The ΔC_p of sublimation corresponding to an equation based on vapor-pressure data (cf. Phipps, CA 44,1056of) is -32 cal/mole degree. A least-squares treatment with an assumed value of ΔC_p of -15 cal/mole degree, and 2 arbitrary const. also fit the data well and yield the equation $\log P(\text{mm}) = -24,917T^{-1} - 7.5513 \log T + 38.920$, valid from 1200 to 1660°K for the dissoch. pressure and the value 89 kcal/mole for the heat of sublimation of 1400°.

CA 46, 1419b

Corrosion Experiments with Gaseous Boron Trifluoride
F. Hudswell, J. S. Nairn, and K. L. Wilkinson (At. Energy Research Establishment, Harwell, Berks, Engl.)
J. Applied Chem. (London) 1, 333-6 (1951)

Metals, alloys, and other compds. which may be used with BF_3 were contacted with this gas at 25 cm Hg at temps. up to 200°. The extent of reaction was detd. by the change in the gas pressure over the sample. It was found that the following can be used in app. for handling dry BF_3 : stainless steel, mild steel, Cu, Ni, Monel metal, brass, and Al. The more noble metals

and Pyrex glass can be used up to about 200°. Acaldite cement, fired pyrophyllite, and polytetrafluoroethylene can be used up to 80°. Some plastics were resistant, but others cannot be used with BF_3 .

CA 46, 1857d

Thermodynamic Functions. Al_4C_3 , Si, SiO_2 , SiC, AlF_3 and Na_3AlF_6 .
L. I. Ivanova (Saratov State Univ.)
J. Gen. Chem. U.S.S.R. 21, 491-9 (1951) (Engl. translation)

See CA 45, 5014c.

CA 46, 2249a

Sodium Aluminum Fluoride

Erling Brodal and Henning Guldhav (to Aktieselskapet Norsk Aluminium Co.)
U.S. 2,567,544, Sept. 11, 1951.
Production in presence of silica.

The production of alk. Na compds. from fluorspar in presence of silica is described.

CA 46, 3334g

Liquids and Vapors as Heat-Transfer Media in the Temperature Range of 200 to 400°

Hermann Schulze

Chem.-Ing.-Tech. 23, 565-9 (1951)

Water, fused salts, liquid metals and alloys, and org. substances are discussed. Some phys. data are given.

CA 46, 3382g

Catalytic Properties of Fluorides of Alkali and Alkaline-Earth Metals

A. A. Tolstopyatova (Moscow State Univ.)

Vestnik Moskov. Univ. 6, No. 3, Ser. Fiz.-Mat. i Estestven. Nauk No. 2, 49-57 (1951)

Dehydrogenation-dehydration of EtOH passed at the rate of 0.2 ml/min over 15 g of ThO_2 (pptd. from a 10% $\text{Th}(\text{NO}_3)_4$ soln. with 20% NH_4OH at 50°, washed and dried at 120°) gave the following % decompn. and gas (% CO_2 , C_2H_4 , CO , H_2): at 287°, 4.1% (1.5, 11.5, 3.1, 84.2); at 338°, 5.8 (3.6, 24.5, 6.8, 65.1); at 348°, 10.4 (4.6, 27.3, 10.9, 57.5); at 360°, 14.8, (5.2, 31.3, 9.1, 54.4); at 420°, 43.3 (9.2, 39.1, 6.9, 44.8). Dehydrogenation to AcH predominates at lower temps; the part of dehydration to C_2H_4 increases with the temp. The apparent activation energies E_{H_2} and $E_{\text{H}_2\text{O}}$, for dehydrogenation and dehydration, resp., are 14.7 and 21.8 kcal/mole. At the same feed rate, on 12 g CaF_2 (pptd. from a 10% soln. of $\text{Ca}(\text{NO}_3)_2$ with 10% NaF, washed and dried at 120°), the data were: at 460°, 2.5%

(7.5, 0, 2.7, 89.8); at 495°, 4.3 (7.0, 2.1, 4.0, 86.8); at 510°, 7.8 (8.0, 5.2, 3.4, 83.5); at 526°, 11.9 (8.5, 4.9, 5.0, 81.6). The catalytic activity of CaF₂ is new. Despite its identical structure with ThO₂ and the near equality of the cation and anion radii, the activity of CaF₂ is considerably lower, and the part of dehydration is very much smaller; the activation energies are $E_{H_2} = 26.0$, $E_{H_2O} \sim 36$ kcal/mole. CaF₂ promoted with a trace of Fe (by pptn. of 10% CaCl₂, contg. some Fe, with 10% NH₄F at 50°) detectable with NH₄CNS, is active at lower temps. With 15 g catalyst, the data are: at 375°, 6.0 (1.6, 2.5, 1.0, 92.7); at 400°, 15.6 (3.5, 4.6, 2.5, 89.4); at 425°, 18.2 (3.7, 5.6, 5.4, 85.1); in addn. to these products, about 2% CH₄ was found in the gas with this catalyst. It can be only partially regenerated by air, and the activation energies can be detd. only approx.: $E_{H_2} \sim 35$, $E_{H_2O} \sim 53$ kcal/mole. It is striking that E is higher with promoted than with unpromoted CaF₂, although reaction with EtOH begins at lower temps. with the promoted CaF₂. The ratio E_{H_2}/E_{H_2O} is approx. const., = 0.7, with ThO₂ and with promoted or unpromoted CaF₂. For other fluorides, approx. data of the degrees of decompn. of EtOH are: 15.6 g SrF₂ (pptd. from 10% Sr(NO₃)₂ with 10% NaF at 50° and dried at 120°), at 345, 394, 426°, resp., 3.1, 6.0, 10.4%; 12 g LiF (dried at 120°), at 348, 394, 434, 450, 484°, resp., 2.4, 3.7, 2.4, 7.0, 11.7%; 15 g NaF (dried at 120°), at 348, 394, 460°, resp., 1.7, 2.3, 4.6%; 21 g KF, 370 and 460°, resp., 2.3 and 13.0%. Temps of equal catalytic activity, corresponding to 10% decompn., are: SrF₂ 425, KF 450, LiF 470, NaF 490, CaF₂ 526°. With SrF₂, LiF, and NaF, 85-90% of the gas is H₂, i.e., dehydrogenation is by far predominant; with KF, about 50% of the gas is H₂, 25% CO₂, large amts. of CH₄ and satd. hydrocarbons. Rough values of the activation energies are, for LiF and NaF, 8-9 kcal/mole, for SrF₂ 13 kcal/mole.

CA 46, 3441d

Fluorine-Active Substances

Hans Bode and Ernst Klesper (Chem. Staats-inst. Hamburg, Ger.)
Z. anorg. u. allgem. Chem. 267, 97-112 (1951)

When gaseous F which is free of HF, reacts with K, Rb, or Cs halides at low temps. (140-220°), substances higher in F than MF are obtained. The phenomenon was not observed with Li and Na halides. For Rb and Cs, according to the exptl. conditions, a limit formula of MF₃ seems to be reached. The reaction mechanism and the structure of the new substances are discussed.

CA 46, 3715d

The Importance, Manufacture, and Use of Inorganic Fluorine Compounds
K. Kersten and E. Pieschel (Dohna/Sa, Ger.)
Chem. Tech. (Berlin) 3, 296-8 (1951)

A general discussion is given of the importance and manuf. of HF, synthetic cryolite, NaF, AlF₃, silicofluorides, and fluosilicic acid, and the use of F salts in the preservation of wood.

CA 46, 3816h

Theory of the Electric Breakdown of Solid Dielectrics

A. A. Vorob'ev and E. K. Zavadovskaya (S.M. Kirov Polytech. Inst., Tomsk)
Doklady Akad. Nauk S.S.S.R. 81, 375-7 (1951)

It is assumed that elec. breakdown takes place when the energy accumulated by the electrons and transferred to the lattice is sufficient to break the bond between lattice points. The energy increment of an electron per sec is $\Delta w = eEu$, where E = field strength and u = group velocity, and hence $\Delta w = (e^2 E^2 / m) \tau(w)$, where $\tau(w)$ is the time elapsing until a collision, and is a function of w ; the reciprocal $1/\tau$ is the probability for an electron to undergo collision or deflection per unit time. This energy is transferred to the lattice; on the assumption that all of it is spent in disruption of the lattice, one has $(e^2 E^2 / m) \tau(w) \Delta t = \alpha U$, where U = lattice energy, and the time Δt of the duration of the breakdown is of the order of 10^{-8} sec. If τ were independent of E , one should have proportionality between E^2 and U . Data for alkali halides, RbI, KI, RbBr, RbCl, NaI, KCl, NaBr, NaCl, KF, NaF, LiF (in the order of increasing U) do not bear it out. More nearly, there is a linear relation between E and U (with the points for KBr, NaI, and NaBr deviating considerably from the straight line). Linearity between E and U means that τ is inversely proportional to E . If the dissocn. energy is used instead of U , i.e., if it is assumed that elec. breakdown is accompanied by dissocn. into neutral atoms rather than into ions, no linear relation is obtained. Consequently, elec. breakdown corresponds to dissocn. of the lattice into ions. Over the time interval τ , the energy accumulated by the electron, $\Delta w = (e^2 E^2 / m) \tau^2(w)$, and the exptl. data lead to the conclusion that τ is inversely proportional to $E^{1/2}$. The decrease of τ with increasing E holds only at sufficiently high E , possibly when the kinetic energy of the electrons becomes comparable with the vibration energy of the lattice points.

CA 46, 4305d

Growth of Alkali Halides from the Vapor on Single-Crystal Substrates of Alkali Halides

L. G. Schulz (Univ. of Chicago)
Acta Cryst. 5, 130-2 (1952)

Alkali halides of the NaCl-type structure (LiF, NaF, LiCl, KF, NaCl, NaBr, KCl, KBr, KI, and RbI) were deposited from the vapor phase by evapn. in a vacuum onto cleavage surfaces of LiF, NaCl, KCl, and KBr. It was found by electron diffraction that the crystals of the initial deposit were oriented with their crystallographic axes parallel to those of the substrate for all deposit-substrate combinations. Through the examn. of deposits that had an av. thickness of only a few at. layers, the mechanism of crystn. of the initial deposit was detd.

CA 46, 4871h

The Halides of Niobium and Tantalum. III. The Vapor Pressures of Niobium and Tantalum Pentafluorides

Fred Fairbrother and Wm. C. Frith (Univ. Manchester, Engl.)

J. Chem. Soc. 1951, 3051-6; cf. CA 44, 2879f

The vapor pressures of NbF_5 and TaF_5 were measured by a static method using a Bourdon-type sickle gage and by b.p. detns. under a no. of controlled pressures. Measurements near the b.p. were made in an app. in which the whole interior of the gage chamber and sickle were plated with a thin film of Ni deposited by thermally decomp. $\text{Ni}(\text{CO})_4$ in order to eliminate reactions of MF_5 and traces of moisture with the glass. NbF_5 , m. 80.0° , b. 234.9° , $\Delta H_{\text{vap}} + 12.9$ kcal, $\log p_{\text{mm}} = 8.439 - 2.824/T$. TaF_5 m. 95.1 , b. 229.2° , $\Delta H_{\text{vap}} 13.0$ kcal, $\log p_{\text{mm}} = 8.524 - 2.834/T$. Trouton's const. TaF_5 25.9, NbF_5 25.4. A mixt. of the fluorides prepd. directly by fluorination of com. ferrocolumbium is an excellent Friedel-Crafts-type catalyst.

CA 46, 4875c

Growth of Alkali Halide Crystals from the Vapor Phase and from Solution Onto Substrates of Mica

L. G. Schulz (Univ. of Chicago)

Acta Cryst. 4, 483-6 (1951) (in English); cf. CA 45, 5989e

Electron-diffraction patterns were taken in 2 positions differing by 30° in the same app. in which the films were formed by deposition from vapor onto muscovite cleavage surfaces. KF , NaCl , NaBr , KCl , NaI , KBr , KI , NH_4I , and RbI are oriented to the larger at. network in mica. LiCl with a mismatch of 30% and NaF showed a (111) fiber structure; the latter showed considerable diln. with crystals having random orientation. LiF was unique in orienting to the smaller hexagonal mica network. Salts, such as RbI with a_0 greater than 5.32\AA ., showed a double-positioned type of angular orientation when grown from the vapor phase but only a single-positioned orientation when grown from soln. Crystal growth from soln. was studied by exposing the salt deposited on the mica to moist air and evapg. H_2O after returning it to the camera. The growth of salts with a_0 less than 6.5\AA . supported the oriented nucleus hypothesis, whereas the growth of salts with a_0 greater than 6.5\AA . supported the monolayer hypothesis. Successive deposits of different alkali halides yielded films having the same orientations as the first salt deposited. A deposit of KBr thicker than about 0.5\AA . was sufficient to cause deposited LiF to have the same angular orientation as the KBr . A film of MgF_2 , amorphous and nonporous, and about 0.5\AA . thick was sufficient to upset the orientation of deposits. Close at. matching at the interface was not required for an oriented overgrowth.

Forms of the Complex Fluoroaluminates in Aqueous Solutions

G. S. Savchenko and I. V. Tananaev (N. S. Kurnakov Inst. Gen. Inorg. Chem. Acad. Sci. U.S.S.R., (Moscow)

Zhur. Obshchei Khim (J. Gen. Chem.) 21, 2235-45 (1951)

By potentiometric measurements with a quinhydrone electrode, the variation of the pH in the binary solns. $\text{Al}(\text{NO}_3)_3 + \text{H}_2\text{O}$, $\text{HF} + \text{H}_2\text{O}$, and $\text{HNO}_3 + \text{H}_2\text{O}$, with the concn. of the electrolyte is almost linear. In the ternary systems, $\text{Al}(\text{NO}_3)_3 + \text{HNO}_3 + \text{H}_2\text{O}$ and $\text{HNO}_3 + \text{HF} + \text{H}_2\text{O}$, at const. sum $\text{Al}(\text{NO}_3)_2 + \text{HNO}_3$ or $\text{HNO}_3 + \text{HF} = 0.1 \text{ M}$, the variation of the pH is almost linear in the ratio $\text{HNO}_3:\text{Al}(\text{NO}_3)_3$ or $\text{HNO}_3:\text{HF}$, resp., i.e., is detd. solely by the content of HNO_3 ; there is no indication of an interaction between either $\text{Al}(\text{NO}_3)_3$ and HNO_3 or HF and HNO_3 . In the system $\text{Al}(\text{NO}_3)_3 + \text{HF} + \text{H}_2\text{O}$, at the const. concn. sums $\text{Al}(\text{NO}_3)_3 + \text{HF} = 0.01, 0.03, \text{ and } 0.1 \text{ M}$, the pH passes through a max. lying, in all 3 cases, at the ratio $\text{HF}:\text{Al}(\text{NO}_3)_3 = 2$. Inasmuch as increase of the acidity is due only to HNO_3 , it must be concluded that, at higher ratios $\text{HF}:\text{HNO}_3$, there is a displacement of NO_3^- ions by F^- ions, i.e., at the max., a reaction $\text{Al}(\text{NO}_3)_3 + 2\text{HF} \rightarrow \text{AlF}_2\text{NO}_3 + 2\text{HNO}_3$, or $\text{Al}^{+++} + 2\text{HF} \rightarrow \text{AlF}_2^+ + 2\text{H}^+$. The same general picture is found in the systems $\text{AlCl}_3 + \text{HF} + \text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 + \text{HF} + \text{H}_2\text{O}$; in all cases, there is an undissocd. ion AlF_2^+ . The amt. of H_2SO_4 displaced, and the degree of progress of the formation of the AlF_2^+ ion, can be detd. with the aid of data of the variation of the pH with the concn. in the system $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$. By thermal measurements of the temp. rise Δt on mixing, as a function of the ratio $\text{HF}:\text{Al}$, in the systems $\text{Al}(\text{NO}_3)_3 + \text{HF} + \text{H}_2\text{O}$, and $\text{AlCl}_3 + \text{HF} + \text{H}_2\text{O}$ the heat evolved increases with the relative amt. of HF in the soln., and passes through a max. at the ratio $\text{Al}:\text{HF} = 2$, in agreement with the pH measurements; the temp. rise Δt can attain 1° . These results again reveal the formation of AlF_2^+ . There is no indication of the presence of AlF_3 , or of more highly coordinated ions. Nor is there, at the concns. used, any indication of an ion AlF^{++} , there being no singularity at the ratio $\text{HF}:\text{Al} = 1$. In the light of these conclusions, the soln. of cryolite in Al salt solns. should be explained by formation of AlF_2^+ ions, $3\text{NaF} \cdot \text{AlF}_3 + 2\text{Al}^{+++} \rightarrow 3\text{AlF}_2^+ + 3\text{Na}^+$. Contrary to Brosset (CA 37, 13-8), the easy soln. of CaF_2 in AlCl_3 solns. should be attributed not to formation of AlF_6^{---} ions, but to the reaction $\text{CaF}_2 + \text{Al}^{+++} \rightarrow \text{AlF}_2^+ + \text{Ca}^{++}$, and the analogous reaction with Be^{++} ions should be formulated $\text{CaF}_2 + 2\text{Be}^{++} \rightarrow 2\text{BeF}^+ + \text{Ca}^{++}$. It is incorrect to explain the difficulty of the decompn. of cryolite by evapn. with H_2SO_4 , by a stability of AlF_6^{---} ions; actually 2/3 of the total F in cryolite are split off very easily, $\text{AlF}_6^{---} + 4\text{H}^+ \rightarrow \text{AlF}_2^+ + 4\text{HF}$, and only the remaining 1/3 is difficult, and requires twice-repeated evapn. to dryness.

CA 46, 4986i

Separation of Iron and Nickel from Fluorides

Melvin A. Perkins and Monroe Couper (to U.S.A., represented by A.E.C.)

U.S. 2,588,041, Mar. 4, 1952

Sludge produced in making F by electrolysis of $\text{KF} \cdot 2\text{HF}$ is treated with an equal wt. of H_2O , filtered, the filter cake agitated with 23% NH_4OH for 3 hrs, filtered and washed. The filtrate is evapd. 15-20% to produce NiF_2 , and then to dryness producing K and NH_4 fluorides.

CA 46, 5276a

Alkali Aluminum Fluoride

Erling Brodal and Henning Guldhav (Aktieselskapet Norsk Aluminium Co.)

U.S. 2,592,113, Apr. 8, 1952

See Brit. 621,569 (CA 43, 7201b)

CA 46, 5278a

Sodium Aluminum Fluoride

Kenjiro Yamamoto (to Nippon Light Metals Co.)

Japan. 180,937, Nov. 15, 1949

To 320 g of an impure HF contg. 19% HF and 3% SiF_4 is added 56 g $(\text{Al}(\text{OH})_3)$ contg. 55% Al_2O_3 to make $\text{AlF}_2(\text{OH})$, then there is added 24 l. sea water (treated with 10 g NaOH per 3 l. and filtered to remove $\text{Mg}(\text{OH})_2$). The ppt. is allowed to settle, the clear upper layer is removed by decanting, and the ppt. is washed with water and heated at 500° to yield 90 g 5 $\text{NaF} \cdot 2\text{AlF}_3$.

CA 46, 5795h

Aluminum Fluoride

National Smelting Co., Ltd., and Arnold J. Edwards

Brit. 656,374, Aug. 22, 1951

AlF_3 is prepd. by passing gaseous HF upward through a fluidized bed of particles of Al_2O_3 and $\text{Al}(\text{OH})_3$ at $350-650^\circ$, the heat required for raising the temp. being wholly derived from the reaction itself if the mixt. contains a major portion of Al_2O_3 . When a considerable proportion of $\text{Al}(\text{OH})_3$ is present, addnl. heat is supplied by burning fuel. The reaction may be performed batchwise, but preferably is conducted in two or more stages. The beds of the aluminous material are superimposed, and the gas is passed in series up through them, while the aluminous material overflows from each bed to the one below.

CA 46, 5797i

Sodium Fluoride

Edward A Heisler (to Allied Chemical and Dye Corp.)

U.S. 2, 585,387, Feb. 12, 1952

Na_2SiF_6 slurry, which may be a by-product from fertilizer manuf., is treated in a continuous manner with Na_2CO_3 while withdrawing a reaction mixt. of $\text{Si}(\text{OH})_4$ and cryst. NaF . This mixt. is sent to a classifier. The small crystals are returned to the first reactor while the larger crystals and the $\text{Si}(\text{OH})_4$ go to a second reactor where NaOH is added to neutralize the acid. NaF crystals and Na_2SiO_3 soln. are recovered from the second reactor.

CA 46, 6450h

Dielectrics with a High Dielectric Strength

E. K. Zavadovskaya

Doklady Akad. Nauk S.S.S.R. 82, 709-12 (1952); cf. *ibid.* 81 375 (1951)

The previously established formula for the dielec. strength of solid dielectrics of the NaCl type, $E_s = ((7.683(a + b)/(R_A + R_B))w_A w_B) - 3.9$, expresses a relation between the close-packing of the lattice, characterized by the factor in (), and the valence bond, characterized by the factor $w_A w_B$. Calcns. by this formula of E_s for LiF , NaF , KF , LiCl , NaCl , KCl , RbCl , NaBr , KBr , RbBr , LiI , NaI , KI , RbI , MgO , CaO , BaO , and FeO are in good agreement with data of lattice energies. Fluorides, oxides, sulfides, and carbides can be expected to have a high E_s , except for certain impurity-semiconductor oxides such as Cu_2O , CdO , Ag_2O , MoO_2 , or SnO_2 which have high lattice energies but low E_s . This inconsistency is probably due to pos. type of elec. cond. and the impurity-conductor nature of these oxides; with increasing field strength, the cond. increases rapidly and breakdown occurs at relatively low field strengths. High polarizability also favors loss of elec. strength; this may lead to a low E_s , despite a high lattice energy, particularly in sulfides and selenides. In solids the first stage always consists in a perturbation of the elec. strength through liberation of electrons; the second stage is the breakdown of the lattice proper. The first stage is easiest in sulfides, then in oxides, and then in fluorides. In gases the breakdown consists wholly in the first stage.

CA 46, 6470b

Cryoscopy in Molten Lithium Borate. Cryoscopy of Fluorides

Georges Zarzycki

Compt. rend. 234, 1370-1 (1952); cf. CA 46, 3371b

Cryoscopic detns. of LiF , NaF , KF , BeF_2 , MgF_2 , CaF_2 , SrF_2 , BaF_2 , ZnF_2 , CdF_2 , PbF_2 , and AlF_3 in molten LiBO_2 showed that all were completely ionized. Natural cryolite, Na_3AlF_6 , was ionized into particles, i.e., did not form AlF_6^{3-} complexes.

Cryoscopy in Fused Cryolite and Ionic Constitution of Dissolved Aluminum
Maurice Rolin

Bull. soc. franc. elec. 2, 35-56 (1952)

The mechanism of Al electrolysis was investigated to define the phys.-chem. constitution of Al solns. in fused cryolite. The mol. state of the fused cryolite and the dissolved Al are represented by: $\text{Na}_3\text{AlF}_6 \rightarrow \text{AlF}_3 + 3\text{F}^- + 3\text{Na}^+$, and $\text{Al}_2\text{O}_3 \rightarrow \text{AlO}_2^- + \text{O}^{--} + \text{Al}^{+++}$. The fundamental mechanism of the Al electrolysis can be said to be a direct discharge of its ions and the discharge of the Na^+ ions to be only a secondary and parasitic phenomenon. The normal course of the electrolysis is thus defined as that in which only the Al ions are discharged, and the cryolite, though ionized, does not participate in the electrolysis. A 3-part diagram represents the mechanism of the electrolysis, showing in the first part the ionization of the non-electrolyzed cryolite, in the second the discharge of the Al ions, and in the third the case of eventual formation of AlO^+ ions, from which the liberation of Al atoms proceeds by the transfer of electrons.

CA 46, 6883b

Magnetochemistry of the Heaviest Elements. V. Uranium Tetrafluoride-Thorium Tetrafluoride Solid Solutions

J. K. Dawson (At. Energy Research Establishment, Harwell, Berks, Engl.)

J. Chem. Soc. 1952, 1185-6; cf. CA 46, 2863h

Owing to an arithmetical error, the concns. of U in the solid solns. previously reported were wrong. Corrected values for the susceptibilities and magnetic moments of the U(IV) ion are given that differ considerably from the previous values. The susceptibility at room temp. and the moment extrapolated to infinite diln. now agree within exptl. error with the values predicted for 2 unpaired spins with the orbital contribution to the moment completely quenched ($\chi = 3333 \times 10^{-6}$, $\mu = 2.83$). These values imply a $6d^2$ electron configuration for the uranous ion, rather than the $5f^2$ arrangement indicated by the values first reported. This agrees with the configuration indicated by the earlier work on urania-thoria solid solns.

CA 46, 6919h

The System Ammonium Fluoride-Sodium Fluoride-Water at 25°

Helmut M. Haendler and Avis Clow (Univ. of New Hampshire, Durham)

J. Am. Chem. Soc. 74, 1813 (1952)

Schreinemakers' wet-residue method (CA 40, 5328-8) was used in the study. Chem. and x-ray analyses established the compn. of the phases. No double salts are formed, and NH_4F and NaF are the only solid phases. There is no evidence for the existence of hydrated NaF in the equil. mixt.

CA 46, 7405i

Cryoscopic Study of Solutions of Certain Metallic Oxides in
The Eutectic Cryolite-Sodium Fluoride

Georges Petit

Compt. rend. 234, 1281-3 (1952)

Cryolite and the eutectic cryolite-NaF contain, resp., 25% and 14 mol % AlF_3 , and m. at 1008° and 885° , resp. The eutectic is an excellent solvent on account of nonvolatility and const. m.p. Its cryoscopic const. is only 27, as compared with 41 for cryolite. Results at the 2 temps., are plotted and discussed for La_2O_3 , ThO_2 , Al_2O_3 , CeO_2 , CaO and B_2O_3 .

CA 46, 7416i

Fusion Diagrams of the Ternary Systems of the Fluorides
of Lithium, Sodium, Potassium and Rubidium

E. P. Dergunov

Doklady Akad. Nauk S.S.S.R. 58, 1369-72 (1947); Chem. Zrntr. (Russian Zone Ed.) 1949, I, 655; cf. CA 45, 9414a

The fusion diagrams of the alkali fluorides have theoretical interest because of the formation of solid solns. and eutectics showing large m.p. reductions. For the binary system LiF-RbF the m.p. lowering from the lowest-melting component (Rb, 780°) to the eutectic is 330° . The m.p. lowering for the ternary system LiF-NaF-RbF is only slightly greater (354°). The explanation for the fact that the m.p. lowering is only slightly greater in the ternary system is probably that the tightest possible packing has already been reached in the binary system. The properties of the individual alkali fluorides and the 6 possible ternary systems are reviewed. In the ternary system LiF-KF-RbF , the crystn. curve goes as a straight line from the LiF-RbF side to the LiF-KF side of the LiF-KF-RbF triangular fusion diagram (m.p. $450-492^\circ$; crystn. zone: the solid soln. 75.4%; LiF 24.6%). In the system NaF-KF-RbF , the crystn. curve shows a min. in the neighborhood of the NaF-RbF side (m.p. $644-710^\circ$; crystn. zone: solid soln. 55.6%; NaF 44.4%). In contrast to these 2 systems, the system LiF-NaF-RbF shows 3 crystn. zones (NaF 59.4, LiF 21.1, RbF 19.5%). The ternary eutectic point is at 426° ; NaF 6.5, LiF 46.5, RbF 47 mol %.

CA 46, 7417f

Liquid-Solid Equilibria in the Quaternary System Containing NaCl , KCl , CaCl_2 , NaF , KF , and CaF_2 . (The three corresponding reciprocal ternary systems, the system containing three fluorides, and the binary system containing KF and CaF_2)

Mohammad Ishaque (Faculte sci., Paris)

Bull. soc. chim. France 1952, 127-38

Cooling curves were used to det. equil. diagrams for the various systems. Twelve solid phases were found, consisting of the 6 simple salts; 3 double salts, $2\text{KCl} \cdot 3\text{CaCl}_2$, $\text{CaCl}_2 \cdot \text{CaF}_2$, and $\text{KF} \cdot \text{CaF}_2$; 1 series of mixed crystals, without

a miscibility gap, in the system NaCl and KCl; and 2 series of mixed crystals, with a miscibility gap, within the system NaF and KF. Twelve ternary invariant points of three kinds were found: (1) eutectic, (2) peritectic, and (3) a ternary min. where the invariance is due to the fact that the solid and liquid phases keep the same compn. Eight different types of diagrams showing the following solid phases were found; (1) NaCl, NaF, and CaF₂, (2) KCl, CaF₂, and 2KCl.CaCl₂ (congruent f.p.), (3) KCl, CaF₂, and KF.CaF₂ (congruent f.p.), (4) NaCl, CaCl₂, CaF₂, and CaCl₂.CaF₂ (incongruent f.p.), (5) CaCl₂, CaF₂, 2KCl.3CaCl₂ (congruent f.p.), and CaCl₂.CaF₂ (incongruent f.p.), (6) KCl and two series of mixed crystals contg. NaF and KF, (7) CaF₂, KF.CaF₂ (congruent f.p.), and 2 series of mixed crystals contg. NaF and KF, and (8) NaF and 1 series of mixed crystals contg. NaCl and KCl.

CA 46, 7418d

Thermodynamics of Beta-KHF₂, Including Heats of Dissociation, of Fusion, and of the Alpha-Beta Transition
Merton L. Davis (Univ. of Michigan, Ann Arbor)
Univ. Microfilms (Ann Arbor, Mich.), Pub. No. 3487, 177 pp. (Microfilm \$2.21, Paper enlargements \$17.70); Dissertation Abstracts (formerly Microfilm Abstracts) 12, 130-1 (1952)

CA 46, 7449i

Hydroxytrifluoroborates

I. G. Ryss and M. M. Slutskaya (Dnepropetrovsk Met. Inst.)
Zhur. Obschchei Khim. (J. Gen. Chem.) 22, 41-8 (1952)

(1) KHF₂, 0.1 mole, was added to 4.1 g soln. contg. 0.1 mole HF, the soln. was cooled to 0°, and 0.1 mole H₃BO₃ was added with stirring. The yield of KBF₃OH was 11.6 g. The salt can be recrystd., contrary to the statement of Wamser (CA 42, 4430i). It is insol. in, and is not decompd. by, EtOH or Iso-AmOH. (2) NaBF₃OH cannot be prepd. by this method with an adequate yield and sufficiently pure. To obtain better products, mix aq. NaHF₂:H₃BO₃ = 2:1 moles at 0°, with 50-100 ml H₂O per mole H₃BO₃. Evap. the filtrate from the small amt. of NaF in vacuo or ppt. with a 4-fold vol. of EtOH. Mean yields are about 50% of the theory. NaBF₃OH is easily sol. in H₂O, very little sol. (0.3%) in EtOH, and is not decompd. by the latter. This compd. is very different from the alleged NaOH.BF₃ described by Meerwein and Pannwitz (CA 29, 1060-1). (3) On standing, the acidity of aq. KBF₃OH solns. decreases. The decompn. can be $3\text{BF}_3\text{OH}^- \rightleftharpoons 2\text{BF}_4^- + \text{H}_3\text{BO}_3 + \text{F}^-$ (I) or $2\text{BF}_3\text{OH}^- \rightleftharpoons \text{BF}_2(\text{OH})_2^- + \text{BF}_4^-$ (II). The equil. yield of BF₄⁻ increases slightly with the diln., particularly in the concn. range 0.33-0.11 M; this is taken to indicate a prevalence of the process I. The yield of BF₄⁻ also increases slightly with the temp. The calcd. heat of reaction I is 4.2 kcal.; for II, the calcd. heat of the reaction is less than 1.4 kcal. The order of the formation of BF₄⁻ is somewhat lower than first. (4) The soly. of KBF₃OH in H₂O cannot be detd. with accuracy on account of the slow decompn. of the solns.

CA 46, 7864e

Physicochemical Analysis of Ternary Aqueous Systems of Fluorides of Alkaline Earth Metals and Alkali Metals. I. Ternary Systems $\text{BaF}_2\text{-KF-H}_2\text{O}$ and $\text{BaF}_2\text{-NaF-H}_2\text{O}$
 Sh. T. Talipov and V. A. Khadeev (Central Asian State Univ., Tashkent)
 Zhur. Obshchei Khim. (J. Gen. Chem.) 20, 774-82 (1950); J. Gen. Chem. U.S.S.R. 20, 813-21 (Engl. translation).

The ternary systems were investigated by analyzing satd. solns. and wet residues according to the Schreinemakers method, all at 25° . No double salts or solid solns. are formed in either system. The soly. of BaF_2 in KF and in NaF was detd. at concns. of alkali fluoride up to 0.5 M. The exptl. results agree well with those predicted by the Debye-Huckel theory in its second approximation. Values for KF concn. (M) and for the soly. of PbF_2 (M) are, resp.: 0.0, 9.23×10^{-3} , 1.087×10^{-2} , 6.20×10^{-3} ; 5.011×10^{-2} , 1.50×10^{-3} ; 0.1001, 7.5×10^{-4} ; 0.5020, 2.2×10^{-4} . The values obtained for the soly. of PbF_2 in NaF are similar.

II. Ternary systems $\text{SrF}_2\text{-KF-H}_2\text{O}$ and $\text{SrF}_2\text{-NaF-H}_2\text{O}$. Ibid. 783-8.

No double salts or solid solns. are formed in either system, the diagrams being qualitatively identical with those for the corresponding Ba compds. Soly. of SrF_2 was studied at concns. of NaF and KF up to 0.01 M. Values of NaF concn. (M) and SrF_2 soly. (M) are, resp.: 0.00, 9.62×10^{-4} , 1.995×10^{-3} , 4.51×10^{-4} ; 3.990×10^{-3} , 2.00×10^{-4} ; 6.982×10^{-3} , 9.3×10^{-5} ; 1.096×10^{-2} , 5.0×10^{-5} . Data obtained with KF are similar.

CA 46, 7923f

The Influence of the Cation Radius on the Energy of Formation of Addition Compounds. III. The Systems Alkali Fluoride-Alkali Chromate, Molybdate, and Tungstate

O. Schmitz-Dumont and Albert Weeg (Univ. Bonn, Ger.)

Z. anorg. u. allgem. Chem. 265, 139-55 (1951); cf. CA 44, 3829f

The systems $\text{MF-M}_2\text{CrO}_4$, $\text{MF-M}_2\text{MoO}_4$ and $\text{MF-M}_2\text{WO}_4$ (M = alkali metal) were investigated thermally and by x-ray analysis. $\text{NaF-Na}_2\text{CrO}_4$, $\text{LiF-Li}_2\text{MoO}_4$ and $\text{LiF-Li}_2\text{WO}_4$ have simple eutectics and form no compds. In all other systems a compd. of the compn. $\text{M}_3\text{ZO}_4\text{F}$ exists (Z = Cr, Mo, or W). $\text{Na}_3\text{MoO}_4\text{F}$ and $\text{Na}_3\text{WO}_4\text{F}$ melt incongruently. All others melt congruently. The energy of complex formation ($\text{MoO}_4^{--} + \text{F}^- = (\text{MoO}_4\text{F})^{---}$) is negative. X-ray analysis of the fluorochromates, fluoromolybdates, and fluorotungstates show that they can be sepd. into 4 groups which contain salts isotypical with one another: (1) $\text{Na}_3\text{MoO}_4\text{F}$, $\text{Na}_3\text{WO}_4\text{F}$; (2) all fluorochromates; (3) $\text{K}_3\text{MoO}_4\text{F}$, $\text{K}_3\text{WO}_4\text{F}$; $\text{Rb}_3\text{WO}_4\text{F}$; (4) $\text{Rb}_3\text{MoO}_4\text{F}$, $\text{Cs}_3\text{MoO}_4\text{F}$, $\text{Cs}_3\text{WO}_4\text{F}$.

IV. The Systems Alkali Fluoride-Molybdenum (VI) Oxide

O. Schmitz-Dumont and Irmgard Heckman, Ibid, 267, 277-92 (1952)

Congruently melting $\text{M}_3\text{MoO}_3\text{F}_3$ occurs in the systems with KF, RbF, and CsF. In the system NaF-MoO_3 , $\text{Na}_3\text{MoO}_3\text{F}_3$ melts incongruently. $\text{Li}_3\text{MoO}_3\text{F}_3$ does not exist. The energy of complex formation of the compds. is positive. The compds. crystallize in the cubic system, and hydrolyze in damp air to $\text{M}_3\text{MoO}_4\text{F}$.

Double Fluorides of Uranium Hexafluoride

H. Martin, A. Albers, and H. P. Dust (Univ. Kiel, Ger.)

Z. anorg. u. allgem. Chem. 265, 128-38 (1951); cf. CA 43, 6102d

UF₆ (free from HF) forms fluouranates (VI) with AgF and the alkali fluorides (except LiF) at temps. below 100°. Double salts of definite compn. are obtained: 3AgF·UF₆, 3NaF·UF₆ (citron yellow), 3KF·2UF₆ (gold yellow), 2RbF·UF₆ (citron yellow). All the compds. hydrolyze immediately with H₂O. At temps. above 100°, the Na and K salts give off F along with UF₆ to form colorless fluouranates (V).

Magnetochemistry of the Heaviest Elements. VI. Plutonium Dioxide-

Thorium Dioxide and Plutonium Tetrafluoride-Thorium Tetrafluoride Solid Solutions

J. K. Dawson (At. Energy Research Establishment, Harwell, Engl.)

J. Chem. Soc. 1952, 1882-6; cf. CA 46, 2863h, 6883b

Solid solns. of PuF₄-ThF₄ and PuO₂-ThO₂ were prepd. from very pure materials, with the concn. of Pu varying from 100% to 2%. X-ray diffraction studies indicated the formation of true solid solns. The magnetic susceptibilities of most of these were measured at a no. of temps. from 90° to about 450°K., by the microbalance method (cf. CA 45, 3669h), but for low concns. only values at 300°K are given. To obtain the true paramagnetism of the Pu(IV) ion corrections for the diamagnetism of the various ions were applied. The tabulated results give χ_g (gram susceptibility, χ_m (Molar susceptibility) and $\chi_{Pu(IV)}$ (gram-ion susceptibility corrected for diamagnetism). Above 200°K PuF₄ obeys the Curie-Weiss law, but the (1/ χ)-T line curves up somewhat below 200°K. Extrapolation to infinite diln. of the PuF₄ values at 300° indicates that the susceptibility of Pu(IV) is approx. 3020x10⁻⁶, which is in reasonable agreement with that calcd. for a 5f⁴ electron configuration with L-S coupling. The susceptibility of PuO₂ is considerably lower than that of PuF₄ and does not obey the Curie-Weiss law. The results for ThO₂ indicate a very rapid increase in $\chi_{Pu(IV)}$ between 10 at. % and infinite diln., and the value at infinite diln. is about the value for a 5f⁴ configuration, although there is some evidence that 6d levels are occupied. The methods of prepn. and testing for purity are outlined.

Properties of Solutions of Beryllium Fluoride.III.

I. V. Tananaev and E. N. Deichman

Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1951, 26-31; cf. CA 43, 6049h

The systems BeF₂-H₂O, Be(NO₃)₂-H₂O, and BeF₂-Be(NO₃)₂-H₂O were studied by investigating η and d . at 25° and f.p. at salt concns. up to 2 M. In all cases η and d . increase and the f.p. decreases with increasing salt concn. In the system BeF₂-H₂O, values for BeF₂ concn. (M), $\eta \times 10^3$ (25°), and f.p.

are, resp.: 0.0, 8.85, 1.0108, 0.0; 0.4, 10.00, 1.0115, -1.6°; 1.0, 11.77, 1.0353, -4.2°; 1.4, 13.14, 1.0375, -6.9°; 2.0, 15.68, 1.0699, -10.3°. The corresponding values for $\text{Be}(\text{NO}_3)_2$ solns. are: 0.4, 10.17, 1.0302, -0.2°; 0.8, 11.61, 1.0590, -1.00°; 1.4, 14.56, 1.4563, -2.00°; 2.0, 17.71, 1.7708, -3.0°. The f.p.-concn. curves in the $\text{BeF}_2\text{-H}_2\text{O}$ system are composed of two straight-line portions intersecting at about 1.1 M BeF_2 , but in the system $\text{Be}(\text{NO}_3)_2\text{-H}_2\text{O}$ the f.p. decreases smoothly with increasing concn. In the ternary system $\text{BeF}_2\text{-Be}(\text{NO}_3)_2\text{-H}_2\text{O}$, values for η and $d.$ at 25° and for f.p. were obtained at ratios of $\text{BeF}_2/\text{Be}(\text{NO}_3)_2$ from 0.1 to 3.0 using a total concn. of $\text{BeF}_2 + \text{Be}(\text{NO}_3)_2 = 2.0$ M. Values for $\text{BeF}_2/\text{Be}(\text{NO}_3)_2$ ratio, $\eta \times 10^3$ (25°), $d.$ (25°), and f.p. are, resp.: 0.2, 17.11, 1.1330, -4.5°; 0.6, 16.61, 1.1179, -6.0°; 1.0, 16.21, 1.1061, -7.2°; 1.2, 16.17, 1.1030, -7.4°; 1.6, 16.00, 1.0985, -7.8°; 2.0, 16.13, 1.0957, -8.1°. The curves of $\text{BeF}_2/\text{Be}(\text{NO}_3)_2$ ratio against η and against f.p. show a sharp break at a ratio of 1.0. This is interpreted as an indication of the formation of the ion BeF^+ by the reaction $\text{BeF}_2 + \text{Be}^{++} = 2\text{BeF}^+$, existence of the ion having been indicated by previous work.

CA 46, 8557g

Solubility of Magnesium Fluoride in Solid Lithium Fluoride

Y. Haven

Rec. trav. chim. 69, 1505-18 (1950)

By using exptl. values detd. previously for the ionic cond. of LiF-MgF_2 mixed crystals (CA 45, 4111h) the soly. of MgF_2 in solid LiF is calcd. as 0.04-4.6 mol. % over the temp. range 400-700°. The energy of soln. of MgCl_2 in LiCl , MgF_2 in LiF , and Li_2O in LiF is also calcd., and the data are discussed in relation to Goldschmidt's theory of formation of mixed ionic crystals. In addn. to the necessary similarity in ionic r , the gain in polarization energy on soln. of the solute is also an important criterion for formation of mixed crystals, particularly in cases where the solute contains ions having a valency different from that of the solvent ions. This gain in energy is necessary to compensate the loss of Madelung energy on soln. of the solute, and is provided by polarization of the solvent lattice consequent on the charged lattice defects arising from the differently charged solute ions.

CA 46, 8598b

Corrosion by Fluorine and Fluorine Compounds

Ralph Landau (Scientific Design Co., New York, N.Y.)

Corrosion 8, 283-8 (1952)

The extreme reactivity of F is coupled with the high resistance of F compds. to chem. attack, as it tends to displace other elements and no other element is sufficiently reactive to displace F. While F is near O and Cl in the periodic table, its -2.85 v. electronegativity is the highest known so F tends to displace O and Cl from their compds. The heat of reaction of F is much greater than for O and Cl and while metals that

resist oxidation may also resist F, contaminants, especially org. materials, may react so rapidly as to initiate ignition of backing metal. Ni and Monel are resistant in clean systems; Cu, Al, and Mg are less resistant but may be used for special purposes. In the presence of moisture, when HF is formed, Monel has better resistance than Ni. Teflon or Al 2S disks should be used in valves seating on Monel. General characteristics of the fluorocarbons are given and some specific fluorocarbon materials are described. Safety precautions in handling F are discussed.

CA 46, 8819a

Sodium Bifluoride

Ernest A. Winter (to Tenn. Corp.)

U.S. 2,602,726, July 8, 1952

NaHF_2 is produced from H_2SiF_6 by treating the H_2SiF_6 first with NaF to form HF and Na_2SiF_6 , which latter is filtered off, dried, and calcined. The SiF_4 formed may be recycled to conc. the H_2SiF_6 before treatment, and the NaF is recycled to ppt. more Na_2SiF_6 . The HF formed above is concd. and mixed with NaF to ppt. NaHF_2 , which is filtered and dried. In this way NaHF_2 may be made from such cheap materials as the waste gases from superphosphate manuf.

CA 46, 9270g

Zirconium Tetrafluoride

Harley A. Wilhelm and Kenneth A. Walsh (to U.S.A., A.E.C.)

U.S. 2,602,725, July 8, 1952

A nonhygroscopic ZrF_4 is produced by treating ZrCl_4 with anhyd. HF at 50° until at least 90% conversion has occurred and then continuing to completion of the reaction at 300° . The product does not fume in moist air. By employing a complex of ZrCl_4 with POCl_3 , all of the HF contamination may be removed by distn. If a product of higher d. is desired, it may be obtained by subliming the original product at 800° .

CA 46, 9356h

The Magnetic Behavior of Nonmetallic Solid Substances

J. H. van Santen (N. V. Philips Gloeilampenfabrieken, Eindhoven, Netherlands)

Chem. Zentr. 1950, I, 1823

A summary on the magnetic behavior of nonmetallic substances, including discussion of the causes of at. dia- and paramagnetism, the Curie-Weiss law, the orbital moment and the spin moment of the individual atom, counter effects on the atom, and exchange forces as the cause of ferro- and anti-ferromagnetism. The ions of the rare earths and the ions of the elements of the Fe group are considered. Agreement is not so good for the latter group; the measured magneton value corresponds only to the electron spin. Compds.

considered are: $K_2Mn(CN)_6$, $K_3Fe(CN)_6$ (good agreement), $K_4Fe(CN)_6$, $K_3Co(CN)_6$, $K_2Ni(CN)_4$ (moment 0), $Fe(NH_3)_6Cl_2$, $Fe(NH_3)_6Cl_3$, $Co(NH_3)_6Cl_2$, $Co(NH_3)_6Cl_3$, K_3CoF_6 , $Co(NH_3)_2F_3$ (diamagnetic), $CrCl_3$, $MnCl_2$, $FeCl_2$, $FeCl_3$, Cr_2O_3 (moment in agreement with the value for the electron spin only), MnO (same as preceding), Mn_2O_3 , FeO , CoO , NiO (antiferromagnetic), Fe_3O_4 (ferromagnetic), TiO_2 , CrO_3 , MnS (antiferromagnetic), and the systems Cr-S and Fe-S (ferromagnetic within the intervals CrS_{1.10-1.18} and FeS_{1.09-1.14}). The significance of magnetic measurements for the explanation of the structure of chem. compds. is discussed, with $K_2B_2H_6$, $H_2S_2O_4$, and Hg_2Cl_2 being used as examples.

CA 46, 9965a

A Criterion of the Electrolytic Dissociation of Fused Salts

Genevieve Sutra

Compt. rend. 234, 1283-4 (1952); cf. CA 46, 3357h

The idea is developed that when an ion is formed by fusion of a salt the entropy (of fusion) should be about $3/2 R$ or 3 cal. About this value is found for the noble gases, HCl and HI. Heat of fusion, with temp. and entropy are given for NaCl, NaF, KCl, TlCl, AgCl, AgNO₃, NaNO₃ and KNO₃. These entropies are usually nearly twice those for one ion, for there are two ions here. Some salts, as KNO₃, show a lower value, perhaps owing to incomplete ionization. Data are also given for CaCl₂, BaCl₂, PbCl₂, PbI₂, HgI₂, and $K_2Cr_2O_7$. Total dissocn. should give about 9 cal. for the entropy, but most values shown are considerably below this figure. The dichromate gave a higher value, attributed to dissocn. of the dichromate ion. Similar data are given for cryolite and LiBO₂. The former appears to yield 4 ions, the latter more than 2, owing, perhaps, to a dissocn. of the borate ion (cf. Zarzycki, CA 46, 3371b).

CA 46, 10022i

Electrolysis of Fused Salts

A. J. Rudge, H. Hill, W. N. Howell, and Imperial Chemical Industries, Ltd.
Brit. 675,209, July 9, 1952

An app. is described for the production of F by the electrolysis of a mixt. of HF and an alkali metal fluoride. No diaphragm is used in the app. because constructional features, such as the placement of the electrodes, prevent mixing of evolved F with the H produced at the cathode. The F rises along the vertical surfaces of the C anode.

CA 46, 10712i

Broader Regularity in the Periodic System.

D. Balarev and St. Andreev.

Annuaire univ. Sofia. II, Fac. sci., Livre 2, 46, 159-75 (1950)

Available data on the phys. properties of oxides, and the oxide-formation power of the elements of the principal groups and the subgroups are reviewed. It is found that the sp. grs. of oxides and the heats of formation of the higher oxides, chlorides, sulfides, fluorides, bromides, and iodides show period regularities.

Bond Strengths in Boron Trifluoride and the Tetrafluoroborate Ion

J. Goubeau and W. Bues (Univ. Gottingen, Ger.)

Z. anorg. u. allgem. Chem. 268, 221-8 (1952)

The B-F bond strengths were calcd. to be 6.86×10^5 dynes/cm in BF_3 and 5.278×10^5 dynes/cm in BF_4^- from the ultraviolet and Raman spectra of B^{10}F_3 and B^{11}F_3 (Gage and Barker, CA 33, 6717-4; Yost, et al., CA 32, 7344-5; Bailey, et al., CA 31, 3784-5, 7755-6) and the Raman spectra of NaBF_4 . The stronger binding in BF_3 is caused either by partial double bond character of the BF_3 bonds or by greater ionic character of the BF_4^- bonds. The B-F bond distances in the 2 compds. and the relative B-C bond strengths in Me_3BNH_3 and Me_3B (Z. anorg. u. allgem. Chem. 268, 1 (1952)) support the first explanation.

Preparation and Physical Properties of Niobium Pentafluoride.

J. H. Junkins, R. L. Farrar, Jr., E. J. Barber, and H. A. Bernhardt (Union Carbide and Carbon Corp., Oak Ridge, Tenn.).

J. Am. Chem. Soc. 74, 3464-6 (1952)

NbF_5 is prepd. by fluorinating Nb with elemental F at 300° . Analysis of warming and cooling curves resulted in the estimates: m.p. $78.9 \pm 0.2^\circ$, heat of fusion 8600 cal/mole. The vapor-pressure data for purified liquid NbF_5 (10 to 1286 mm) are described by: $\log P_{\text{mm}} = 8.3716 - 2779.3/T$, where T is temp., $^\circ\text{K}$. From this equation the b.p. is estd. to be $233.3 \pm 0.5^\circ$. From the heat of fusion and the vapor pressure of NbF_5 at the m.p., the following expression approximating the vapor pressure over the solid is calcd.: $\log P_{\text{mm}} = 14.397 - 4900/T$. The vapor pressure at the triple point is 3.0 mm., and the heat of sublimation is calcd. to be 22,400 cal/mole. The liquid d , (g/cc) measured in the range 86 - 125° is given by: $d. = 2.8026 - 9.81 \times 10^{-4}t - 6.16 \times 10^{-6}t^2$, where t is temp., $^\circ\text{C}$. Thermodynamic quantities calcd. from the vapor-pressure data and corrected for deviation from ideality by the d . measurements are: $\Delta C_p = -8.5$ cal/degree-mole; $\Delta H_v = 16,800 - 8.5 T$; $\Delta S_v = (16,800/T) - 8.5$. The compd. is more stable toward hydrolysis than either RuF_5 or UF_6 . There is no evidence of decompn. of NbF_5 at temps. up to 255° .

The Crystal Structure of K_2TiF_6 .

Stanley Siegel (Argonne Natl. Lab., Chicago)

Acta Cryst. 5, 683-4 (1952)

K_2TiF_6 is trigonal and the structure is of the K_2GeF_6 type. The unit cell dimensions are $a = 5.715 \pm 0.002$, $c = 4.656 \pm 0.001$ A. Each Ti atom is linked to 6 F atoms at the corners of a distorted octahedron, with Ti-F = 1.91 A. This leads to a Ti^{4+} radius of 0.58 A. Each K is bonded to 12 F atoms, of which 6 are at a distance of 2.87 A., 3 at 2.75 A., and 3 at 3.08 A.

CA 46, 10809d

The kinetics of the Acid and Alkaline Hydrolysis of Methyl Fluoride in Water
D. N. Glew and E. A. Moelwyn-Hughes (Univ. Cambridge, Engl.)
Proc. Roy. Soc. (London) A211, 254-65 (1952)

The kinetics of the reaction are studied experimentally. The influence of additional solutes is studied by using HClO_4 , KClO_4 , NaF , CH_3OH , HF , and KBr . The reaction of methyl fluoride with hydroxyl ions is studied in detail. Calcd. and experimental activation energies are compared for MeF , MeBr , MeI , and MeCl .

CA 46, 10838g

Thermodynamic Properties of the Fluorine Atom and Molecule and of Hydrogen Fluoride to 5000°K.

Leland C. Cole, M. Farber, and G. W. Elverum, Jr. (California Inst. of Technol., Pasadena)
J. Chem. Phys. 20, 586-90 (1952); cf. Butkow and Rozenbaum, CA 44, 10477i.

The evaluation of the thermodynamic functions of the F atom and mol. and HF from 100°K to 5000°K were made by statistical calcs. from available spectral consts. for the atom and for HF; for F the consts. were derived or estd. from the Raman shift in gaseous F_2 , the equil. internuclear distance from electron diffraction measurements, and the heat of dissozn. These results were combined with the thermodynamic functions of H_2 to evaluate the heats and free energies of dissozn. and dissozn. consts. for the equilibria $\text{F}_2 = 2\text{F}$, $\text{HF} = 1/2\text{H}_2 + 1/2\text{F}_2$, and $\text{HF} = \text{H} + \text{F}$.

CA 46, 10839h

The Effect of Cation Radius on the Energy of Formation of Addition Compounds.
V. The Systems Alkali Dtitanate - Alkali Fluoride
O. Schmitz-Dumont and A. Hildegard Schulz (Univ. Bonn, Ger.).
Monatsh. 83, 638-49 (1952); cf. CA 46, 7923g

The systems $\text{MF-M}_2\text{Ti}_2\text{O}_5$, where M was K, Rb, or Cs, were studied by means of thermal analysis and x-rays. In the Rb and Cs systems there was a congruently melting compd., $3\text{M}_2\text{Ti}_2\text{O}_5 \cdot 2\text{MF}$, while there was none with K; the Cs compd. decompd. at room temp. As for previously investigated systems ($\text{MF-M}_2\text{CO}_3$), the energy of formation increased with cation radius to a max., then decreased, although in the present case the anions do not exist separately in the lattice, and therefore the addn. compds. are not true complex salts. Although Li_2TiO_3 and Na_2TiO_3 are definite compds., K_2TiO_3 could not be prepd. free from $\text{K}_2\text{Ti}_2\text{O}_5$ and K_2O but x-rays showed its presence; the Rb and Cs compds. behaved similarly.

A Single-Crystal Neutron-Diffraction Determination of the Hydrogen Position in Potassium Bifluoride.

S. W. Peterson and Henri A. Levy (Oak Ridge Natl. Lab., Oak Ridge, Tenn.)
J. Chem. Phys. 20, 704-7 (1952); cf. CA 46, 2369e

Neutron-diffraction measurements on KHF_2 single crystals show that the H atom occupies the central position, within 0.1 A., in the linear F-H-F ion. The data also indicate asymmetry in thermal motion, which suggests that the HF_2^- undergoes rotatory oscillation with appreciable amplitude. The study demonstrates the usefulness of single-crystal neutron-diffraction data for crystal structure detn.

The Affinities of Chromic Ion and Gallium Ion for Fluoride Ion

Archie S. Wilson and Henry Taube (Univ. of Chicago)
J. Am. Chem. Soc. 74, 3509-12 (1952)

The equil. existing in solns. contg. Cr^{3+} , H^+ , F^- , and ClO_4^- are studied by a spectrophotometric method which utilizes the change in optical d. of a soln. of Fe^{3+} when F^- is added. The quotients $(\text{CrF}^{2+})(\text{H}^+)/(\text{Cr}^{3+})(\text{HF})$, $(\text{CrF}_2^+)(\text{H}^+)/(\text{CrF}^{2+})(\text{HF})$, and $(\text{CrF}_3)(\text{H}^+)/(\text{CrF}_2^+)(\text{HF})$ at 25° and ionic strength 0.5 are estd. to be: 26.0, 2.5 (approx.), and 0.3 (approx.), resp. The equil. are established slowly. The hydrolysis quotient for Fe^{3+} , $(\text{FeOH}^{2+})(\text{H}^+)/(\text{Fe}^{3+})$, and the corresponding quotient for Ga^{3+} at 25° and ionic strength 0.5 are: 1.6×10^{-3} and 1.2×10^{-3} , resp. The quotient $(\text{GaF}^{2+})(\text{H}^+)/(\text{Ga}^{3+})(\text{HF})$ is $1.2(\pm 0.2) \times 10^2$.

The Reaction of Fluorine with Zinc, Nickel, and Some of their Binary Compounds. Some Properties of Zinc and Nickel Fluorides.

Helmut M. Haendler, Wm. L. Patterson, Jr., and Walter J. Bernard (Univ. of New Hampshire, Durham)
J. Am Chem. Soc. 74, 3167-8 (1952); Am. Doc. Inst. Doc. 3503 (film or photo-print \$1.00); cf. CA 46, 1837h

The reaction of F with Zn, ZnO, ZnBr_2 , ZnS, Ni, NiO, Ni_2O_3 , and NiS is investigated. ZnF_2 and NiF_2 are the only non-volatile products observed; the crystal structures of these fluorides are checked by x-ray diffraction. Both are tetragonal; for ZnF_2 , $a_0 = 4.7021 \pm 0.0003$ A., $c_0 = 3.1328 \pm 0.0005$ A.; for NiF_2 , $a_0 = 4.6505 \pm 0.0003$ A.; $c_0 = 3.0837 \pm 0.0005$ A. Ds. detd. pycnometrically in benzene are 5.00 ± 0.05 g/cc for ZnF_2 and 4.72 ± 0.05 g/cc for NiF_2 . ZrF_2 m. $875 \pm 3^\circ$.