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GENERAL INFORMATION CONCERNING FLUORIDES

By

Mary E. Lee

OAK RIDGE NATIONAL LABORATORY · U.S. ATOMIC ENERGY COMMISSION

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February 19, 1952

AIRCRAFT NUCLEAR PROPULSION DIVISION

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Oak Ridge, Tennessee

Contract No. W-7405-eng-26

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Date Issued: AP[illegible] 1952

GENERAL INFORMATION CONCERNING FLUORIDES

Abstract

This report is a compilation of abstracts, taken from Chemical Abstracts (1907 thru Sec. 4, 1952), containing information concerning the fluorides of aluminum, barium, beryllium, calcium, cesium, lead, lithium, magnesium, potassium, rubidium, sodium, strontium, and uranium.

CA 6, 174-4

Measurements of Specific Heats at Low Temperatures
with the Copper Calorimeter
F. Koref
Ann. Physik, 36, 49-73

.....The following substances, for certain temperature intervals (given in parentheses) have the following mean at. or mol. heats: Li, (-191 to -80), 3.61; (0 to -78), 5.15: (+19 to -75), 5.44: Na, (-191 to -83), 5.60; (0 to -77), 6.34; K, (-191 to -80), 6.14; (0 to -78), 6.51; NaF, (-191 to -82), 7.31; (0 to -75), 10.43; KF, (-192 to -82), 9.06; (0 to -76), 11.21; CaF_2 (-190 to -84), 9.69; (0 to -73), 14.90; $Ca(OH)_2$, (-191 to -80), 11.30; (0 to -78), 17.53; (+18 to -73), 18.41;..............

CA 7, 1849-6

Equilibrium in Binary Systems of Fluorides
N. A. Pushin and A. V. Baskov
J. Russ. Phys. Chem. Soc., 45, 82-101

A study of the solidification curves of several binary systems of fluorides gave the following results; AlF_3 gives definite compounds, $AlF_3 \cdot 3MF$, in which M = Li, Na, K, Rb, Cs. With Na, K and Rb it also forms compounds, $2\ AlF_3 \cdot 3\ MF$ existing in 2 modifications, and separated by a particular temperature. For Na this temperature is 600°, for K 300°, for Rb 350°. The systems $NaF\text{-}PbF_2$, and $NaF\text{-}CdF_2$ are represented by 2 very slightly concave (toward the X-axis) curves intersecting at the eutectic point. No solid solutions were observed in the systems investigated.

CA 7, 2512-5

Electrometallurgy of Aluminum
P. P. Fedotiev and V. L. Ilyinskii
Z. anorg. Chem., 80, 113-54

An investigation of NaF and AlF_3 mixtures showed the following m. ps.: NaF, 990°; eutectic $NaF\text{-}Na_3AlF_6$, 985°; $3\ NaF \cdot AlF_3$, 1000°; 46.5 mol % AlF_3, 685°, a minimum. The volatility of AlF_3 did not allow of higher readings....

CA 8, 31-8

Theory of the Production of Aluminum
R. Lorenz, A. Jabs and W. Eitel (Frankfurt a/M)
Z. anorg. Chem., 83, 39-50

A thermal and optical study of the systems Al_2O_3 - cryolite and NaF-cryolite (cf. Fedotiev and Ilyinskii, CA 7, 2512 and Pascal and Jouniaux CA 7, 2904). The system Na_3AlF_6 (m.p. 999°) - Al_2O_3 was followed up to 50 mol. % Al_2O_3; mixed crystals were formed on the Na_3AlF_6 side containing 20% Al_2O_3 and the eutectic was at 973-8° and 32-3% Al_2O_3. The results for the system Na_3AlF_6-NaF agree with those of Fedotiev and Ilyinskii, with the exception that the eutectic was found to be at 886° and 23% Na_3AlF_6, and a narrow field of mixed crystals is shown on the NaF side.

CA 9, 405-6

Specific Heats. II Alkali Halides
J. N. Brönsted (Copenhagen)
Z. Elektrochem. 20, 554-6 (1914)

The specific heats of 17 halides have been determined at a mean temperature of 10° in a Cu calorimeter. With the exception of CsCl, the mol. heat increased with mol. wt. for the same halogen, and for a single halogen, with the weight of the metal. The individual values were LiF 9.66, NaF 10.96, NaCl 11.85, NaBr 12.10, NaI 12.31, KF 11.60, KCl 12.04, KBr 12.27, KI 12.30, RbF 12.04, RbCl 12.25, RbBr 12.29, RbI 12.34, CsF 12.09, CsCl 12.56, CsBr 12.38 and CsI 12.39.

CA 9, 2024-6

Investigations on the Temperature-Coefficients of the Free Surface-Energy of Liquids between -80° and 1650°.
VII. The Specific Surface-Energy of the Molten Halides of the Alkali Metals.
F. M. Jaeger (Groningen)
Verslag Akad. Wetenschappen 23, 611-27 (1914)

The surface tension of a number of molten salts of the alkali metals was determined with the same app. which has been previously used for other liquids (cf. CA 9, 738). The necessary measurements of the d. of the various salts as a function of temperature required for the calcn. of the molar surface-energy have not yet been completed and will be published later. The variation with temperature of the specific surface-energy in ergs/cm² (X_t) of all the salts may be represented by the expression $X_t = a - b(t - t_s) + c(t - t_s)^2$ in which t_s is the m.p. and a, b and c are constants. The values of t_s, a, b, and c, resp., of the various salts are as follows: LiF, 840, 255.2, 0.126, 0; LiCl, 608, 140.2, 0.076, 0; NaF, 990, 201.6, 0.106, 0; NaCl, 801, 114.1, 0.071, 0; NaBr, 768, 106.5, 0.069, 0; NaI, 660, 88.2, 0.053, 0; KF, 858, 143.2, 0.087, 0; KCl, 780, 97.4, 0.072, 0; KBr, 734, 88.8, 0.070, 0; KI, 681, 78.3, 0.064, 0; RbF, 765, 132.0, 0.131, 0.00012; RbCl, 720, 98.3, 0.086, 0; RbBr, 685, 90.7, 0.069, 0; RbI, 642, 80.3, 0.065, 0; CsF, 692, 107.1, 0.088, 0.0004; CsCl, 646, 91.3, 0.077, 0; CsBr, 631, 83.6, 0.063, 0; CsI, 620, 91.6, 0.056, 0. From these results it is apparent that X_t as a function of t is very nearly a straight line in all cases. The following conclusions are drawn from the observations: (1) in the case of the four halides of the same alkali metal the temperature coefficient b of X decreases continually with increasing at. wt. of the halogen atom; (2) at the same temperature the value of X for the same halide of all the alkali metals decreases gradually with increasing at. wt. of the alkali metal; at the same temperature X for the four halides of the same alkali metal gradually decreases with increasing at. wt. of the halogen atom. The relations, however, do not possess a simple additive character. Finally, reasons are given for believing that the liquid Li salts possess a higher degree of molar complexity than the salts of the other alkali metals.........

CA 9, 2828-4

Thermal Analysis of Mixtures of Alkali Hydroxides with the Corresponding Halides

I. Compounds of Potassium
Giuseppe Scarpa
Atti accad. Lincei 24, I, 738-46 (1915)

It has long been known that some metallic oxides can combine with their respective halogen salts to form definite and stable compds. (called hydroxyhalides). Considerable work has been done on these compds. in the wet way but very little has been done at high temps. on the behavior of the oxides with the halides. Ruer (Z. anorg. Chem. 49, 365(1906) studied the system $PbO-PbCl_2$, Sandonnini (Atti accad. Lincei 23, I, 959 (1914) studied $PbO-PbBr_2$ and $PbO-PbF_2$ and Truthe (CA 6, 2372) studied $Cu_2O-Cu_2Cl_2$. The 1st pairs form well-defined hydroxyhalides while the last 2 show no formation of compds. S. has extended these data and this paper is a report on the K compds. The systems KOH-KF, KOH-KCl, KOH-KBr, KOH-KI were investigated. The study of these systems is made difficult by the fact that it is hard to find a container that is not attacked by KOH and by the fact that KOH tends to absorb large amts. of moisture and CO_2 from the air. The mixts. were placed in a Ag crucible (since this material is little acted upon by fused KOH in the absence of O at moderate temps.); this is placed in an Fe cylinder, covered with a porcelain cover and the whole put in a resistance furnace in a current of H_2O- and CO_2-free N. A Ag-Ni thermoelement made and calibrated in the lab was used to measure the temps. since a Pt-PtRd couple is attacked. The Ag-Ni couple was covered with a small Ag cylinder in making the solidification p. detns. and the slight changes in the Ag and Ni were found to be without appreciable effect on the e.m.f. For temps. above 900° (for KOH-KF mixts. containing much KF) a Pt crucible and Pt-PtRh couple were used with success. The KOH used was 89.53% KOH, 1.47% K_2CO_3 and 9% H_2O; the latter was removed by heating it 45 min. at 500° in the furnace in an atm. of N. The m.p. of this KOH was 380° (Hevesy (CA 4, 2763) found 360° and Neuman and

Bergve (CA 8, 3533) found 345°) and the point of transformation was 260° (Hevesy, 248°). The KF solidified at 857° (Plate (CA 2, 502) found 859.9° and Karandezen (Centr. Min. Geol. 1909) found 867°). The solidification ps. of all the mixts. of KOH and KF stand between those of the 2 components which are completely miscible in the solid state and give mixed crystals of 1 kind only. Thus the point of transformation of KOH that results from the solidification p. curve gradually falls with the increase of the concn. of KF. The KCl used in the study of KOH-KCl m. 776°. In this system the primary crystn. curve falls from the solidification p. of KCl to that of KOH and shows an elbow at 430° at 67 mol. % KOH. The mixts. from 36 to 67 mol. % KOH show, besides the primary arrest, a secondary arrest of crystn. at 430°; the mixts. from 0 to 25 and 47 to 100 mol. % KOH show an interval of crystn. due to the formation of mixed crystals. This system belongs to the 4th type of Roozeboom since it gives 2 kinds of mixed crystals and a miscibility break. The point of transformation of KOH is markedly lowered by KCl and at 82 mol. % KOH is 120°. The point on the descending crystn. curve limiting the solid soln. of KCl in KOH could not be accurately detd. The KBr used in the system KOH-KBr solidifies at 760°. The solidification diagram of this system shows that the 2 components, if the formation of mixed crystals in the mixts. containing only small amts. of KOH is disregarded, are completely miscible in the liquid state. The eutectic arrest is at 300° with 75 mol. % KOH and disappears at 0 and 85 mol. % KOH. The point of transformation of KOH is rapidly lowered at first by the addition of KBr but becomes nearly constant at 205° with 90 mol. % KOH. The KI used in the system KOH-KI solidifies at 695°. The primary crystn. curve descends from the m.ps. of the 2 components and intersects at the eutectic at 250° at 73 mol. % KOH. The point of transformation of KOH lies a little above the eutectic arrest. The system KOH-KF gives solid solns. in all proportions; KOH with KCl and KBr gives solid solns. of 2 kinds with a miscibility break; KOH and KI gives a simple eutectic.

II. Compounds of Sodium, Ibid. 955-61

In continuing the expts. described above the systems NaOH-NaF, NaOH-NaCl, NaOH-NaBr and NaOH-NaI were studied. The methods and technic were the same. The NaOH attacks Ag less than KOH and since it is stable at high temps. higher temps. could be used without any decompn. taking place. The NaOH used was 97.46% NaOH, 1.64% Na_2CO_3 and 0.9% H_2O. The m. and solidification points of NaOH are 310° and 290° (Hevesy found 318.4° to 299.5° and Neumann and Bergve found the solidification p. to be 300°); the m.p. of NaF was 1005°. The system NaOH-NaF showed the formation of mixed crystals with miscibility break, while KOH-KF gave 2 kinds of solid solns. The primary curve of crystn. lies between the solidification ps. of the 2 components and shows a slight break of 90 mol. % NaOH. For mixts. from 20 to 90 mol. % NaOH there is a 2nd arrest at 360°. The pt. of transformation of NaOH is somewhat lowered and forms, with the limit of the solid soln. of NaF in NaOH, a eutectic which shows a max. at 80 mol. % NaOH and which disappears at 5 and 100 (?) mol. % NaOH. In mixts. of 5 to 80 mol. % NaOH it was possible to det. the duration of the eutectic arrest, but from 80 to 100 mol. % NaOH the arrest due to the transformation was also present. The system NaOH-NaCl shows a diagram similar to the preceding. The NaCl m. 806°. The primary crystn. curve shows a break at 350° and 75 mol. % NaOH; from 10 to 75 mol. % NaOH there is a 2nd arrest at 360°. The pt. of transformation of NaOH is rapidly lowered by small amts. of NaCl with the solid soln. of NaCl in NaOH as the limit and the formation of an eutectic arrest which is at a max. at 73 mol. % NaOH and disappears at 5 and 100% NaOH. The solidification p. of NaBr is 776°. The system NaOH-NaBr shows complete miscibility in the liquid state. The primary crystn. curve shows 2 branches which intersect at the eutectic, 260° and 80 mol. % NaOH. There is not even a slight tendency to form solid solns. The NaI m. 665°. The system NaOH-NaI gives a decomposable compd. From the solidification p. of NaI the primary crystn. curve descends regularly to 65 mol. % NaOH where there is a distinct break; then it descends further and intersects the descending solidification p. curve from the solidification p. of NaOH in a eutectic at 220° and 83 mol. % NaOH. In the mixts. up to 65 mol. % NaOH there is a 2nd arrest in the solidification p. curve at 300° which has a max. duration at 40 mol. % NaOH. This arrest coincides with the formation of a compd. decomposable on melting; 2 NaOH · 3 NaI is probably its formula. The pt. of transformation of NaOH in a mixt. containing 3 mol. % NaI is practically the same as that of pure NaOH. Thus the systems NaOH-NaF and NaOH-NaCl give solid solns. of 2 kinds with a miscibility break; NaOH-NaBr gives a simple eutectic; NaOH-NaI gives a compd. decomposable at fusion (probably 2 NaOH · NaI).

CA 10, 1477-6

Thermal Analysis of the Mixture of the Alkali Hydroxides with the Corresponding Halides III.
Compounds of Lithium
Giuseppe Scarpa
Atti accad. Lincei 24, II, 476-82(1915)

In 2 preceding papers (CA 9, 2828) the behavior of KOH and NaOH with the K and Na halides was described; it was found that the tendency to give compds. increases from K to Na. S. has now extended these expts. to Li to see if with its smaller electroaffinity compared with Na there is a further increase in this tendency. The same methods and app. were used as before. The LiOH used contained 98.5% LiOH, 0.8% Li_2CO_3 and 0.7% H_2O. The Li salts were dehydrated in a Pt crucible. The m.p. of LiOH was found to be 462° (DeForcrand, Compt. rend. 142, 1255(1906) found 445°); that of LiF is 840°. The system LiOH-LiF shows complete miscibility in the liquid state and gives solid solns. in limited proportions. The primary crystn. curve drops from that of LiF to a eutectic at 430° at 80% LiOH and rises to the f.p. of LiOH. The freezing curve shows the eutectic arrest from 5 to 85 mol. % LiOH. LiCl m. 605°. The primary crystn. curve of the system LiOH-LiCl drops from the f.p. of LiCl to a eutectic at about 290°, showing a break at 50 mol. % LiOH and then rising to the m.p. of LiOH. The eutectic arrest for mixts. of 45-100 mol. % LiOH lies at about 285° and shows a max. duration at about 65 mol. % LiOH. Mixts. from 0 to 50 mol. % LiOH show another arrest at 315° which has a max. duration at 40 mol. % LiOH. This arrest corresponds to the formation of a compd. decompg. on fusion, which is probably 2 LiOH-3 LiCl, LiBr m. 550°. The diagram of the system LiOH-LiBr is similar to that of LiOH-LiCl. The eutectic lies at 275° with 45 mol. %

LiOH. Mixts. of 0 to 70 mol. % LiOH show a eutectic arrest which disappears between 75 and 100 mol. %; at the latter compns. there is an arrest at 310° which is max. at 75 mol. % and corresponds to the decomposable compd. 3 LiOH · LiBr. LiI m. 440°. The primary crystn. curve of the system LiOH-LiI drops from the m.p. of LiOH to the eutectic 180° at 45 mol. % LiOH and shows a strong break at 75 mol. % LiOH and then rises to a temp. of 310° at 80 mol. %, which must be due to the formation of a compd. not stable at the m.p.; it must be 4 LiOH · LiI. The results show that the tendency to give compds. between the alkali hydroxides and the halogen salts of the same metal increases gradually on passing from K to Na to Li or with diminishing electroaffinity of the ion. This agrees with the theory of Abegg and Bodlander (Z. anorg. chem. 20, 453(1903)) on electroaffinity and formation of complexes. The results of the 3 papers are summarized thus:

	Fluorides	Chlorides	Bromides	Iodides
LiOH	xx	2LiOH·3LiCl	3LiOH·LiBr	4LiOH·LiI
NaOH	xx	xx	V	2NaOH·3NaI
KOH	x--x	xx	V	V

xx indicate mixed crystals with a break, x--x mixed crystals in any proportion, V formation of a simple eutectic.

CA 11, 414-5

Investigations on the Temperature Coefficient of the Free Molecular Surface Energy of Liquids between -80° and 1650°. XV. The Determination of the Specific Gravity of Molten Salts and of the Temperature Coefficient of their Molecular Surface Energy.
F. M. Jaeger and Jul. Kahn (Groningen)
Proc. Acad. Sci. Amsterdam 19, 381-97 (1916)

The methods used for the determination of density are described. The d. of liquids was determined with a pycnometer, or, in the case of compounds, such as the low-boiling aliphatic amines, which absorb CO_2 and H_2O with avidity, with a volumeter. With inorganic salts of high melting point the d. was determined by the hydrostatic method, using a float of Pt, suspended by a fine Pt wire from the pan of an analytical balance. Following are the results for the compounds whose sp. surface energy was given in CA 9, 2024; first the temperature range used is given, then the empirical formula expressing the d. as a function of the temperature, then the value of $\delta\mu/\delta t$ in ergs per degree; when only one value of the latter is given it was sensibly const.

LiF, 887-1058°, $d^{t^\circ}_4 = 1.798-0.0004375(t-850)$, 0.40-0.58

LiCl, 626-732°, $d^{t^\circ}_4 = 1.501-0.000432(t-600)$, 0.47

$LiNO_3$, 288-546°, $d^{t°}_{4}$ = 1.755-0.000546 (t-300), 0.45

NaF, 1017-1214°, $d^{t°}_{4}$ = 1.942-0.000564 (t-1000), 0.52

$NaCl$, 823-885°, $d^{t°}_{4}$ = 1.549-0.0000626 (t-800), 0.48

$NaBr$, 787-880°, $d^{t°}_{4}$ = 2.306-0.00072 (t-780)-0.0000008$(t-780)^2$, 0.53

NaI, 675-724°, $d^{t°}_{4}$ = 2.698-0.0001061 (t-700), 0.63

Na_2SO_4, 926-1046°, $d^{t°}_{4}$ = 2.061-0.000483 (t-900), 0.30

Na_2MoO_4, 804-1063°, $d^{t°}_{4}$ = 2.795-0.000629(t-700) 1.2 between 700-800, 0.98 (800-1035), 0.56 (1035-1171)

Na_2WO_4, 917-1330°, $d^{t°}_{4}$ = 3.673-0.0009275 (t-930) + 0.000000337 $(t-930)^2$, 0.64 (700-1000), 0.98 (1515-1600)

$NaNO_3$, 350-550°, $d^{t°}_{4}$ = 1.914-0.000672(t-300), 0.24 (320-360), 0.34 (350-425), 0.45 (425-600)

$NaPO_3$, 905-1007°, $d^{t°}_{4}$ = 2.193-0.00044(t-800), 0.43 up to 1200°, 0.61 up to 1270, and 1.1 at 1500

KF, 913-1054°, $d^{t°}_{4}$ = 1.878-0.000669 (t-900), 0.33 (900-960), 0.45 (960-1060), 0.83 (1275-1310)

RbF, 820-1006°, $d^{t°}_{4}$ = 2.873-0.000967(t-825) -0.000000247$(t-825)^2$, 1.0 (802-887), 0.56(887-1037), 0.40 at higher temp.

CsF, 720-824°, $d^{t°}_{4}$ = 3.611-0.001234(t-700), 0.72 up to 930°, diminishing to 0.36 at 1100°

KCl, 785-878°, $d^{t°}_{4}$ = 1.539-0.0005947 (t-750), 0.68

KBr, 751-802°, $d^{t°}_{4}$ = 2.106-0.000799 (t-750), 0.76

KI, 700-751°, $d^{t°}_{4}$ = 2.431-0.001022 (t-700), 1.58 (730-765), 0.67 (765-815), 0.41 at higher temp.

K_2SO_4, 1102-1291°, $d^{t°}_{4}$ = 1.872-0.000545 (t-1100), 0.90

$CsBr$, 662-742°, $d^{t°}_{4}$ = 3.125-0.00134 (t-650), 0.90 (660-700), 0.57 (860-970)

CsI, 639-701°, $d^{t^{o}}_{4}$ = 3.175-0.001222 (t-640), 0.82

Cs_2SO_4, 1040-1220°, $d^{t^{o}}_{4}$ = 3.034-0.000711 (t-1040) -0.000000494 $(t-1040)^2$, 1.91 (1036-1100), 1.16 (1100-1220), 0.70(1220-1425) 0.43 up to 1530°

$CsNO_3$, 445-575°, $d^{t^{o}}_{4}$ = 2.824-0.001114 (t-400), 1.18 to 600; decreasing rapidly to 0.42

CA 16, 1039-8

Vapor Pressure of Some Salts II
H. V. Wartenberg and H. Schulze
Z. Elektrochem. 27, 568-73 (1921); cf. CA 15, 2376

Measurements have been made of the vapor pressures of LiCl, CsCl, RbCl, LiBr, CsBr, RbBr, NaF, KF, LiF, CsF, RbF, NaI, CsI, and RbI at a number of temperatures between the b.p. of the salt and 200-300° below the b.p. The vapor-pressure curves of the different fluorides are widely separated from one another; those of the other classes of salts lie closer together the higher the at. wt. of the halogen.

CA 16, 2431-9

The Regularity of the Molecular Volumes
of Inorganic Compounds
Fr. A. Henglein
Z. anorg. allgem. Chem. 120, 77-84 (1921); cf. CA 16, 1343

....the densities of lithium, sodium and potassium fluorides are 2.587, 2.726 and 2.669, resp.

CA 16, 3799-6

Studies at High Temperatures XV The Vapor Pressures
of the Alkali Fluorides
Otto Ruff, Gerhard Schmidt and Susanne Megdan
Z. anorg. allgem. Chem. 123, 83-8 (1922); cf. CA 16, 190

Vapor pressure-temperature curves for the fluorides of Cs, Rb, K, Li and Na are given between pressures of about 50 mm. Hg and 1 atm. For exptl. methods cf. CA 16, 190. The curves are roughly parallel, and the order of metals given above is the order of decreasing vapor pressure at any temperature. For any given pressure Rb has a curve about 160° above Cs, K about 80° above Rb, Li about 180° above K, and Na about 30° higher yet. The centigrade boiling points are:

LiF	NaF	KF	RbF	CsF
1670	1705	1498	1408	1253

Heats of vaporization, the Ramsay-Young consts., and critical temperatures (from the Guldberg-Guy rule) are calculated.

CA 16, 4118-1

Vapor Pressure of Some Salts III
H. V. Wartenberg and O. Bosse
Z. Elektrochem. 28, 384-7 (1922); cf. CA 15, 2376

The vapor pressure of AgCl, the chloride, bromide and sulfide of Cu, the chloride, bromide and fluoride of Pb and the chloride, bromide, fluoride and sulfide of Tl has been measured at different temperatures by the method previously employed. Determinations have been made of the vapor d. of the fluorides of K, Rb and Cs at different temperatures. These data show that alkali fluorides exist as simple mols. in the vapor state.

CA 17, 2376-5

Measurements of the Density of Aluminum Halides,
with Mercury as the Pycnometer Liquid
Wilhelm Biltz and Walter Wein
Z. anorg. allgem. Chem. 121, 257-65 (1922)

Assuming AlF_3 d. = 3.10, mol. vol. = 27.1

CA 17, 3273-1

Fusibility of the Ternary System: NaF, CaF_2, AlF_3
P. P. Fedotieff and W. P. Iljinsky
Z. anorg. allgem. Chem. 129, 93-107 (1923)

The results of the study are given in the accompanying diagram. The black portions denote the unrealizable regions. The invariant points occur at 780, 705, and 675°.

CA 19, 1368-4

Thermal Analysis of the System LiF-MgF_2
G. Tacchini
Gazz. chim. ital. 54, 777-80 (1924)

Sardonnini (Gazz. chim. ital. 41, 377 (1914); cf. CA 7, 3284) studied the system LiCl and $MgCl_2$ and found that it gave a continuous series of mixed crystals. T. examined the system LiF-MgF_2. 30 g. of mixts. of the pure salts were fused in a Pt crucible by means of a small Pt-resistance elec. furnace. The results are given in a table and a diagram. The temp.

on cooling was followed to 300° but showed no eutectic arrest in any of the mixts. The curve for the beginning of crystn. falls from 840°, the m.p. of LiF, to a min. of 670° at 68.2 mol. % MgF_2, rises slightly to 690° at 78.99 mol. % MgF_2 and then rises sharply to 1060° at 88.5 mol. % MgF_2. The app. was not suited for observing the m.ps. of higher mixts. of MgF_2, which is estd. to be about 1400° (Beck, CA 4, 279). The form of the diagram and the lack of a eutectic in all mixts. lead T. to conclude that mixed crystals are formed in all ratios. Owing to the fact that the components have different cryst. forms it is believed that the mixed crystals are decomposed but thermal evidence of this decomposition could not be obtained.

CA 19, 2581-9

Solid Solutions of Compounds of Elements of
Different Valencies
G. Bruni and G. R. Levi
Atti accad. Lincei (V), 33, ii, 377-84 (1924)

The results of X-ray analysis confirm the conclusion reached from those of thermal analysis (cf. Tacchini, CA 19, 1368) that Li and Mg fluorides form solid solutions, the mixed crystals undergoing decomposition at a low temperature. At the ordinary temperatures, solid solutions of the LiF type contg. up to 20% MgF_2 may be prepd. The replacement of a certain No. of MgF_2 mols. by a corresponding No. of double LiF mols. causes neither appreciable change in the LiF space lattice nor the appearance of new lines in the corresponding X-ray photograms, but, just as in other similar cases, the formation of the mixed crystals is accompanied by a slight increase in the volume of the elementary cell.

CA 19, 2890-6

The Crystalline Reticuli of Lithium and
Magnesium Fluorides and their Isomorphism
A. Ferrari
Atti accad. Lincei (6), 1, 664-71 (1925)

The structure of MgF_2 was determined by the powder method. The results show that it has a rutile type of structure with the following dimensions for the elementary cell containing the MgF_2 mol.: a = 4.65 A.U., C = 30.06 A. U., C/a = 0.6596. The d. deduced is 3.14. The vols. of the elementary cells containing 4 mols. in the case of LiF and 2 in that of MgF_2 are practically equal.

CA 20, 559-7

A Study of the Fluorides and Double
Fluorides of Aluminum
Martin Tosterud
J. Am. Chem. Soc. 48, 1-5 (1926)

Hydrated Al fluoride of compound $Al_2F_6 \cdot 18\ H_2O$ was prepared from Al hydrate and aq. HF. Anhyd. AlF_3 was prepared by heating the hydrate to 200°. X-ray photographs show a transition at 115-120°. The compounds $4\ KF \cdot Al_2F_6$ and $4\ RbF \cdot Al_2F_6$ were prepared in the cryst. form by subjecting the gelatinous substance to a temperature of 270° in a closed system. Two forms of the K salt, one monoclinic and the other orthorhombic, were found; the Rb salt was orthorhombic. Cond. measurements suggest the existence of an NH_4Al fluoride and NaAl fluoride.

CA 20, 2111-1

The Thermochemistry of Fluorine. II.
H. V. Wartenberg
Z. anorg. allgem. Chem. 151, 326-31 (1926)

From older data in connection with new heat of formation the following heats of formation are calculated. LiF 144.7, NaF 136.2, KF 134.2, RbF 132.8, CsF 131.5, BaF_2 278.9, TlF aq. 80.5, CaF_2 289.4, SrF_2 289.3, MgF_2 264.3, ZnF_2 193, CdF_2 aq. 173.7, FeF_2 aq. 177.2, MnF_2 aq. 206.1, CoF_2 aq. 172.8, NiF_2 aq. 171.4, AlF_3 331.5, FeF_3 aq. 253.1, CuF_2 aq. 129.8, AgF 50.1, PbF_2 156 kg-cal.

CA 21, 2436-9

Researches on the Electrometallurgy of Magnesium and
its Alloys. Pressure of the Binary System Lithium
Fluoride-Magnesium Fluoride
V. P. Hyniski and P. F. Antipine
Trav. inst. russe chim. appl. 1925, No. 84, 3-8;
Chimie et industrie 17, 601 (1927)

The fusibility of the system $LiF-MgF_2$ was determined by mixing given weights of the previously dried salts, melting in a Pt-Ir crucible, and obtaining the cooling curve by means of a Pt-Pt-Rh couple by taking readings every 15 sec., the rate of cooling being 20° per min. Pure LiF m. 837°, pure MgF_2 1225°. The eutectic mixt. contains 53% MgF_2 and m. 718°. Between 0 and 53% MgF_2 there is no eutectic, showing that LiF gives continuous solid solutions with MgF_2. At 90% MgF_2 there is another eutectic point, showing that there are no solid solutions along this branch of the curve. The solidified mixtures with high LiF contents are white and have a porcelain-like structure. Cryst. structure appears with increase in MgF_2, and with 85-90% on cooling the crucible is filled with MgF_2 needles. All the mistures contract on cooling. The fused eutectic readily dissolved

10% of MgO, and the cooling curve of the system MgF_2-LiF-MgO indicated that crystn. started at 753°; hence, the soly. of MgO is sufficient to allow for its electrolysis in the eutectic at 753°.

CA 21, 3801-8

The Fusibility of the Mixtures of Lithium and Magnesium Fluorides

V. P. Ilyinskii and P. F. Antipin
Ann. inst. anal. phys. chem. 3, 464 (1926)

The eutectic lies at 718°, solid solns. being formed on the LiF side.

CA 22, 732-8

Electrodeposition of Magnesium from Molten Fluorides

George Grube
Z. Elektrochem. angew. physik. Chem. 33, 481-7 (1927)

The ternary system for BaF_2, MgF_2, NaF was studied and the results were plotted in a diagram to determine the point of lowest m.p. About 1% of MgO could be dissolved in the different fusion mixtures. A eutectic m. 800° with the compn. BaF_2, $BaF_2 \cdot MgF_2$, $MgF_2 \cdot NaF$ and contg. 1% MgO gave a deposition of Na with Mg. The eutectic m. 850° with the compn. MgF_2, $BaF_2 \cdot MgF_2$, $MgF_2 \cdot NaF$ and contg 1% MgO deposited Mg only. 900° is the best working temp. for this system. A cathode c.d. of 5 amp. per sq. cm. yields 50% Mg; 6 amp. per sq. cm.: 53%; 7 amp. per sq. cm.: 48% Mg. A fusion contg. 20% MgF_2 and 80% BaF_2 (m. 890°) with a cathode c.d. 5 amp. per sq. cm. at 920° gave 52% yield of Mg. In most cases the Na is deposited rather than Mg, but in the cases in which Mg is deposited the Na is probably held in the complex Mg-NaF_3 as part of the ion NaF_3^-.

CA 22, 3851-8

Salt-Like Hydrides. III.

M. Proskurnin and I. Kazarnovskii
Z. anorg. allgem. Chem. 170, 301-10 (1928)

App. is described in which the d. of the hydrides can be determined pycnometrically with the exclusion of air. The d. of the hydrides of Na, K, Rb and Cs is determined and given as follows: for NaH 1.38 ± 0.04, KH 1.47, RbH 2.60 ± 0.07, CsH 3.42 ± 0.1. Moissan's values are much too low. In taking up H, a large contraction of the metal lattice takes place, which is greater for the alkali hydrides than for the alk. earth hydrides. Thus with LiH the vol. contraction in % is 24.6, with NaH 26.6%, KH 40.0%, RbH 40.7%, CsH 44.9%, CaH_2 4.2%, BaH_2 13.3%. Comparison of the mol. vol. of the hydrides with the halogenides shows a great similarity between the hydrides and fluorides. Mol. vol. of LiH is 9.8, LiF 9.98, LiCl 20.53, while for CaH_2 mol. vol. is 24.8, CaF_2 24.6, $CaCl_2$ 50.0. The ion radius of the H ions is 1.45 A. U.

CA 23, 747-5

Dilatometric Measurement of the Thermal Expansion of Unstable Crystalline Salts
W. Klemm, W. Tilk and S. V. Mullenheim
Z. anorg. allgem. Chem. 176, 1-22 (1928)

..... d_4^{25} MgF_2 3.13, ZnF_2 4.95, LiOH 1.43, NaOH 2.02, KOH 2.12 Anion vols. MgF_2 6.4, ZnF_2 5.8, LiOH 10.4, NaOH 8.0, KOH 3.6.

CA 23, 1058-3

Fluorescence and Solid Solution
Mabel K. Slattery
Proc. Nat. Acad. Sci. 14, 777-82 (1928)

NaF and LiF, activated to fluorescence by the addn. of small amts. of U, show no difference in crystal structure from the pure salts. This may be due to replacement of Li or Na by U in the lattice at random points, no distortion being expected since U has a quite small atomic radius. Mixts. of LiF and NaF (5% to 50% LiF) and a small and uniform amt. of U were fused. The fluorescent lines show a shift from the positions found in the pure fluorophors, but this shift is the same for all mixts., the increase in intensity of the LiF lines being the only change in going from the 5% to the 50% LiF mixt. Also the amt. of shift of the NaF x-ray diffraction lines is the same for all mixts. It thus appears that some Li had entered the NaF lattice but the remainder had crystallized separately. It finally appears that an increase in crystal dimensions causes an increase in wave-length of the fluorescent emission.

CA 23, 1320-9

The Fluorine Tension of Metal Fluorides and the Chemical Constants for F and HF
Karl Jellinek and A. Rudat
Z. anorg. allgem. Chem. 175, 281-320 (1928)

..... heat of formation PbF_2 155,600.

CA 23, 4874-9

Melting Point Diagram of Cryolite-Barium Fluoride
Naoto Kameyama and Eiichi Masuda
J. Soc. Chem. Ind. (Japan) 31, 1134 (1928); Suppl. Binding 32, 271B (1928)

The cryolite used contained 24.30% Al_2O_3 and 0.04% matter insol. in H_2SO_4 and HCl. BaF_2 was prepd. by double decompn. of $BaCl_2$ and NaF, and the purified product contained 0.19% NaF and 99.48% BaF_2. The NaF used was purified by pptg. contaminating sulfate with benzidine chloride. Cooling curves show a eutectic point at 835°, the eutectic mixt. being composed of BaF_2 62.5% by wt. No compd. was found.

BaF_2 in the mixt.	Beginning of freezing	Eutectic point
0 by wt.	1014°	.....
20	982	819.5
40	931	830
55	877	837
61	844	834
64	840	835
67.5	856	835
70	875	833
77.5	944	828
85	1025	820
100	1324	.....

CA 24, 2927-3

The Mixed-Crystal Series Calcium Fluoride-Strontium Fluoride
Erich Rumpf
Z. physik. Chem., Abt. B. 7, 148-54 (1930)

It was shown by means of Debye-Scherrer photographs that the mixed-crystal series CaF_2-SrF_2 satisfies the additivity rule of Vegard.

CA 24, 4208-3

Equilibrium in the Fused State between Potassium, Sodium, and their Fluorides
E. Rinck
Compt. rend. 190, 1053-4 (1930); cf. CA 24, 1787

The reaction between fused Na and K and their fluorides was studied by heating the various mixtures in Ni tubes. At 1000° the equil. const. has a value of 0.29.

CA 25, 4164-1

Densities of Molten Cryolite and of Molten
Mixtures of Cryolite and Barium Fluoride
Naoto Kameyama and Atsushi Naka
J. Soc. Chem. Ind., Japan 34, Suppl. binding 140-2 (1931)

The ds. of molten cryolite and molten mixts. of cryolite and BaF_2 were detd. by the buoyancy method; they decrease with increasing temp. The interpolated ds. at 1050° are as follows (the 1st. no. in each case indicates the percentage by wt. of BaF_2 in the melt, and the 2nd the d. in g. per cc): 0, 2.03; 21.8, 2.37; 50.0, 2.91; 62.5, 3.19; 71.6, 3.74.

CA 26, 5000-9

The Melting Diagram of the Systems: $KF-AlF_3$ and
$LiF-AlF_3$
P. P. Fedotiev and K. Timofeev
Z. anorg. allgem. Chem. 206, 263-6 (1932)

In both systems stable compds. of the cryolite type $3KF \cdot AlF_3$, m. 1025°, and $3\ LiF \cdot AlF_3$, m. 790°, were found. In melting KF with AlF_3 there is probably an unstable compd. $KF \cdot AlF_3$ with transition point at 575°, there is no evidence of a similar compd. of LiF with AlF_3.

CA 27, 2410-8

Determination of Corrosion of Iron, Chromium
and Nickel and of Corrosion- and Heat-Resistant
Alloys of these and other Metals
R. Mueller, G. Hahn and H. Krainer
Berg-U. Huttenmann, Jahrb. 80, 74-8 (June 10, 1932); Met.
Abstracts (in Metals and Alloys) 4, 32

The electrolysis of melts of fluorides requires heat- and corrosion-resisting materials. In a melt of MgF_2 at 950°, Fe was the least and Ni the most resisting, with Cr in between; after 6 hrs. Fe showed an av. loss of 10.3%, Cr 9.3%, and Ni a very slight increase in wt. due very likely to a thin film formed on the surface. Cr-C steels show at first with increasing C content a deterioration; with higher C content near the eutectic point an improvement takes place. Ni steels show with increasing Ni content an increase in corrosion resistance. Si has a slight improving influence. Cr and Ni increase the resistance considerably. Addn. of Al, Mo or Cu seems also to have a favorable effect. Replacement of Ni by Co leads to strong corrosion. In general, under the influence of molten MgF_2, pure Ni is the most resistant, highly alloyed Cr-Ni steels are a close second, while the typical heat-resisting C-Si steels are comparatively strongly attacked. The actual loss in material for all tests is tabulated.

CA 27, 3660-6

Determination of Freezing Points of the
System MgF_2-BaF_2-CaF_2
G. Fuseya, M. Mori and H. Imamura
J. Soc. Chem. Ind. Japan 36, Suppl. binding 175-6 (1933)

For obtaining a molten bath of low fusing point suitable for producing Mg from MgO, the MgF_2-BaF_2-CaF_2 system has the advantage of no co-deposition of Ba or Ca with Mg. In this system the lowest f.p. lies at 40% MgF_2, 42% BaF_2 and 18% CaF_2 and at 817° the addn. of 10% NaF lowers the f.p. to 790°.

CA 28, 400-5

Thermal Analysis of the System Lithium Fluoride-
Lithium Metaborate
I. I. Kitaigorodskii, T. A. Popova and O. K. Botvinkin
Ann. inst. anal. phys.-chim. (Leningrad) 6, 135-9;
J. Phys. Chem. (U.S.S.R.) 4, 380-2 (1933)

A thermal investigation of the system LiF-$LiBO_2$ was undertaken with the object of finding a glass capable of transmitting ultra-violet rays. The melting diagram contains a max. corresponding to the complex compd. 2 LiF · $LiBO_2$. Two polymorphic transformations in this compd., at 545° and 585°, were detd., also two in LiF, at 812° and 762°, and one in $LiBO_2$ at 785°. Eutectics were found at 688° for LiF-2 LiF · 3 $LiBO_2$, contg. 66% $LiBO_2$, and at 710° for $LiBO_2$-2LiF · 3 $LiBO_2$, contg. 80% $LiBO_2$.

CA 28, 1241-2

The Relationship between the Densities of Some
Salts in the Solid and the Liquid State. Determinations
of the Diameters and Densities of Molecules of
Salts and of the Atoms of Alkali Metals.
A. E. Makovetzkii
J. Phys. Chem. (U.S.S.R.) 4, 423-30 (1933)

The ds. of solid alkali halide salts were obtained by calcn. from data for d. of salts in the liquid state. On this basis empirical relationships are found.

CA 29, 32-2

Specific Heats of Light-Metal Fluorides at High Temperatures
A. N. Krestovnikov and G. A. Karetnikov
Legkie Metal 3, No. 4, 29-31 (1934)

The sp. heats of MgF_2, BaF_2 and Na_3AlF_6 were detd. between 300° and 1000° and that of NaF between 300-800°. Results: NaF 0.2474 + 1.88 x

$10^{-4}t + 2.53 \times 10^{-8}t^2$; MgF_2 $0.2151 + 1.73 \times 10^{-4}t + 2.66 \times 10^{-8}t^2$; BaF_2 $0.1091 + 0.711 \times 10^{-5}t + 2.96 \times 10^{-8}t^2$; Na_3AlF_6 $0.2459 + 2.51 \times 10^{-4}t - 1.255 \times 10^{-7}t^2$.

CA 29, 976-4

The Vapor Pressures of Zinc, Cadmium, Magnesium,
Calcium, Strontium, Barium, and Aluminum Fluorides
Otto Ruff and Leon Le Boucher
Z. anorg. allgem. Chem. 219, 376-81 (1934)

The b. ps., heats of evapn. and Trouton consts. are: MgF_2 2260, 69.8 cal., 27.9; CaF_2 2500, 80.3, 29.0; SrF_2 2460, 78.2, 28.6; BaF_2 2260, 69.8, 27.9; ZnF_2 1500, 45.7, 25.8; CdF_2 1748, 53.5, 26.4; AlF_3 sublimes at 1260, 78.0, -. If the vapor-tension curves are plotted (abscissas: 1/T; ordinates: log p), they are practically straight lines and intersect at $1/T = 10^{-4}$ and log p = 7.48.

CA 29, 3570-4

Effect of Chemical Combination on Atomic Constants
in Crystalline Binary Compounds
Ugo Panichi
Mem. accad. Lincei (6), 5, 471-578 (1934)

Several more or less qual. relations gained from a consideration of the changes which certain phys. consts. (at. vol., at. refraction, at. lattice energy) undergo in the act of forming a cryst. binary compd. A_mB_n, chiefly of a metal and a nonmetal, are discussed. New ds. are reported: CaI_2 4.30, SrF_2 4.06, AgF 7.10 and AlI_3 about 4.

CA 29, 5728-4

The Equilibrium Diagram of the System Barium
Fluoride-Magnesium Fluoride
Usaburo Nishioka and Masazo Okamoto
Kinzoku-no-Kenkyu 12, 220-5 (1935)

The equil. diagram of the system BaF_2-MgF_2 was constructed by measurements of sp. gr. and n of the salt mixts. in addn. to thermal and x-ray analyses. In this system a compd. $BaF_2 \cdot 2\,MgF_2$ (41.5% MgF_2) was formed through the peritectic reaction, MgF_2 + melt (21% MgF_2) $\rightleftharpoons BaF_2 \cdot 2\,MgF_2$, at 930°. The compd. and BaF_2 formed a simple eutectic (17% MgF_2), the eutectic point being 912°. By quenching the melt of this salt mixt., a glassy mass could not be obtained.

CA 29, 6497-3

Specific Heat of Calcium Fluoride at
High Temperatures
A. N. Krestovnikov and G. A. Karetnikov
Legkie Metal 4, No. 3, 16-18 (1935); cf. CA 29, 32-1

Between 300° and 1000° the sp. heat = $0.24871 + 4.251 \times 10^{-6}t + 5.844 \times 10^{-9}t^2$.

CA 29, 7770-9

Equilibrium Diagram of the System BaF_2-MgF_2
Masazo Okamoto and Usaburo Nishioka
Science Repts. Tohoku Imp. Univ. 1st Ser., 24, 141-9 (1935)

The equil. diagram of the BaF_2-MgF_2 system was detd. by means of thermal and x-ray analyses, microscopic examn., and measurements of sp. gr. and n. In the system a compd. $BaF_2 \cdot 2\, MgF_2$ is formed at 930°. This compd. in turn forms a eutectic with BaF_2 at 912° with 83 wt. % of the latter.

CA 30, 4095-9

Electrometallurgy of Aluminum
Paul Drossbach
Z. Elektrochem. 42, 65-70 (1936); cf. CA 28, 6639-6

Temp. - compn. diagrams are given for the binary systems, Na_3AlF_6-Li_3AlF_6, Na_3AlF_6-Al_2O_3 and Li_3AlF_6-Al_2O_3 and for the ternary system composed of all 3 compds. Exptl. electrolyses were made with mixts. of 65% Na_3AlF_6, 30% Li_3AlF_6 and 5% Al_2O_3. Data are given on the polarization potential and current yield under various conditions of c.d., temp. and distance between electrodes. The max. current yield obtained was 86%. The operation and elec. connections are described for a tube voltmeter for use with both a. c. and d. c.

CA 30, 4097-1

Reactions Occurring in the Production of Aluminum
by the Electrolysis of Cryolite-Alumina Melts
Paul Drossbach
Z. Elektrochem. 42, 144-7 (1936)

The e. m. f. at 950° for the decompn. of AlF_3 into its elements is given as 3.4 to 3.7v. and for NaF, 4.4 to 4.6v. These values are calcd. from available thermodynamic data. The primary reaction in the electrolysis of cryolite and alumina is the decompn. of NaF (cf. CA 18, 3516). Al and O_2 are formed by the depolarizing action of Al_2O_3.

CA 30, 4097-3

Decomposition Potentials of Molten Potassium and Sodium Fluorides
V. S. Molchanov
Legkie Metal. 4, No. 5, 28-31 (1935)

By use of a special graphite cell the decompn. potential of KF and NaF was detd. by breaks in the current-potential curve. Results: KF, 900°, 2.13v.; 940°, 2.00v; 980°, 1.70v.; NaF, 860°, 2.95v.; 920°, 2.80v.; 968°, 2.63v. and 1022°, 2.45v.

CA 31, 2894-5

Anomalous Mixed Crystals in the System SrF_2-LaF_3
J. A. H. Ketelaar and P. J. H. Willems
Rec. trav. chim. 56, 29-35 (1937)

The system SrF_2-LaF_3 was examd. by means of x-rays and d. detns. Between 0 and 30 mol. % LaF_3 anomalous mixed crystals of the fluoride structure of pure SrF_2 are formed, the lattice parameter increasing from 5.782 to 5.827A. The isomorphous replacement of Sr^{++} by La^{+++} is accompanied by a filling of vacant spaces in the lattice structure by F ions, similar in character to the formation of the so-called luteo structure.

CA 31, 4569-3

Reaction in Equilibrium of Water Vapor, at High Temperatures, with Some Metallic Fluorides
Louis Domange
Ann. chim. 7, 225-97 (1937)

....The heats of reaction (with water vapor) in cal. are: MgF_2, 900-1100°, -44300; CaF_2, 900-1100°, -48500; BaF_2, 900-1100°, -37250; PbF_2, 600-750°, -37200. The heat of formation of each of these fluorides was calcd.

CA 32, 407-1

Crystallization of Calcium Fluoride from Melts
E. V. Tsekhnovitser
J. Phys. Chem. (U.S.S.R.) 10, 88-99 (1937)

CaF_2 was melted in ZrO_2 crucibles at 1400-1500° and on crystn. gave individual crystals up to 5 mm. and those of dendritic fluid type up to 10 mm. Slight decompn. takes place at 1500° leading to a CaO content of 3%. Above 1300° the reaction $CaF_2 + 2\ NaCl \longrightarrow CaCl_2 + 2\ NaF$ takes place, both products being volatile.

CA 32, 1582-6

Decomposition Potential of Aluminum Oxide in Fused Fluorides

I. P. Tverdovskii and V. S. Molchanov
J. Applied Chem. (U.S.S.R.) 10, 1011-19 (in German 1019) (1937)

The decompn. potentials of cryolite at 1030°, 1058° and 1110° are, resp., 1.98, 1.80, and 1.55v.; for the mixt. NaF 90 + AlF_3 10% (mol.%), 2.16v. at 1000°; for NaF 51.5 + AlF_3 48.5%, there are 2 points of inflection, 1.44 (for 1000°) and 2.70v. (at 885°); for the mixt. Na_3AlF_6 plus 12% (by wt.) Al_2O_3, 1.37 and 1.45v. at 965° and 1000°, resp., and for 20% Al_2O_3, 1.50 and 1.55v., resp. The results showed a rectilinear relation with the temp.; thus the electrolysis is a homogeneous process in almost all electrolytes under investigation. The depolarization action of Al_2O_3 on F at the anode caused an accumulation of AlF_3, and the O liberated at the anode formed CO_2. Data are tabulated and plotted. 29 references.

CA 32, 3247-5

Double Decomposition in the Absence of a Solvent. XXXVI. Irreversible Reciprocal System of Sodium and Potassium Fluorides and Bromides

N. S. Dombrovskaya and Z. A. Koloskova
Ann. secteur anal. phys.-chim., Inst. chim. gen. (U.S.S.R.) 10, 211-28 (1938); cf. CA 31, 1686-4

The irreversible reciprocal system KF + NaBr $\rightleftharpoons$ NaF + KBr was studied (cf. Bergman and D., CA 31, 1686-2). According to the thermochem. reaction effect equal to 11.6 kg.-cal. the equil. is shifted toward the side NaF + KBr. By means of a stable diagonal section of NaF + KBr, representing a simple eutectic system, the square of the system (obtained by projecting the crystn. surface on the prism base, representing the property diagram of the system) is divided into 2 independent ternary systems: (1) NaF + KBr + KF with 1 ternary eutectic point at 570° and 7.5% NaF + 56% KBr + 36.5 KF, and (2) NaF + KBr + NaBr with 2 fields: (1) NaF and (2) solid solns. of bromides. A considerable no. of sections in this region showed that the line of mutual crystn. divides these fields in the form of a very oblique curve with a min. at 583° and the compn. 16.5% NaF, 29.5% KBr and 54% NaBr. The space diagram shows the presence of 3 fields of crystn: 1 field of continuous solid solns. and 2 fields of the components NaF and KF. The crystn. vols. of the solid phases are in accord with the direction of the reaction of double decompn.

CA 32, 4290-8

Beryllium Fluoride
Seri Holding S.A.
Fr. 822,302, Dec. 28, 1937

Be fluoride practically free from oxide is prepd. by heating dry $Be(OH)_2$ with pure dry NH_4HF_2 in theoretical amt. The temp. is preferably 450-500° so that sublimation of the Be fluoride is prevented.

CA 32, 5271-8

Surface Tension of Molten Mixtures Containing Cryolite
Emile Elchardus
Compt. rend. 206, 1460-2 (1938)

The surface tension (α) of cryolite alone or with addn. of amts. not exceeding 20% of NaF or AlF_3, was detd. by measuring the pressure necessary to force a bubble of gas through the molten mixt. at a temp. approx. 20° above the m.p. Addn. of AlF_3 lowers, of NaF raises α, while that of Al_2O_3 has little effect. On passing downward through the m.p. α first decreases then rapidly increases and then decreases again; or conversely increases with increased temp.; this is attributed to rapid increase in ionic dissocn. near the m.p. Cryolite when solid is Na_3AlF_6; on fusion, apart from ionic dissocn., it becomes a mixt. of AlF_3 and NaF. A labile form exists, probably $(Na_3AlF_6)_2$, which melts 8° lower than the ordinary Na_3AlF_6.

CA 32, 7686-2

Beryllium Fluoride
Seri Holding (Soc. anon.)
Fr. 826,405, Mar. 31, 1938

Dry $Be(OH)_2$ or BeO is caused to react at a high temp. (700-750°) with gaseous HF, which should be dry or contain not more than 20% of moisture. BeF_2 may be prepd. in a continuous manner.

CA 32, 7808-7

The Heat Capacity and Entropy of Barium Fluoride,
Cesium Perchlorate and Lead Phosphate
K. S. Pitzer, W. V. Smith, and W. M. Latimer
J. Am. Chem. Soc. 60, 1826-8 (1938)

The heat capacities were measured from 15° to 300°K. With these data, and by use of the Debye sp. heat equation to extrapolate from 0° to 15°K, the entropies were calcd. by graphical integration of $C_p = f(\log T)$. For BaF_2, $Pb_3(PO_4)_2$ and $CsClO_4$; $S^{\circ}291.1 = 23.03 \pm 0.1$, 85.45 ± 0.4 and 41.89 ± 0.2 cal. deg^{-1} $mol.^{-1}$, resp.

CA 33, 3227-9

Mixed-Crystal Formation between Several Fluoride Salts of Different Formula Types

E. Zintl and A. Udgard

Z. anorg. allgem. chem. 240, 150-6 (1939)

Mixts. of the binary systems LiF-MgF_2, CaF_2-ThF_4, CaF_2-YF_3 and SrF_2-LaF_3 were studied. The prepn. of the constituents is given. For the first pair mixts. contg. 5, 10 and 15 mol. % MgF_2 were tested with x-rays, characteristics lines of the latter already being strong for the 5% mixt. No mixed crystals could be found at 9 mol. %. The lattice const. of LiF does not change on melting with MgF_2. Calcns. on data for a mixt. of 33.5 mol. % YF_3 and 66.5 mol. % CaF_2 indicate crystals of the interstitial type. From a 66.6 mol. % SrF_2 and 33.3 mol. % LaF_3 a lattice const. of 5.849A. and a d. of 4.88 indicate the interstitial type of cryst. Three mixts. of 9.22, 18.6 and 27.3 mol. % CaF_2 for the fourth pair were prepd. From the lattice const. and d. the interstitial-type crystal was again indicated. The vacant lattice position type was also considered but found incompatible with the data.

CA 33, 3228-3

Mixed Crystals of Cryoliths with Clays

E. Zintl and W. Morawietz

Z. anorg. allgem. Chem. 240, 145-9 (1939)

Three mixts. of Na_3AlF_6 and α-Al_2O_3 were prepd. which contained 5, 10 and 15% of the last. The 15% mixt. showed corundum lines with x-rays but they were not present in the others. Measurements of d. gave 2.974, 2.980 and 2.977 for pure Na_3AlF_6, 5% and 10% Al_2O_3, resp. Of the various cases considered only that for formation of Na_3AlF_6 and Al_3AlO_6 gave calcd. ds. comparable to the values found. The coupling of Al and Na is explained.

CA 33, 4525-7

Electrolytic Refining of Aluminum

J. Z. Zaleski and A. Kotowicz

Przemysl Chem. 22, 536-48 (1938)

Expts. on electrolytic refining of Al in 3, horizontal, fused layers were performed in lab. as well as on a semitech. and industrial scale. The lab. investigations consisted in the detn. of the m.p. and the sp. gr. of the ternary system AlF_3- BaF_2- NaF, as well as of the m.p. of the exhausted anode alloys and of the sp. gr. of the fresh anode alloys, both in liquid state....

CA 33, 8367-2

Beryllium Fluoride
Carlo Adamoli (to Perosa Corp.)
Can. 383,438, Aug. 15, 1939

BeF_2 nearly free from oxide is prepd. by reaction of dry NH_4HF_2 with dry $Be(OH)_2$ in substantially stoichiometric proportions at 450-500°.

CA 33, 8367-3

Anhydrous Beryllium Fluoride
Carlo Adamoli and Gino Panebianco (to Perosa Corp.)
Can. 383,440, Aug. 15, 1939

Gaseous HF is made to react with $Be(OH)_2$ at high temp. in app. impermeable to HF.

CA 34, 1237-7

Vapor Pressures of Some Salts at High Temperatures
I. I. Naryshkin
J. Phys. Chem. (U.S.S.R.) 13, 528-33 (1939)

From the exptl. data on the vapor pressures at temps. from 750 to 1000°, the values of A and B in the August equation, $\log p = -(A/T) + B$, are: 8810.6, 7.982 for NaCl; 8133.0, 7.580 for KCl; 9756.0, 8.463 for KF; 11387.7, 8.654 for NaF; and 5000, 4.35 for AlF_3. The heats of evapn. and the extrapolated b. ps. are: NaCl, 40.2 Cal., 1454°; KCl, 37.2, 1457°; KF, 44.6, 1473°; NaF, 51.9, 1702°; AlF_3, 59.0, (sublimes). These values are fairly close to the av. values of other workers.

CA 34, 6143-1

Magnetic Susceptibilities of Some Fluorides
Abdul Awwal Chowdhury
Current Sci. 8, 550 (1939)

By using a Gouy balance, the following mass-susceptibility ($X\ 10^6$) data were obtained: MgF_2, 0.40 (28°); AlF_3, -0.16 (29.2°); CdF_2, -0.25 (29°); CrF_3, 91.20 (32°); FeF_3, 122.00 (32°); CuF_2, 23.00 (32.2°); ZnF_2, -0.37 (26.6°); CoF_3, 10.90 (29°); BiF_3, -0.23 (29.8°); "HgF_2(oxy)," -0.26 (29°); "HgF_2(ous)," -0.24 (29°); $KBeF_2$, -0.60 (28.6°).

CA 35, 361-7

Determination of Crystal Densities by the Temperature - of - Flotation Method. Density and Lattice Constant of Lithium Fluoride
Clyde A. Hutchison and Herrick L. Johnston
J. Am. Chem. Soc. 62, 3165-8 (1940)

A method is described for detg. the ds. of crystals to the fifth decimal place, which is a combination of "temp. flotation" of small crystals with calibration of the flotation liquid by hydrostatic weighings. By this means the d. of LiF was found to be $d_{25} = 2.63905 \pm 0.0001$. This value of the d. was used to compute the lattice const. of LiF. With the at. wt. of F taken to be 19.00 and Avogadro's No. taken as 6.064×10^{23}, this yields $a_{25} = 4.01736 \pm 0.00004$A. However, an addnl. uncertainty that may be as high as 0.00050A. is involved because of an uncertainty of 0.01 unit in the at. wt. of F. Corrected to a wave-length scale which also uses $N = 6.064 \times 10^{23}$ and takes the d. of NaCl (20°) as 2.1638, recent x-ray measurements of Straumanis (cf. CA 32, 4124-8) yield $a_{25} = 4.01732 \pm 0.00004$A. in complete agreement with the above figure. An addnl. uncertainty of at least 0.00020A. is involved because of a min. uncertainty of 0.0002 unit in the d. of NaCl. The possible future utility of a combination of d. and x-ray measurements on LiF in providing a standard of wave-length measurements, in detg. the precise value of Avogadro's No. or in comparing the at. wt. of F with that of Cl is indicated.

CA 35, 2055-9

Activity Coefficients of Sodium and Potassium Fluorides at 25° from Isopiestic Vapor-Pressure Measurements
R. A. Robinson
J. Am. Chem. Soc. 63, 628-9 (1941); cf. CA 35, 367-2

A table gives the molalities of solns. of KCl and NaF or KF that are isopiestic at 25°; from these data the activity coeffs. were calcd.; the coeff. for KF is very close to that of NaCl, whereas NaF has a much lower coeff., close to that of RbI.

CA 35, 3514-6

Density of Fused Salts of the Systems KF-NaF, K_3AlF_6-Na_3AlF_6 and (K_3AlF_6 + Na_3AlF_6)-BaF_2-Al_2O_3
G. A. Abramov
Trans. Leningrad Ind. Inst. 1939, No. 1,
Sect. Met. No. 1, 49-58 (in Eng. 59)

For the mixts. KF-NaF the d. for each compn. decreases linearly with rising temp. and the d. - temp. curves are almost parallel to one another. The mol. vols. of these mixts. at 1000° decrease linearly with increasing mole fraction of NaF. The d. of K_3AlF_6-Na_3AlF_6 mixts. increase linearly with drop in temp., whereas their mol. vols. as a function of the compn. at 1000° and 1100° deviate slightly from the law of additivity. The mol. vols. v_t at any temp. can be expressed by: $v_t = 136-36.5a + [0.047a + 0.069 (1-a)] (t-1000)$, where t is temp. and a is content of Na_3AlF_6 in mole fractions, assuming that the mol. vols. are subject to the law of additivity. The d. decreased linearly with rising temp. for the mixts. of $(K_3AlF_6 + Na_3AlF_6)$-BaF_2. The Na and K cryolites were taken in equimol. proportions. Their mol. vols. as a function of compn. at 1000° and 1100° decrease linearly with increasing mole fraction of BaF_2. The mol. vol. can be computed from $v_t = 136(1-a-b) + 99.5a + 35b + [0.069 (1-a-b) + 0.012b + 0.047a] (t-1000)$, where a is mole fraction of Na_3AlF_6 and b is mole fraction of BaF_2 in the mixt. Addn. of Al_2O_3 decreased the d. in all cases. The drop was large in presence of large amounts of BaF_2 in the mixt.

CA 35, 3514-9

Density of the Fused Salts of the Ternary Systems NaF-AlF_3-CaF_2 and NaF-AlF_3-BaF_2

G. A. Abramov and P. A. Kozunov
Trans. Leningrad Ind. Inst. 1939, No. 1, Sect. Met. No. 1, 60-73

The d. of both systems increases linearly with decreasing temp., and with increasing amts. of CaF_2 or BaF_2 the d. rises considerably. The mol. vols. of NaF and cryolite with CaF_2 or BaF_2 are subject to the law of additivity. The mixts. of NaF and AlF_3 have a max. d. situated near the compn. corresponding to cryolite. This max. is shifted to the side of NaF, the shift being greater the higher the temp. It is shown that cryolite dissocs. into Na ions and a complex ion contg. Al. The complex ion dissoc. into simple ions particularly with rising temp.

CA 35, 3549-9

Behavior of Fluorides of Sodium and Aluminum and Cryolite During their Fusion

K. P. Batachev
Trans. Leningrad Ind. Inst. 1939, No. 1, Sect. Met. No. 1, 40-8

NaF is considerably volatile and changes compn. during fusion in the open. In fusing cryolite in the open there is a fractional evapn. of the AlF_3 along with the substitution of F for O. The vapors of AlF_3 are converted to α-alumina in the surrounding air. Anhyd. AlF_3 can be prepd. by distn. in an incompletely hermetically sealed app. in an atm. of AlF_3 and HF.

CA 35, 4664-9

The Phase Diagrams for the Systems KF-MgF_2 and RbF-MgF_2
H. Remy and W. Seemann
Rec. Trav. Chim. 59, 516-25 (1940) (in German)

In the KF-MgF_2 system, the compds. $KF \cdot MgF_2$ (I) and 2 $KF \cdot MgF_2$ (II) were found. From melts with 50 to 78.5 mol. % KF, mixed crystals of I and KF first sepd., then rearranged on further cooling to give II, or mixed crystals of II with I, or with KF. The products obtained in this range were pale green. With more than 78.5% KF, there were no mixed crystals, II and KF sepg. directly from the melt. In the RbF-MgF_2 system, there were no mixed crystals; the compds. $RbF \cdot MgF_2$ and 2 $RbF \cdot MgF_2$ were found. The products contg. 50-75 mol. % RbF were greenish.

CA 37, 303-2

Fusibility Diagram of the System LiF-KF-MgF_2
A. G. Bergman and S. P. Pavlenko
Compt. rend. acad. sci. (U.R.S.S.) 30, 818-19 (1941) (in English)

The phase diagram of the system is given and discussed in detail.

CA 37, 823-1

Fusion Diagram of LiF-KF-NaF
A. G. Bergman and E. P. Dergunov
Compt. rend. acad. sci. (U.R.S.S.) 31, 753-4 (1941) (in German)
cf. CA 37, 303-2

The ternary system, of which the components m. 844, 856 and 990°, resp., consists of 3 binary systems, KF-NaF with a eutectic at 710° contg. KF 60 and NaF 40 mol. %, LiF-NaF eutectic at 652° contg. NaF 39 and LiF 61 mol. %; and LiF-KF with a eutectic at 492° contg. 50 mol. % of each. The Li binaries form neither solid solns. nor double compds. The diagram of the ternary system consists of 3 distinct crystn. areas. Of the total area NaF occupies 55, KF 23.7 and Li 21.3%. The eutectic triple point is at 454°. At this point the compn. is NaF 11.5, KF 42 and LiF 46.5 mol. %, or 11.7, 59.2 and 29.1% by wt., resp. The sp. gr. at the eutectic point is 1.99-2.13 at 460-860°. The results indicate that this ternary system is suitable for fused-salt baths at 460-1000°.

CA 37, 823-3

Fusion Diagram of the System LiF-NaF-MgF_2
A. G. Bergman and E. P. Dergunov
Compt. rend. acad. sci. (U.R.S.S.) 31, 755-6 (1941) (in German)

The binary system LiF-MgF_2 has a eutectic at 742° contg. 33 mol. % of MgF_2. This system forms a continuous chain of solid solns. NaF and MgF_2 form a compd. NaF · MgF_2, m. 1030°. This compd. forms a eutectic with NaF, m. 830°, NaF 75 mol. %, and a eutectic with MgF_2, m. 1000°, MgF_2 64 mol. %. The ternary system LiF-NaF · MgF_2 has a eutectic point 708°, at which it contains 62 mol. % of LiF. The system LiF-NaF-NaF · MgF_2 has a eutectic at 630°, at which it contains MgF_2 10, NaF 43 and LiF 47 mol. % or 17.1, 49.4 and 33.5% by wt., resp. The system LiF-MgF_2-NaF · MgF_2 has a eutectic at 684° and a compn. MgF_2 29, NaF 12 and LiF 59 mol. %, or 47.0, 13.11 and 39.89% by wt.

CA 37, 2982-7

Thermal and Röntgenographic Studies of the
System BeF_2-MgF_2
Giovanni Venturello
Atti accad. sci. Torino, classe sci. fis., Mat. nat. 76, I, 556-63 (1941); Chem. Zentr. 1942, I, 1114

The system BeF_2-MgF_2 plays an important role in the industrial production of Be. After introductory remarks on the prepn. of BeF_2 from BeO and HF with the application of NH_4F, results of a thermal investigation show a solidus line indicating complete miscibility of the two fluorides. The region studied extended from pure MgF_2 to pure BeF_2. In the region about and above 90% BeF_2 the measurements are uncertain. X-ray measurements in general confirm these results. They show the presence of BeO formed from the partial transformation of BeF_2 under the exptl. conditions employed. Debye x-ray diagrams with photometric curves are given.

CA 37, 3661-6

The Heats of Formation of Chromium (III) Fluoride,
Chromium (IV) Fluoride, Chromium (III) Chloride and
Magnesium Fluoride
H. V. Wartenberg
Z. anorg. allgem. Chem. 249, 100-12 (1942); cf. CA 36, 6097-6

.... A combination of data gives the thermochem. equation $Mg + 2\ HF \cdot aq \rightarrow MgF_2 + H_2 + aq. + (109.5 \pm 0.7)$ kg:cal. Finally a value of 261.4 ± 1 kg.-cal. per mol. is obtained for the heat of formation of MgF_2.

CA 37, 4971-2

The Electrolysis of Molten Salts
P. Drossbach
Matallwirtschaft 21, 61-3 (1942); Chem. Zentr. 1942, II, 13

....The structure of molten salts is discussed. Measured polarization potentials are given for fused LiF and PbF_2.

CA 39, 852-4

Entropies in Homologous Series of Saltlike Solids
W. D. Treadwell and B. Mauderli
Helv. Chim. Acta 27, 567-71 (1944) (in German)

$S_{298} = 14.286 (\log K + \beta \log A) + (-25.244)$ for NaF-KF
K is mol. wt. of the cation; A, that of the anion
$\beta = 1$ for 1-1 salts, $\beta = 2$ for 2-1 salts

CA 39, 1351-9

Heat Contents at High Temperatures of MgF_2 and CaF_2
B. F. Naylor
J. Am. Chem. Soc. 67, 150-2 (1945)

High-temp. heat contents above 298.16°K. of MgF_2 and CaF_2 (fluorite) were detd. from room temp. to about 1773°K. From these data heats of fusion and m. ps. also were obtained. The results are summarized by algebraic equations and a table giving the heat content and entropy increments above 298.16°K. at 100° intervals. The sp. heat relations are MgF_2 (s): $C_p = 16.93 + 0.00252T-(220,000/T^2)$, $MgF_2(l)$: $C_p = 22.57$, $CaF_2(\alpha)$: $C_p = 14.30 + 0.00728T(46,900/T^2)$, $CaF_2(\beta)$: $C_p = 25.81 + 0.00250T$ and $CaF_2(l)$: $C_p = 23.88$.

CA 39, 1807-1

Lattice Spectrum, Specific Heat and Thermal Expansion of LiF and NaF
Bisheshwar Dayal
Proc. Indian Acad. Sci. 20A, 138-44 (1944); cf. CA 39, 459-4

The lattice spectrum, sp. heat, and thermal expansion of LiF and NaF are calcd. by methods based on Raman dynamics of crystal vibrations. The mutual repulsion of the nearest F ions is considered in addn. to those existing between the neighboring ions Li and F for the calcn. on LiF. An exponential form of the repulsive potential is assumed, and the consts. are evaluated from exptl. data. Good agreement is obtained for LiF.

CA 39, 4542-6

Thermal Analysis of the System NaF-BeF_2.
X-ray Phase Analysis of the System NaF-BeF_2
A. V. Novoselova, M. E. Levina, Yu. P. Simanov and A. G. Zhasmin
J. Gen. Chem. (U.S.S.R.) 14, 385-402 (1944) (English summary)

By means of x-ray and thermal analysis of the system NaF-BeF_2 the following double salts were established: Na_2BeF_4 which melts congruently at 615°, whereas at 220 and 330° its polymorphic transformations occur; $NaBeF_3$ which melts with decompn. at 360-70°; $NaF \cdot 2\,BeF_2$ which decomposes at 280° without melting. BeF_2, prepd. from $(NH_4)_2\,BeF_4$ by distn. of NH_4F, suffers polymorphic changes at 425° and 528° and softens at 600°, with occurrence of transparency at 780°. Molten BeF_2, on cooling, solidifies to a glass without formation of any of its cryst. forms. On solidification of melts of BeF_2 with NaF the former seps. in a cryst. form. An analogy was detected between the x-ray data of this form of BeF_2 and that of α-quartz; this material has the following const. with hexagonal cell structure: a = 4.72A., c = 5.18A.

CA 40, 3953-6

Anomalous Behavior of Fused Cryolite
T. R. Scott (Council Sci. and Ind. Research, Melbourne, Australia)
Nature 157, 480-1 (1946)

Natural cryolite (Na_3AlF_6) fused in Pt gives a "wetting" melt that may creep over the edge of the crucible. The addn. of 0.02% Pb or Bi and comparable amts. of Tl makes the melt nonwetting. Tl is volatile, and its effect is temporary. The addn. of 5% of other compds. does not interfere with the effect of Pb or Bi. With K_3AlF_6, 5% Pb or 0.25% Bi is required to make the melt nonwetting. Melts of synthetic cryolite prepd. in Pb vessels are nonwetting; prepd. in rubber or Pt, are wetting. Melts of Na_2SO_4, NaF, Na_2WO_4, and K_2SO_4 are affected like cryolite; melts of NaCl and $NaPO_3$ are not. PbF_2 forms a wetting melt in Pt which becomes nonwetting on the addn. of twice its wt. of cryolite. No theoretical explanation if given.

CA 40, 4943-7

Fusion Diagram of the System KF-NaF-MgF_2
A. G. Bergman and E. P. Dergunov
Compt. rend. acad. sci. (U.R.S.S.) 48, 329-31 (1945)

The KF-NaF-MgF_2 system studied is one of the 4 triple systems forming the faces of the compn. tetrahedron of a quadruple system of Li, K, Na, and Mg fluorides, which is being investigated primarily to find fluoride fluxes for the refining of nonferrous metals and their alloys. The compds. in the KF-NaF-MgF_2 system det. the nature of the quadruple system as a whole, as the fourth component, LiF, does not form any addnl. compds. and serves only as a solvent. The method used was the visual-polythermal method, where the temps. at which the first crystals appear and the last disappear are detd. by means of a Pt/Pt-Rh thermocouple. The formation of 3 compds.-2 KF · MgF_2, KF · MgF_2, and NaF· MgF_2 - divides the compn. triangle into 4 simple systems. The resulting 3 eutectics correspond to the following temps. and compn. (in mol. %): eutectic (1) at 975° - 53.5% MgF_2 (I), 33.0% NaF (II), and 13.5% KF (III); eutectic (2) at 798° - 22.5% I, 62.5% II, and 15.0% III; and eutectic (3) at 685° - 6.5% I, 34.5% II, and 59.0% III. The transition triple point occurs at 710° and has the following compn.: 11.0% I, 39.0% II, and 50.0% III.

CA 41, 2313 g

Results of Low-Temperature Research. I. The
Molecular Heat of Lithium Fluoride between 18° and 273.2° abs.
Klaus Clusius (Univ. München)
Z. Naturforsch 1, 79-82 (1946)

The Debye continuum theory is only qualitatively valid for LiF at these low temps. The characteristic temp. θ_D has a min. of 607° at 80° abs., increasing to 648° at 273° abs., and 752° at 18° abs. At 18° abs. the av. at. heat (one-half mol. heat) C_v is 0.0065 cal/g. atom, which is about 1/1000 of the value at room temp.

CA 42, 4811 e

The Low-Temperature Heat Capacities, Enthalpies,
and Entropies of UF_4 and UF_6
F. G. Brickwedde, H. J. Hoge, R. B. Scott (Natl. Bur. of Standards)
J. Chem. Phys. 16, 429-36 (1948)

The heat capacity of UF_4 was measured from 20 to 350°K. and that of UF_6 from 14 to 370°K. Molar heat capacities are tabulated at 5° intervals and extrapolated to 0°K. From them the entropies and enthalpies of the compds. are found by integration and are tabulated. The triple-point temp. of UF_6 is 337.212°K. and the heat of fusion is 19,193 joules per mole.

CA 42, 6194 b

The Electrolytic Conductivity of Crystals IV. An
Experimental Study of the Mixed-Crystal System: SrF_2-LaF_3
Ugo Croatto and Maria Bruno (Univ. Padova, Italy)
Gazz. chim. ital 78, 95-105 (1948)

In continuation of investigations of the fluorite lattice (cf. CA 38, 4172-3, 6152-9) pure SrF_2 and anomalous mixed crystals of SrF_2-LaF_3 were studied conductometrically. Pure SrF_2 and LaF_3 were prepd. by pptn. from their aq. nitrates by pure HF, filtration, repeated evapn. with HF, and heating to a red heat. The mixed crystals were prepd. by repeated pulverization and heating, at 1100° of mixts. of SrF_2 and LaF_3 until x-ray examn. showed that equil. was reached. Röentgenographic and d. data on the mixts. are tabulated. The technique of making the cond. measurements is described in detail, and the results obtained at various temps. are given in graphs and tables. By application of the general principles developed in the previous part, it was possible to calc. on a quant. basis the lattice disorder and relative energy consts. of pure SrF_2, the transference Nos., and the mobility of the individual points of cond. The lattice disorder was found to be of purely ionic nature.

CA 42, 6695 i

Complex Formation between Alkali Metal Fluorides and Fluorides of Metals of the Fourth Group

E. P. Dergunov and A. G. Bergman (N.S. Kurnakov Inst.
Gen. Inorg. Chem. Acad. Sci. U.S.S.R., Moscow)
Doklady Akad. Nauk S.S.S.R. <u>60</u>, 391-4 (1948)

The binary system $KF-ThF_4$ shows eutectic points at 664° (17 mol. % ThF_4), 750° (33), 878° (57), and 954° (80), and maxima corresponding to K_3ThF_7 (870°), $KThF_5$ (906°), and $KF \cdot 3\ ThF_4$ (960°), the latter being a new type of compd. The system $RbF-ThF_4$, has the eutectic points 664° (15 mole % ThF_4), 762° (37), 848° (54), and 1000° (80), and maxima corresponding to Rb_3ThF_7 (974°) $RbThF_5$ (852°), and $RbF \cdot 3\ ThF_4$ (1004°). Stability of complexes of the type $Me_3^1\ ThF_7$ increases with the ionic radius of the cation; the Rb salt is more stable than the K salt, and Na and Li salts could not be obtained. Complex compds. of the type $M_2^1\ ThF_6$, analogous to $(NH_4)_2\ SiF_6$, are nonexistent; hence, the type $M_3^1\ ThF_7$ cannot be structurally related to $(NH_4)_2-SiF_6 \cdot NH_4F$, especially as the former show an unprecedently sharp max. on the melting diagram. The ternary system $KF-RbF-ThF_4$ shows an uninterrupted series of solid solns. of the 3 complex compds. with KF and with RbF, indicating perfect isomorphism of the K and the Rb complexes. The $KF-RbF-ThF_4$ triangle is divided into 3 tetragons, $KF-K_3ThF_7-Rb_3ThF_7-RbF$, $K_3ThF_7-KThF_5-RbThF_5-Rb_3ThF_7$, and $KThF_5-KF \cdot 3\ ThF_4-RbF \cdot 3\ ThF_4-RbThF_5$, and one triangle $KF \cdot 3\ ThF_4-ThF_4-RbF \cdot 3\ ThF_4$.

CA 42, 6696-c

Complex Formation between Alkali Metal Fluorides and Fluorides of Metals of the Third Group

E. P. Dergunov (N.S. Kurnakov Inst. Gen. Inorg.
Chem. Acad. Sci. U.S.S.R., Moscow)
Doklady Akad. Nauk S.S.S.R. <u>60</u>, 1185-8 (1948)

Melting diagrams are given for the binary systems: $NaF-YF_3$, deep min. at about 700°, 30 mole % YF_3; $LiF-YF_3$, eutectic 744°, 17 mole % YF_3; $KF-YF_3$, eutectic 756°, 14, compd. K_3YF_6 m. 996°; $RbF-YF_3$, eutectic 752°, 9, compd. Rb_3YF_6 m. 1064°; $CsF-YF_3$, eutectic 673°, 4, compd.

Cs_3YF_6 m.1075°; NaF-LaF_3, deep min. at 808°, 27 mole % LaF_3, incongruent compd. $NaLaF_4$, inflection pt. 920°; KF-LaF_3, eutectic 620°, 22, incongruent compd. $KLaF_4$, inflection pt. 770°; RbF-LaF_3, eutectic 582°, 20.5, incongruent compd. $RbLaF_4$, inflection pt. 684°; CsF-LaF_3, 1st eutectic 600°, 12, compd. (congruent) Cs_3LaF_6 m.795°, 2nd eutectic 726°, 34. Congruently m. compds. with sharp maxima are thus: K_3YF_6, Rb_3YF_6, Cs_3YF_6, and Cs_3LaF_6; incongruently m. compds.: $NaLaF_4$, $KLaF_4$, and $RbLaF_4$. The deep min. in the system NaF-YF_3, indicative of solid soly., confirms the isomorphism of the ions Na^+(0.98A.), CA^{++}(1.06A.) and Y^{+++} (1.06A.). The tendency to form complex compds. of the cryolite type falls from Al to La, i.e., with increasing ionic radius. Thermal stability of compds. with the same complex anion increases from Li to Cs, i.e., with increasing radius of the cation.

CA 42, 7190b

Double Fluorides of Potassium or Sodium with
Uranium, Thorium, or Lanthanum
W. H. Zachariasen (Univ. of Chicago)
J. Am. Chem. Soc. 70, 2147-51 (1948)

Many double fluorides were found in the system KF-UF_4, KF-ThF_4, KF-LaF_3, NaF-UF_4, NaF-ThF_4 and NaF-LaF_3 by the x-ray diffraction method. The observed diffraction intensities can with good approximation be attributed to the heavy atoms since the scattering powers of K, Na, and F are small compared to those of U, Th, and La. Since a small number of degrees of freedom is involved, the number and positions of the heavy atoms within the unit cell can be detd. from the intensity measurements. The vol. of the unit cell, V, and the number of heavy atoms within it, N_X, are thus accurately known exptl. quantities. The vol. of the unit cell for fluorides of the heavy elements under consideration can with good approximation be attributed to the F atoms alone, with the heavy-metal atoms fitting the interstices between the anions. The vol. requirement of a F atom may be set at V_F = 18A.^{3}; exptl. values are for UF_3 18.1, UF_4 19.4 U_2F_9 16.9, α-UF_5 19.0, β-UF_5 17.0, UF_6 19.3, LaF_3 18.2. The mean values for the vol. requirement of a K or a Na atom obtained from a number of known crystal structures are V_K = 21A.^{3} and V_{Na} = 7A.^{3}. $V = N_AV_A + N_FV_F$, where N_A and N_F are, resp., the number of alkali atoms and of F atoms per unit cell, and V_A is the vol. requirement of an alkali atom. N_A, N_X, and N_F are not independent, since the valences must be balanced. Thus N_A and N_F can be detd. in terms of the experimentally known V, V_F, V_A, and N_X. In the systems AF-XF_4, $N_A = (V-4N_XV_F)/V_A + V_F)$ and $N_F = (V + 4N_XV_A)/V_A + V_F)$; in the systems AF-$XF_3$, $N_A = (V-3N_XV_F)/(V_A + V_F)$ and $N_F = (V + 3N_XV_A)/(V_A + V_F)$. In addn. to the terminal compds. the following phases were observed: In the KF-UF_4 system: KU_6F_{25}, KU_3F_{13}, KU_2F_9, KUF_5, α-K_2UF_6, β_1-K_2UF_6, β_2-K_2UF_6, α-K_3UF_7, and α'-K_3UF_7; in the KF-ThF_4 system: KTh_6F_{25}, KTh_2F_9, $KThF_5$, α-K_2ThF_6, β_1-K_2ThF_6 and K_5ThF_9; in the KF-LaF_3 system: α-$KLaF_4$, β_1-$KLaF_4$; in the NaF-UF_4 system: $NaUF_5$, α-Na_2UF_6, β_2-Na_2UF_6, γ-Na_2UF_6, and Na_3UF_7; in the NaF-ThF_4 system: $NaTh_2F_9$, β_2-Na_2ThF_6, δ-Na_2ThF_6, and Na_4ThF_8; in the NaF-LaF_3 system: β_2-$NaLaF_4$. Crystal structure data are given also for KNp_2F_9, KPu_2F_9, $NaPuF_5$ $RbPuF_5$, $KPuF_5$ and $NaPuF_4$.

CA 42, 7190h

Complex Formation and Solid Solutions in the Ternary System Potassium Fluoride, Rubidium Fluoride and Magnesium Fluoride

E. P. Dergunov and A. G. Bergman (Inst. Gen. Inorg.
Chem., Acad. Sci. U.S.S.R., Moscow)
J. Phys. Chem. (U.S.S.R.) 22, 625-32 (1948) (in Russian)

KF, m. 856°, and RbF, m. 780°, form a continuous series of solid solns. without a min. KF and MgF_2 form 2 compds., namely, $KMgF_3$, m. 1090°, and K_2MgF_4 (a transition point at 872°); the 2 eutectics are at 12.5 mol % MgF_2 and 785° and at 68% MgF_2 and 1028°. The RbF-MgF_2 system forms the compds. $RbMgF_3$, m. 912°, and Rb_2MgF_4 m. 792°, and the eutectic at 19% MgF_2 and 686° and at 62.5% MgF_2 and 883°. In the ternary system, $KMgF_3$ forms solid solns. with any amt. of $RbMgF_3$, and K_2MgF_4 with Rb_2MgF_4. Pure MgF_2 was prepd. by heating NH_4MgF_3 at 700°.

CA 43, 8763 d

Thermodynamics of the System KHF_2-KF-HF, Including Heat Capacities and Entropies of KHF_2 and KF

Edgar F. Westrum, Jr., and K. S. Pitzer
J. Am. Chem. Soc. 71, 1940-9 (1949)

....In the range 330-530°K., the data for KF can be represented by: $H_T-H_{298.16^\circ} = 11.266T + 1.929 \times 10^{-3}T^2 + 6.88 \times 10^{-4}T^{-1}-3761.5$, $C_p = 11.266 + 3.858 \times 10^{-3}T-6.88 \times 10^{4}T^{-2}$.

CA 44, 392d

Dielectric Constants and Polarizabilities of Ions in Simple Crystals and Barium Titanate

Shepard Roberts
Phys. Rev. 76, 1215-20 (1949); cf. CA 43,4061e

The dielec. consts. and polarizabilities of ionic crystals are correlated by means of the Clausius-Mosotti equation. Polarizability changes but slightly with temp. By use of the principle of additive polarizabilities, dielec. consts. are calcd. for PbF_2, $SrCl_2$, K_2O, Li_2O, Na_2O, Rb_2O, AgF, TlI, CuF, CuI, AgI and $KMgF_3$.

CA 44, 892g

Sintering of Salts and Oxides
A. Ya. Zvoryskin and N. I. Timokhina
Zhur. Priklad. Khim. (J. Applied Chem.) 22, 1063-7 (1949)

In further development of the rule of Tammann and Z. (CA 23, 747) establishing the empirical ratio of the temps. of beginning sintering of solid powders and their temp. of fusion, $t_s/t_f = 0.44$ for salts, and 0.8 for oxides and silicates, powders sintered at definite temps. above t_s were tested for mech. strength S by detn. of the min. wt. necessary to crush a specimen of lower diam. 11, upper diam. 19, height 25 mm. For NaF, NaCl, NaBr, KCl, KBr, and KI, $t_s = 285, 204, 181, 216, 190$, and 137°, heated at 500°, S = 25.0, 47.5, 92.4, 65.6, 87.1 and 371.7 g/0.95 sq. cm., increasing, within each halide series, with decreasing lattice energy of the salt. CaF_2, heated at 400-700°, reached only small S of 9.2-56.4.....

CA 44, 896 i

Crystal Modifications of Lead Fluoride
Ya. Sauka
Zhur. Obshcheĭ Khim. (J. Gen. Chem.) 19, 1453-8 (1949)

Large crystals, up to 3 mm., can be obtained by slow pptn. occurring when dil. solns. of $Pb(NO_3)_2$ and of NH_4F are made to diffuse into each other. The product is a mixt. of the 2 known forms of PbF_2, cubic and orthorhombic. The proportion of the cubic form is the higher the slower the reaction. With very dil. solns., almost pure cubic (octahedral) PbF_2 was obtained. Replacement of $Pb(NO_3)_2$ by $Pb(OAc)_2$ favors the cubic form. Interdiffusion of concd. solns. yields almost pure rhombic PbF_2. By goniometric detns., the latter belong to the class of rhombic dipyramids. The rhombic form goes over monotropically into the cubic form. The transition point was redetd., by X-ray and microscopic examn., to 315°, considered more accurate than previous detns. (400, 200, or 280°). The d. of the cubic and rhombic forms are detd. to 7.750 and 8.445 resp. The cubic form can be obtained and maintained at lower temps., altho it is thermodynamically stable only above 315°. Along with the 2 forms of PbF_2, the ppt. contains a small amt. of mixed crystals, the compn. of which $PbF_2 \cdot 0.16\ Pb(NO_3)_2 \cdot 0.13\ H_2O$, corresponds to no definite compd., and which gradually recrystallize into either cubic or rhombic PbF_2.

CA 44, 1306 d

Tables of Osmotic and Activity Coefficients of Electrolytes in Aqueous Solution at 25°
R. A. Robinson and R. H. Stokes
Trans. Faraday Soc. 45, 612-24 (1949)

The data are tabulated for H, Li, Na, K, Rb, Cs, Al, Sc, Cr^{3+}, Y, La, Ce, Pr, Nd, Sm, and Eu chlorides; H, Li, Na, K, Rb, and Cs bromides and iodides; Na and K fluorides; H, Li, Na, K, Rb, Cs, Ag, Tl^+, Cr^{3+}, and Th^{4+} nitrates; Li, Na, K and Cs hydroxides; H, Li, Na and Tl perchlorates; Na and K chlorates; Na and K bromates; Cu^{2+}, Mg, Zn^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Al, and Cr^{3+} sulfates; Li, Na, K, Rb, Sc, and Tl acetates; Li, Na, and K toluenesulfonates; Na and K thiocyanates; NaH_2PO_4; $K_4Fe(CN)_6$; KH_2PO_4 and sucrose.

CA 44, 1313 f

Comparison of the Catalytic Activities of Some
Solid Salts in the Recombination of Hydrogen Free
Atoms (Atomic Hydrogen) and Hydroxyl Free Radicals
(Free Hydroxyl Radicals)
Mikko Tamura and Shoji Shida
Rev. Phys. Chem. Japan, Shinkichi Horiba Commem. Vol. 1946, 115-20

The negative catalytic effect of some solid salts on the combustion of H_2 and some org. compds. may be caused by the recombination of H atoms and OH radicals on the solid surfaces. To test this theory, water vapor was passed thru a Wood's discharge tube, past a thermometer coated with the solid salt, thru a trap cooled with solid CO_2 and alc., and finally was pumped out by a vacuum diffusion pump and an oil pump. The rise in temp. was measured for KF, KCl, KBr, KI, KCl, NaCl, RbCl, LiCl, NaF, LiF, Li_2CO_3, Na_2SO_4, Na_2CO_3, $NaNO_3$, K_2SO_4, NH_4Cl, KNO_3, $MgCl_2$, $Ca(NO_3)_2$, CaF_2, Pt, K_2CO_3, and glass. The order of catalytic activity decreased in the order Rb, K, Na, Li for carbonates, halides, and nitrates and in the order metal, carbonates, nitrates, halides for K and Na salts. The fluorides and sulfates of K and Na are inactive. In general, the more pos. the cation and the less neg. the anion, the more active the salt. For the alkali halides, the smaller the lattice energy, the greater the catalytic activity.

CA 44, 1316 g

Chemical Investigations of Silicates
XII. The System Lithium Fluoride-Beryllium Fluoride
and its Relation to the System Magnesia-Silica
Erich Thilo and Hans Albert Lehmann
Z. anorg. Chem. 258, 332-55 (1949); cf. CA 35, 5054-1

The m.p. diagram of the system $LiF-BeF_2$ (I) was observed to find how closely it serves as a Goldschmidt model for the system $MgO-SiO_2$ (II), in which the ion radii are nearly the same but the valences are doubled. Mixts. in the system I were prepd. by heating LiF and $(NH_4)_2 BeF_4$ together, and the melting curves were followed to 50 mole % BeF_2. Incongruent m.ps. were observed for $Li_3Be_2F_7$ (445°) and $LiBeF_3$ (365°). $LiBe_2F_5$ may exist. The compds. formed in I are explained by the unsatn. and polymerization of BeF_2, considered to be covalent with the Be lacking two electron pairs. The similarity to II is very close, with discontinuities at almost the same compns. Ratios on the abs. temps. of 5 characteristic points in I and II are all close to 2.88. Crystal structures of 4 analogous compds. in I and II are discussed from data of the literature and the authors. Powder X-ray data are given for $LiBeF_3$, and powder and rotation data for Li_2BeF_4, but structures are not worked out. Analyses in I were limited to a detn. of Be in $(NH_4)_2 BeF_4$ by conversion to sulfate and reduction to BeO with hydrogen or illuminating gas at 625° or above. The compds. LiF (845°) and Li_2BeF_4 (475°) were congruent melting, with a eutectic (462°) at 31% BeF_2.

CA 44, 1321 i

The Heats of Vaporization of Uranium Hexafluoride
Joseph F. Masi
J. Chem. Phys. 17, 755-8 (1949)

UF_6 was vaporized in a heavy-wall, Ni-plated calorimeter. The heat of vaporization of the solid was measured at 7 temps. and of the liquid at 4 temps. covering the range from 4° to 90°. The app. was tested before beginning the measurements by obtaining the heats of vaporization of water at 3 temps. The scattering of the data on UF_6 is about 1%. The measured heats of vaporization were used to obtain a consistent correlation of the vapor pressures, heat of fusion, and triple point given in the literature. The results are expressed as vapor pressure equations and an equation of state for the satd. vapor. From these equations and the National Bureau of Standards values for the thermodynamic properties of the solid and liquid, the entropies of the ideal gas are calcd. and compared with those given in the literature from spectroscopic data and mol. structure. The heat of vaporization and entropy at 273.16°K. is 12,023 cal/mole and 87.56 cal/mole degree. At the m.p. (337.21°K) the entropy is 94.20 cal/mole degree. The heat of vaporization is 11.429 and 6859 cal/mole in the solid and liquid state, resp.

CA 44, 1322 f

Dissocn. Energy of Fluorine
E. Wicke
Z. Elektrochem. 53, 212-16 (1949)

The heat conducted by F at 10 mm. pressure from a hot Ni wire to a cool wall was the same as for N at all temps. up to 1000°, showing that little dissocn. occurs at this temp. The result is consistent with the old value of 63 kcal. for the dissocn. heat of F, but inconsistent with the new value 33 kcal. of Schmitz and Schumacher (CA 42, 2869 d). The interpretation of the ClF absorption spectrum, on which S. and S. base their value, is discussed and shown to be doubtful.

CA 44, 1322 g

Heats of Formation of Several Fluorides
H. V. Wartenberg and G. Riteris
Z. anorg. Chem. 258, 356-60 (1949); cf. CA 43, 8255 h

The heat of the reaction $ClF_3 + 3\ NaCl = 3\ NaF + 2\ Cl_2$ was calorimetrically detd. as 86.8 ± 0.3 kcal. (exothermic). Then with the aid of recently detd. heats of formation of NaCl and NaF, $1/2\ Cl_2 + 3/2\ F_2 = ClF_3 + 28.4 \pm 0.3$ kcal. From the hydrolysis reaction calorimetrically measured as $COF_2 + H_2O = 2\ HF$ aq. $+ CO_2 + 26.73 + 0.2$ kcal., and known heats of formation of HF and CO_2 there was obtained $C + 1/2\ O_2 + F_2 = COF_2 + 150.35 \pm 0.5$ kcal. The compd. CF_4 was reacted with K in a special app. contg. an elec. arc, and the heat observed:

$$4\ K + CF_4 = C\ (\text{graphite}) + 4\ KF + 307 \pm 3\ \text{kcal.}$$ Then

$$C\ (\text{graphite}) + 2F_2 = CF_4 + 231 \pm 3\ \text{kcal.}$$

CA 44, 1801 d

Ultraviolet Absorption Spectra of Rubidium and
Cesium Fluorides and the Heat of Dissocn. of Fluorine
A. D. Caunt and R. F. Barrow (Univ., Oxford, Engl.)
Nature 164, 753-4 (1949)

To det. the dissocn. energy, D. of mol. fluorine, the absorption spectra of RbF and CsF were measured in the quartz ultraviolet. At about 900° for RbF and 750° for CsF, continuous absorption is detectable, with max. absorption at 2150A. for RbF and at 2100 for CsF. As the temp. is raised, diffuse bands appear at longer wave lengths. Some 30 for RbF to 2980 and 25 for CsF to 2710 have been measured. From these D_{18} - (RbF) and D_{18} (CsF) were detd.; coupled with the heats of formation, Q(MF), the latent heat of vaporization, L_{18} (MF), they give a value of $D(F_2)$ of 50 ± 6 kcal., which is incompatible with one of 40 + 3 kcal. as detd. from ClF. Further work is necessary to bring these values more into line but it appears certain that the bond strength of mol. fluorine is considerably less than that of mol. chlorine.

CA 44, 2314 f

Improved Crystallization of Lithium Fluoride
of Optical Quality
Donald C. Stockbarger (MIT, Cambridge)
Discussions Faraday Society 1949, No. 5, 299-306

Pure LiF is prepared by bubbling CO_2 through saturated aq. Li_2CO_3 solution at room temperature and mixing the $LiHCO_3$ which is formed with HF solution. The $LiHCO_3$ is added to the HF slowly with agitation, and the addition is stopped while acid is still present in excess. LiF crystals are prepared by lowering the melt, which is contained in a Pt crucible, through a temperature gradient in an air furnace. The major difficulties are the control of the temperature and line voltage, the avoidance of reaction with water vapor, and the avoidance of color in the resulting crystals. Superior crystals can be grown at greater expense in a vacuum furnace. These crystals have much better transmission characteristics in the ultraviolet and infrared than crystals grown in air.

CA 44, 2811 g

A Theory of Dielectric Polarization in
Alkali Halide Crystals
Shepard Roberts (G. Elec. Co., Schenectady, N. Y.)
Phys. Rev., 77, 258-63 (1950); cf. CA 44, 392 d

A theory of dielec. polarization is described in which each ion in an alkali halide crystal is considered as a sep. entity capable of being distorted internally by an elec. field. Three stiffness coeffs. suffice to describe the interaction between the local elec. field and the polarizable ion. The Lorentz internal field is valid for this calcn. Optical and dielec. polarizabilities per mol. and infrared absorption frequencies in alkali halide crystals calcd. by this method are in substantial agreement with exptl. Electronic polarizabilities of free (gaseous) ions are also calcd., and a novel "pseudo-piezoelec." effect is predicted.

CA 44, 2839 a

Heat Capacities at Low Temps. and Entropies
of Magnesium and Calcium Fluorides
S. S. Todd (U.S. Bureau of Mines, Berkeley, Calif.)
J. Am. Chem. Soc. 71, 4115-16 (1949)

The heat capacities of MgF_2 and CaF_2 were measured throughout the range 52 to 298°K. Their entropies at 298.16°K. were calcd. to be 13.68 ± 0.07 and 16.46 ± 0.08 cal/degree/mole, resp.

CA 44, 2839 d

Low-Temp. Research. VII. The Specific Heat of the
Alkali Halides Lithium Fluoride, Sodium Chloride,
Potassium Chloride, Potassium Bromide, Potassium
Iodide, Rubidium Bromide, and Rubidium Iodide between
10° and 273° Abs.
Klaus Clausius, Jochen Goldmann, and Albert Perlick
Z. Naturforsch. 4a, 424-32 (1949); cf. CA 43, 8254b

The sp. heats were measured in a vacuum calorimeter (cf. CA 30, 3707-9). C_p, C_v, and the characteristic Debye temp. Θ are given. Curves are presented to show the deviation from the prediction of the Debye theory that Θ = const. LiF, NaCl, and KCl were investigated at sufficiently low temps. ($\Theta/T > 12$) to include the region of the T^3 law. The values of Θ were, on the contrary, found to reach a min. just above this region, then to increase very rapidly with decreasing temp.

CA 44, 3320 g

An Anomalous Dielectric Effect of Vacuum-Sputtered CaF_2 Layers
Erkki A. Laurila (Finland Inst. Technol, Helsinki)
Phys. Rev. 77, 405-6 (1950)

The change in the capacitance, a.c. and d.c. resistances, and the dielec. const. with time (5 sec. to 14 days) are tabulated for layers of CaF_2 1000, 3000, and 10,000 A. thick.

CA 44, 3327 g

Crystal-Chemical Studies of the 5 f Series of Elements
W. H. Zachariasen (Univ. of Chicago)
Acta Cryst. 2, 288-91 (1949); cf. CA 43, 6484h

XI. The crystal structure of α-UF_5 and of β-UF_5, Ibid 296-8
α-UF_5 is tetragonal body-centered with $a_1 = 6.512 \pm 0.001$, $a_3 = 4.463 \pm 0.001$ kX and 2 stoichiometric mols. per unit cell, space group C^5_{4h} - I 4/m. In the proposed structure each U atom is bonded to 6 F atoms. The UF_6 octahedra are linked by shared corners into endless strings along the a axis. β-UF_5 is also tetragonal body-centered. The unit cell contg. 8 stoichiometric mols. has dimensions $a_1 = 11.450 \pm 0.002$. $a_3 = 5.198 \pm 0.001$ kX space group D^{12}_{2d} - I 42d. A structure is proposed in which each U atom is bonded to 7F atoms. The interat. distances are: α-UF_5, U-6F = 2.20A.; β-UF_5, U-7F = 2.23A.

XII. New compds. representing known structure types. Ibid 388-90
The crystal structures of 55 new compds. of 4f and 5 f elements representing 14 known structure types were detd.: NaCl-type = NpO, PuO, AmO, NpN, PuN, PuC;
CaF_2-type = $PaO_{2.2}$(?), N_pO_2, PuO_2, AmO_2, ActOF, PuOF, α-K_2ThF_6, α-K_2UF_6, α-Na_2ThF_6, α-Na_2UF_6, α-$KLaF_4$, α-$KCeF_4$; LaF_3-type = $ActF_3$, UF_3, NpF_3, PuF_3, AmF_3, $CaThF_6$, $ThOF_2$, $SrThF_6$, $BaThF_6$, $PbThF_6$, $SrUF_6$, $BaUF_6$, and $PbUF_6$; PbFCl-type = ActOCl, ActOBr, PuOCl, PuOBr, PuOI, PrOCl, NdOCl, NdOBr, and YOCl; ZrF_4 type = ZrF_4, HfF_4, ThF_4, UF_4, NpF_4, PuF_4, CeF_4; La_2O_3 type = Act_2O_3, Th_2N_3; Sodium uranyl acetate-type = neptunyl and plutonyl compds.; K_3ZrF_7-type = K_3UF_7, Cu_2Mg-type = $CePt_2$; $CaTiO_3$-type = $CeAlO_3$; UO_2F_2-type = $Np_2O_2F_2$; $LaPO_4$-type = Act $PO_4 \cdot 0.5\ H_2O$; UCl_4-type = $NpCl_4$.

XIII. The crystal structures of U_2F_9 and $NaTh_2F_9$, Ibid 390-3
The compd. U_2F_9 is body-centered cubic with a = 8.4545 ± 0.0005 kX, space group T^3_d - $I\bar{4}3m$, and 4 stoichiometric mols. per unit cube. The positions of the U atoms were detd. from the observed intensities and the positions of the F atoms from spatial considerations. Each U atom is bonded to 9 F with U-9F = 2.31A. The U atoms are structurally equiv. The double fluoride, $NaTh_2F_9$, is body centered cubic with a = 8.705 ± 0.005 kX, space group T^3_d - $I \bar{4}3 m$. The positions of the Th and F atoms are practically the same as for the U and F atoms in the U_2F_9 structure. Suitable positions for the Na atoms were found. The interat. distances are Na - 6F = 2.34 A. and Th -9F = 2.40 A.

CA 44, 3389 f

The Dry Chemistry of Plutonium Fluorides
S. Fried and N. R. Davidson (Argonne Nat'l. Lab., Chicago)
Nat'l Nuclear Energy Ser., Div. IV, 14 B, Transuranium Elements.
Pt. I, 784-92 (1949)

PuF_4 does not react with dry O_2 at temps. up to 600°, whereas PuF_3 at 600° apparently undergoes the reaction $4\ PuF_3 + O_2 \rightleftharpoons 3\ PuF_4 + PuO_2$. PuF_4 decomps. to $PuF_3 + F_2$, presumably, at about 900° in vacuo. This decompn. takes place in vessels of Pt, BeO, and CaF_2. PuF_4 does not decomp. to PuF_3 in vacuum in contact with Pt at 600°. It is suggested that the PuF_4 decompn. is a disproportionation, $2\ PuF_4 \longrightarrow PuF_3 + PuF_5$, followed by decompn. of the PuF_5.

CA 44, 3389 g

Alkali Plutonium (IV) Fluorides
H. H. Anderson (Argonne Lab., Chicago)
Nat'l. Nuclear Energy Ser., Div. IV, 14 B, Transuranium Elements,
Pt. I, 775-8 (1949)

Insol. alkali Pu fluorides were prepd. by wet pptn. methods. Analyses established the formulas $NaPuF_5$, $KPuF_5$ and $RbPuF_5$ for compds. found isomorphous with KUF_5. The $CsPu_2F_9 \cdot 3\ H_2O$ was obtained under analogous conditions, and KPu_2F_9 was found in a sample of unknown history. NH_4PuF_5 and $LiPuF_5$ are probable compds. found under analogous conditions. The potassium compd. is the least sol.

CA 44, 3391 d

The Effect of K and La Ions on the Solubility
of Plutonium (IV) Fluoride
M. Cefola and C. Smith (Argonne)
Nat'l. Nuclear Energy Ser., Div. IV, 14B, Transuranium Elements,
Pt. 1, 822-4 (1949). Cf. CA 42, 821 b

Observations that Pu^{4+} fluoride is insol. in the presence of K and La ions and sol. in the absence of these ions suggests that double fluorides are formed in the latter case. Pptns. of Pu^{4+} with La from a MHF-0.4 M HNO_3 soln. yielded a compd. corresponding to the double fluoride $La_2PuF_{10} \cdot x\ H_2O$ (I). Attempts to prep. a cryst. form of I were unsuccessful. Prepns. of $KPuF_5$ were shown by X-ray analysis (cf. CA 42, 7190 g) to have a rhombohedral structure isomorphous with KUF_5, $KThF_5$, and $NaUF_5$.

CA 44, 3680 f

Alkali Aluminum Fluorides
Erling Brodal and Henning Guldhav (to Aktieselskapet
Norsk Aluminum Co.)
Norw. 72,831, Sept. 19, 1949

Alkali Al fluorides, particularly cryolite, are made by dissolving fluorspar in alkali, adding alkali aluminate and pptg. with CO_2, the quantity of CO_2 is limited so that some free alkali remains in soln., and this is then used for prepg. fresh alkali aluminate by leaching sintered or smelted Ca aluminate. The soln. may be used alternately for extg. the alkali-fluorspar sinter and the Ca aluminate, and when its alkali content has increased sufficiently (e.g., to 150 g/l) the excess alkali is pptd. with CO_2 as bicarbonate and heated to convert the bicarbonate to carbonate, which is then returned to the process.

CA 44, 3681 c

Beryllium Fluoride
Warren S. Peterson and Charles B. Willmore (To Aluminum
Co. of Am.)
U. S. 2,487,270, Nov. 8, 1949

Be is extd. as BeF_2 from beryl or similar Be ores by first removing all but 10-15% of the Si in the ore by smelting with Fe and C, forming granules of the slag, and treating these last with anhyd. HF, first at 450-500° to remove the rest of the Si as SiF_4 and then at about 650° to convert the Be to BeF_2. If Al is present, it will also be converted in this last step and must be sepd. later. The presence of C to reduce H_2O formed during the last step is desirable.

CA 44, 3792 b

New Band Spectra of Diatomic Lead Halides

K. Wieland and R. Newburgh (Zurich, Switz.)
Helv. Phys. Acta 22, 590-1 (1949)

Absorption spectra were obtained in heated vapor for $PbCl^{35}$, $PbBr^{79}$, and PbI. The bands are degraded to the violet (B-system). A further system (A- bands), degraded to the red was observed for PbI, in both absorption and emission. Vibrational consts. were calcd. The dissocn. energies, Do, in kcal. per mole are : PbF, 80.0; PbCl, 72.0; PbBr, 68.5; PbI, 65.5.

CA 44, 3829 f

The Influence of the Cation Radius on the Energy of Formation of Addition Compds. II. The System Alkali Carbonate-Alkali Fluoride and Alkali Sulfate-Alkali Fluoride

O. Schmitz-Dumont and Irmgard Heckmann
Z. anorg. Chem. 260, 49-64 (1949); cf. CA 40, 4312-4

Temp-compn. studies were made of the systems $MF-M_2CO_3$ and $MF-M_2SO_4$ (M = alkali metal). LiF, NaF, and CsF formed only simple eutectics with their corresponding carbonates. The $LiF-Li_2SO_4$ system did not form a congruent-melting compd. KF, RbF, and CsF formed compds., of the general formula M_3SO_4F. A theoretical discussion of the influence of the cation radius on the energy of formation of the compds. is given. KF and RbF formed congruent-melting compds. of the formula M_3CO_3F with their corresponding carbonates.

CA 44, 4210 i

Purification of Certain Alkaline Earth Halides and Crystal Products thereof

Donald C. Stockbarger and Arthur A. Blanchard (to Research Corp.)
U. S. 2,498,186 Feb. 21, 1950

A soln. contg. 60 parts HF is added with stirring to a suspension of 100 parts $CaCO_3$ and 4 parts $PbCO_3$ in 3 l. H_2O in a lead bucket. After settling, the supernatant liquid is decanted. A little addnl. HF is added to the residue and the mixt. evapd. to dryness. The dry ppt., consisting of CaF_2 with about 4% PbF_2 and a small amt. of absorbed H_2O, is transferred to a graphite crucible and fused in an elec. vacuum furnace. The PbF_2 acts as scavenger for the commonly occurring sulfides, sulfates, silica and oxide impurities, and is volatilized with them and the H_2O, leaving a clear, colorless, purified melt of CaF_2. The CaF_2 is allowed to cool in vacuo and yields a large cryst. body of optical quality free from impurities which cause light scattering. Other alk. earth fluorides as well as MgF_2 may be prepd. similarly by using the corresponding carbonates. Optical crystals of natural fluorite can be produced by thoroughly mixing the finely crushed mineral with PbF_2 and fusing.

CA 44, 4321 c

Phase Relations and Structural Phenomena in the
Fluoride - Model Systems $LiF-BeF_2$ and $NaF - BeF_2$
Della M. Roy, Rustum Roy, and E. F. Osborn (State College, Pa.)
J. Am. Ceram. Soc. 33, 85-90 (1950)

Phase equil. data are given for the system $LiF-BeF_2$ and for the BeF_2 end of the systems $NaF-BeF_2$ and $RbF - BeF_2$. The results show them to be weakened models of the systems $ZnO-SiO_2$ and $CaO - SiO_2$, resp., altho the liquid immiscibility does not appear in the fluoride systems as it does in the silicate systems. The m.p. of the cristobalite form of BeF_2, produced by the distn. of $(NH_4)_2 BeF_4$, was detd. as 543 ± 5°, and that of the willemite model (Li_2BeF_4) as 458 ± 5°. A tridymite form did not appear. Data for the compd. $Na_2LiBe_2F_7$ showed that its structure is similar to that of melilite hardsytonite ($Ca_2ZnSi_2O_7$). The value of data on refractory oxide systems obtained by studying their fluoride models is apparent from the similarity of these systems to their silicate counterparts.

CA 44, 4359 a

New Fluorine Compounds
Walter Huckel
Nachr. Akad. Wiss. Gottingen, Math.-physik. Klasse 1946,
No. 1, 55-6

The fluorination of metals with F and ClF_3 in a V 2 A-steel-lined autoclave proceeds easily, often at room temp. HgF_2 (120° for 3 hrs) is prepd. in good yield. AgF_2, CuF_2, TlF_3, CoF_3, PtF_4, and PbF_3 are also prepd. Bulk Cr is unaffected. $(FCN)_3$, b. 150°, is prepd. in good yield from HgF_2 and ICN at 160°.......

CA 44, 4790 f

A Kinetic Study of the Thermoluminescence of LiF
Charles A. Boyd (Univ. of Wisconsin, Madison)
J. Chem. Phys. 17, 1221-6 (1949)

The isothermal decay of the thermoluminescence of single crystals of LiF activated by X-rays has been detd. at various temps. The results are interpreted in terms of a simple reaction-rate mechanism based on a picture of the thermoluminescent process similar to that of Johnson (CA 33, 9144). The analysis of the isothermal decay studies is in agreement with the results of "glow curve" expts. on similar LiF samples where the intensity of luminescence is measured as the temp. of the crystal is heated at a const. rate. Two principal types of electron traps in LiF are found to have trapping energies of 19,800 cal/mole and 45,300 cal/mole., resp.

CA 44, 5750 g

The Ternary Fluoride NaYF$_4$
F. Hund (Univ., Munster, Ger.)
Z. anorg. Chem. <u>261</u>, 106-15 (1950)

Two forms of NaYF$_4$ were prepd. β-NaYF$_4$, high-temp. form, is produced by chilling a melt of YF$_3$ in excess NaF or by pptn. from YCl$_3$ soln. by a large excess of NaF soln. β-NaYF$_4$ is soft, white, d. = 3.87, m. 1100°, cubic with lattice const. a_w = 5.448 ± 0.001A.; 2 mols. per unit cell. 2 Na + 2 Y in (a) 000; 0 1/2 1/2; 1/2 0 1/2; 1/2 1/2 0; 8F in (c) 1/4 1/4 1/4; 1/4 3/4 3/4; 3/4 1/4 3/4; 3/4 3/4 1/4; 3/4 3/4 3/4; 3/4 1/4 1/4; 1/4 3/4 1/4; 1/4 1/4 3/4. α-NaYF$_4$, low-temp. form, ivory-white, brittle, d. = 4.23, is formed by long tempering of β-NaYF$_4$ at 550 - 600° or by slow cooling of the melt of YF$_3$ and excess NaF; it crystallizes in a new lattice with many X-ray lines.

CA 44, 6696 i

The Growth of Artificial Crystals and their Properties
M. Gans
Congr. groupement avance. methodes anal.
spectrograph. produits met. (Paris) <u>11</u>, 61-4 (1949)

Two methods of crystal growth are outlined: (1) The method of Stockbarger is used by Harshaw Chemicals; pure salts are place in a cylindrical Pt crucible terminating in a conical end. This crucible is placed in a 2-compartment furnace, the upper part slightly above, the lower part slightly below, the crystn. temp. The crucible is then slowly lowered thru the furnace. (2) The method of Kyropoulos is used at the O.N.E.R.A. labs. in Toulouse; crystn. is initiated by a crystal seed and the crystal is cooled at a very slow rate. The following tables are given: (1) the infrared transmission of glass, quartz, mica, spinel, sapphire, LiF, CuF$_2$, SrF$_2$, BaF$_2$, NaCl, KCl, KBr, AgCl, KI, and Tl(Br,I); (2) linear dispersion in the infrared of quartz, LiF, CaF$_2$, NaCl, KCl, and KBr; (3) ns and absorption coeffs. of LiF, CaCl$_2$, and KBr.

CA 44, 7124 d

The Compressibility, Viscosity, and Surface
Tension of Aqueous Solutions of Alkali Halides
H. Krishnamurty (Andhara Univ., Waltair)
Current Sci. (India) 19, 87 (1950)

A preliminary report on the detn. of the adiabatic compressibility β, viscosity η, and surface tension σ by ultrasonic measurements for solns. with various concns. of KI, KBr, KF, and NaF. The empirical relations, $\eta = 2.0 \times 10^2 \beta$ and $\sigma = \rho v^{3/2} \times 1.2 \times 10^{-6}$, where ρ is dens. and v is the ultrasonic velocity, are independent of temp. and concn. for all the halide solns.

The adiabatic and apparent molar compressibilities of alkali halides, Ibid 87-8. The apparent molar compressibility ϕ for the KI, KBr, and KF and NaF solns. follows from the values for β. β is not related to concn. by Bachem's equation (CA 30, 7970^6) in the lower concn. ranges, but instead passes thru a max. at approx. 0.3 M. In the same concn. range ϕ is not a linear function of the sq. root of concn. as predicted by Gucker's equation (CA 27, 5233).

CA 44, 7204 d

Problems of the Use of Chemical Fused Salt
Baths for the Separation of High- and Low-Melting Metals
Edmund R. Thews and Martin Stromeyer
Chem. Tech. 2, 157-61, (1950)

CA 44, 7607 e

The Surface Tension of Solids
R. Shuttleworth (Bristol Univ., Engl.)
Proc. Phys. Soc. (London) 63A, 444-57 (1950)

For a one-component liquid, surface free energy and tension are equal. The surface tension of a crystal face is related to, but not equal to, the surface free energy. Thermodynamic formulas of surface physics are reviewed. The surface free energy appears in the expression for the equil. contact angle and in the Kelvin expression for the excess vapor pressure of small drops, but the surface tension appears in the expression for the difference in pressure between the 2 sides of a curved surface. The surface tensions of inert-gas and alkali halide crystals, calc. from expressions for their surface energies, are neg. The surface tensions of homopolar crystals are zero if it is possible to neglect the interaction between atoms that are not nearest neighbors. Surface tensions are calcd. for the (100) faces of the crystals of Ne, A, Kr, and Xe and for the (100) faces of NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI. Except for NaF the calcd. values are neg.

CA 44, 7608 g

Elastic Constants of Lithium Fluoride
R.V.G. Sundara Rao (Indian Inst. Sci., Bangalore)
Current Sci. (India) 18, 336 (1949)

Acoustic velocities in sections (100 and 110) of LiF crystals were detd. by the ultrasonic wedge method (CA 39, 4783-2) and the modified plate method (CA 43, 8787b). The elastic consts. calcd. from the mean acoustic velocities in units of 10^{11} dynes/sq.cm. were: C_{11}, 11.9; C_{12}, 4.58; C_{44}, 5.42. The bulk modulus K in similar units was 7.02. The elastic moduli in units of 10^{-13} cm^2/dyne were: S_{11}, 10.7; S_{12}, 2.97; S_{44}, 18.5. The C_{11} and C_{12} values agree with those of Schaefer and Bergmann (Ultrasonics, 1938, p. 180) but the C_{44} value does not.

CA 44, 8068 h

Soluble Aluminum Fluoride
"Montecatini" Societa Generale per l' industria mineraria
e chimica (Franco Sciacca and Luigi Notarbartolo, inventors)
Ital. 426,332, Oct. 24, 1947

$AlF_3 \cdot 3.5\ H_2O$ is crystd. from AlF_3 solns. by adding a rather large quantity of the same salt at a temp. of 22-50° with stirring. In an example, to 10 cu. m. of AlF_3 soln. (20°Bé) is added 1000 kg. of salt (contg. 52% AlF_3) at 30-50°, under 12 hrs. stirring.

CA 44, 8211 a

The Fluoride Ion as a Base in High-Temp.
Reactions with Polyphosphates
O. F. Hill and L. F. Audrieth (Univ. of Ill., Urbana)
J. Phys. and Colloid Chem. 54, 690-6 (1950)

Reactions of NaF and various Na phosphates in the fused state were studied. The fluoride ion behaves as a strong ionic base in effecting the depolymerization of fused polymetaphosphate and polyphosphate ions.

CA 44, 8217 h

The Ternary Adiagonal, Reciprocal System of the
Fluorides and Chlorides of Sodium and Barium
E. I. Banashek and A. G. Bergman
Doklady Akad. Nauk SSSR 56, 485-6 (1947); Chem. Zentr.
(Russian Zone Ed.) 1948, I, 1167

The surface of the liquidus curves in the system Na_2F_2 - NaCl - BaF_2 - $BaCl_2$ is divided into 5 cryst. fields. The greater portion of this surface (about 51%) represents the field of the compd. $BaF_2 \cdot BaCl_2$. Three triple points were established: a eutectic contg. $BaCl_2$ 59, NaCl 36, and Na_2F_2 5% at 617°; a transition point with BaF_2 37, NaCl 43.5, and Na_2F_2 19.5% at 654°; and a eutectic contg. Na_2F_2 49, $BaCl_2$ 32, and NaCl 19% at 630°.

CA 44, 8274 c

The Vapor Pressure of Plutonium Halides
T. E. Phipps, G. W. Sears, R. L. Seifert, and O. C.
Simpson (Argonne, Chicago)
National Nuclear Energy Ser., Div. IV, 14B, Transuranium Elements,
Pt I, 682-703 (1949)

Vapor pressures of PuF_3, $PuCl_3$, and $PuBr_3$ were measured by a modification of the Knudsen effusion method. The vapor-pressure equation is $\log p_{mm} = E - F/T$. Consts. E. and F, resp., for the halides are: PuF_3 (solid) 12.468, 21,120; (liq.) 11.273, 19400; $PuCl_3$ (solid) 12.726, 15,910; (liq.) 9.509, 12,590; $PuBr_3$ (solid) 13.386, 15,280; (liq.) 10.321, 12,360. Thermodynamic quantities are for PuF_3, $PuCl_3$, and $PuBr_3$, resp: ΔH of sublimation, 96.6 ± 0.5, 72.8 ± 0.6, and 69.9 ± 0.3: ΔH of vaporization, 88.7 ± 0.2, 57.6 ± 0.4, and 56.5 ± 0.2; ΔH of fusion, 7.9 ± 0.5, 15.2 ± 0.7, and 13.4 ± 0.3 kcal/mole.; ΔS of fusion 5.5 ± 0.4, 14.7 ± 0.7, and 14.0 ± 0.4 cal/mole/degree.

CA 44, 8275 h

Aluminum Fluoride Hydrates
Werner Fischer, Eleanore Bock, and Karl Meisel
(Tech. Hochschule, Hannover)
Z. anorg. Chem. 262, 54-60 (1950)

Detailed descriptions are given for the prepn. of hydrated AlF_3 by solution of (a) $Al(OH)_3$, (b) ignited Al_2O_3 (600°) and (c) Al metal in aq. HF. The first two starting materials lead to basic salts, which are not in chem. equil. with the soln. These solns. may contain a peptized colloid that causes the compn. of the resulting fluoride to depend upon the previous history of the material. Neutral AlF_3 hydrates (mono - and tri-) are obtained from solns. of Al metal dissolved in aq. HF. The monohydrate is obtained by long drying on a steam bath; the trihydrate is obtained by exposure of the monohydrate to air satd. with water vapor, followed by drying over concd. H_2SO_4. Debye X-ray diffraction photographs support the claims for the mono- and trihydrates, but cast doubt upon the existence of a 3.5 hydrate.

CA 44, 8611 d

Fluoride Glass
Kuan-Han Sun and Maurice L. Huggins (to Eastman Kodak Co.)
U. S. 2,511,224, June 13, 1950

Moisture-insusceptible glass contg. over 32% AlF_3 and BeF_2 and fluorides and other anions of multivalent elements transmit light thru the visible spectrum and far into the ultraviolet and infrared regions. Cf. CA 30, 4288-8; 43, 5165 f.

CA 44, 8713 b

Effect of Pressure on the Low-Frequency Dielectric
Constant of Ionic Crystals
Sumner Mayburg (Univ. of Chicago)
Phys. Rev. 79, 375-82 (1950)

Data on the pressure dependence of the dielec. const., ϵ , of 5 compds. at 1000 c.p.s. and room temp. are given as a function of hydrostatic pressure, 0-8000 bars. The dielec. consts. decrease with an initial slope $(\partial \ln \epsilon/\partial\ p)\ T\ (X10^{-5}bar^{-1})$: MgO, -0.320 ± 0.019; LiF, -0.448 ± 0.028; NaCl, -0.98 ± 0.06; KCl, -1.05 ± 0.08; KBr, -1.17 ± 0.09. Present lattice theories are capable of explaining these data only if the inner field decreases with increasing pressure.

CA 44, 8740 e

Solubilities of Salts in Water at High Temperature
Harold Simmons Booth and Richard MacPherson Bidwell
(Western Reserve Univ., Cleveland, O.)
J. Am. Chem. Soc. 72, 2567-75 (1950)

A technique for the measurement of solubilities at high temps. and pressures was developed, in which filtration of the satd. soln. is effected by quenching the high-pressure vessel. The solubilities of CaF_2, BaF_2, and LiF and $SrSO_4$ were measured up to, or past, the crit. temp. of water. The previously investigated solubilities of $CaSO_4$ and Na_2SO_4 at high temps. were checked and extended. The dependence of the soly. of LiF in water above its crit. point on the d. of the solvent was measured at several temps. The very low solubilities of the salts investigated in the region of the crit. point made it seem unlikely that the recrystn. from their pure aq. solns. of these salts would be a practical method for the making of synthetic crystals of optical quality unless at appreciably higher temps. and pressures. The precision of the results obtained compared well with other measurements in the same region, most of which required far more complex app.

CA 44, 9233 g

Equilibrium in the System $NaF-AlF_3-H_2O$
V. S. Yatlov and E. N. Pinaevskaya
Zhur. Obshchei Khim. 19, No. 1, 24-31 (1949);
J. Gen. Chem. U.S.S.R. 19, 21-6 (1949)(Eng. Trans.);
cf. CA 7, 1849; 17, 3273.

The system was studied at 25° and at 75° by the thermostatic method of detg. solubilities and by investigating the elec. cond. There are 5 regions where the stable solid phases are: (1) $AlF_3 \cdot 3\ H_2O$; (2) solid solutions of $AlF_3 \cdot 3\ H_2O$ in chiolite, which latter compd. appears to have the formula $3\ NaF \cdot 2\ AlF_3$, corresponding to the compd. found in the binary system $NaF-AlF_3$, rather than $5\ NaF \cdot 2\ AlF_3$, corresponding to the naturally-occurring mineral; (3) chiolite; (4) solid solutions of chiolite in NaF, with no indication of the compd. $11\ NaF \cdot 4\ AlF_3$ previously reported (CA 38, 3542-1), but having an upper limit of soly. corresponding to a Na/Al ratio of 2.7 - 2.8; (5) NaF (not investigated). Binary fluorides of Na and Al dissolve in water with decompn. and, consequently, $3\ NaF \cdot AlF_3$ was not found. The compd. $NaAlF_4$ was not isolated, but it is possible that it is formed as a monohydrate in concentrated solutions of AlF_3.

CA 44, 9234 a

Ternary Reciprocal System of Fluorides
and Chlorides of Lithium and Calcium
G. A. Bukhalova and A. G. Bergman
Doklady Akad. Nauk S.S.S.R. 66, 67-70 (1949)

The 4 binary systems were studied previously (cf. CA 2, 502; 18, 1445). All form simple eutectics except the system CaF_2-CaCl_2, where there is a peritectic point in addition to the eutectic. The reciprocal system has 6 crystn. regions where the solid phases are, respectively, LiF, $CaF_2 \cdot CaCl_2$, $CaCl_2$, and α and β - LiCl. There are 3 eutectic points, lying on a slightly curved line, having values of temperature (°C), equiv. % Ca, and equiv. % F, and with solid phases in equil. as follows: 472, 22.5, 43.0, LiF + CaF_2 + LiCl; 450, 51.0, 6.5, $CaCl_2$ + $CaF_2 \cdot CaCl_2$ + LiCl; and 485, 35.0, 25.0, CaF_2 + $CaF_2 \cdot CaCl_2$ + LiCl. Between adjacent eutectic points there are relative maximum: 492, 30, 30.0, LiCl + CaF_2; and 492, 40.0, 20.0, LiF + $CaF_2 \cdot CaCl_2$.

CA 44, 9234 c

Irreversible-reciprocal System of Fluorides and Iodides
of Sodium and Potassium, of the Transition-to-singular Type
F. P. Platonov
Trudy Moskov. Sel'sko-Khoz. Akad. im. K.A. Timiryazeva
1946, No. 36, 42-56

The 4 lateral binary systems, and 2 diagonal binary systems, and 6 quaternary cross-sections were investigated to characterize the reciprocal system. The system NaI-NaF is a simple eutectic system, the m.p. decreasing from 667° for NaI to a eutectic m. 603°, contg. 18 (mole)% NaF, then rising to 990° for NaF. The KF-KI system is of the same type, the m.p. decreasing from 850° for KF to a eutectic m. 544°, contg. 34% KF, then rising to 680° for KI. NaI and KI form a continuous series of solid solutions, with m.p. of mixtures going through a min. of 583° at 42% KI. KF and NaF form a simple eutectic m. 710°, contg. 40% NaF, and there is a limited range of solid solutions, with KF dissolving in NaF to the extent of approximately 4%, and NaF in KF about 10%. The stable diagonal cross-section NaF-KI forms a simple eutectic, m. 631°, contg. 12% NaF. This is a stable system, since the solid phases are the pure components NaF and KI, and none of the products of their reaction appears in the diagram. The metastable diagonal cross-section KF-NaI has 3 crystn. regions: a NaI region from NaI down to a eutectic m. 578°, contg. 12% KF; a KF region from KF down to a eutectic m. 678°, contg. 78% KF, and a central region characterized by a maximum at 840°, 50% KF, and corresponding to the reaction product NaF. In this central region, below the liquidus curve there are other metastable equil. with the result that the curve showing the temperature of complete solidification decreases from the eutectic at 678° to another eutectic-like point at about 540°, 60% KI, then goes through a maximum of 620° at 50% KI, decreasing to a broad min. of 560° at 30% KI, and rises gradually to the eutectic at 578°. From these data and those of the quaternary cross-sections, a 3-dimensional model was constructed for the reciprocal system, and the conventional planar representation by projection of the model on the compn. plane. The stable diagonal NaF-KI divides the diagram into 2 ternary systems: (1) the NaF-KI-KF system contg. 3 regions where the solid phases are NaF, KI, and KF, resp., and a ternary eutectic point at 542° contg. 95.5% K, 64.5% I; (2) the system NaF-KI-NaI contg. 2 crystn. regions where the solid phases are NaF and solid solution of NaI in KI, with a min. in the copptn. curve at 560°. The entire reciprocal system thus has 3 crystn. regions, where the solid phases are NaF, KF, and solid solutions of NaI and KI. In the NaF region, which occupies most of the diagram because of its smaller soly., the isotherms below 700° intersect at very oblique angles, an indication of the irreversibility of the system and of the fact that this irreversible-reciprocal system is of the transition-to-singular type. A comparison of the system NaF-KCl, NaF-KBr, and NaF-KI shows that increasing heats of reaction (7.6, 9.1, and 10.6 kcal., resp.) are assocd. with increasing areas of crystn. of the stable components in the resp. systems in planar representations (73.73, 77.85, and 82.54% of the total area, resp.) and by increasing vols. of crystn. in 3-dimensional models (82.79, 86.78, and 87.89%, resp.)

CA 44, 9272 e

Electromotive Phenomena Between Metallic Aluminum
and Various Aluminum Salts. I. The Occurrence of An
Electromotive Force Between Aluminum and Solid Salts
Horoski Nozaki and Ken Miyauchi
J. Chem. Soc. Japan, Ind. Chem. Sect., 51, 3 - 4 (1948)

The e.m.f. of the cell Al/salt/Pt is measured at or below 700° under a pressure of 1 - 2 mm. Hg. Salts studies are: Na_3AlF_6 (I), NaF (II), AlF_3 (III), Na_3AlF_6 with 25% Al_2O_3 (IV), Al_2O_3 (V), CaF_2 (VI), and NaCl (VII).

In every system the e.m.f. reaches a maximum at about 660°, while short-circuit currents reach a maximum at slightly higher temperatures. Under atm. pressure the maximum e.m.f. values of the systems lie within a narrow zone (2.0 - 2.3 v.), but under reduced pressure the max. e.m.f. values are small but differ from each other; I 1.68, II 1.86, III 1.65, IV 1.59, VII 1.40, VI 0.54, and V 0.52 v. Maximum short-circuit currents also differ considerably, the values for the systems IV, VII and II being 92, 21, and 2%, resp., of I. The maximum e.m.f. of the cell Zn - Na_3AlF_6/Pt is 0.3 v. and the maximum short-circuit current is only 6% of that of I.

CA 44, 9293 a

Exchange Decomposition in the Absence of Solvent-Complex Formation, Solid Solutions, and Exchange Decomposition in Melts of Strontium and Barium Fluorides and Chlorides

A. G. Bergman and G. A. Bukhalova
Zhur. Obshchei Khim. 19, 603-11; J. Gen. Chem. U.S.S.R. 19,
553-62 (1949) (Engl. Translation)

The 4 pure substances have m.ps.: SrF_2, 1400°; BaF_2, 1280°; $SrCl_2$, 868°; $BaCl_2$, 958°. $SrCl_2$ and $BaCl_2$ form solid solutions over the entire concn. range with a min. m.p. at 847°, 30% $BaCl_2$. SrF_2 and BaF_2 form a similar system, with a min. at about 1270°, 70% BaF_2 · SrF_2 and $SrCl_2$ form the compd. $SrCl_2 \cdot SrF_2$ m. 962°, and there are 2 eutectics: 753°, 13% SrF_2; and 962°, 63% SrF_2. The compd. undergoes a phase transition at 890°, intersecting the liquids curve at 25.5% SrF_2. BaF_2 and $BaCl_2$ form a similar system: $BaF_2 \cdot BaCl_2$ m. 1008°; eutectics at 854°, 19% BaF_2 and 936°, 73.5% BaF_2; and transition point 940°, 30% BaF_2. The system $SrCl_2 \cdot SrF_2$ - $BaCl_2 \cdot BaF_2$ is characterized by solid solutions over the entire concn. range, with a min. m.p. at 906°, 36% $BaCl_2 \cdot BaF_2$. The diagonal binary system $SrCl_2$ - BaF_2 has 4 crystn. regions where the solid phases are: (1) solid solutions of $SrCl_2$ in $BaCl_2$; (2) and (3) α- and β- cryst. modifications of solid solutions of $SrCl_2 \cdot SrF_2$ in $BaCl_2 \cdot BaF_2$; (4) solid solns. of SrF_2 in BaF_2, causing breaks in the liquidus curve at 730°, 3.5% BaF_2; 862°, 15% BaF_2; 923°, 62% BaF_2. The other diagonal system $BaCl_2$ - SrF_2 also has 4 regions: (1) all 4 pure compds.; (2) and (3) α- and β- cryst. modifications of solid solutions of the two binary compds.; (4) solid solutions of SrF_2 in BaF_2, causing breaks in the liquidus curve at 800°, 15.5% SrF_2; 890°, 31.5% SrF_2; 917°, 57% SrF_2. On the basis of the binary diagrams and of 4 quaternary mixtures, planar and 3-dimensional models were constructed for the reciprocal system. The latter shows the crystn. surface to be composed of 4 parts. There is an almost planar surface dropping down rather steeply from the SrF_2 - BaF_2 side to a trough, where the solid phase is a series of solid solutions of SrF_2 in BaF_2. Next there is a saddle, in the central portion of the diagram, the peaks of which correspond to the 2 binary compds., and the surface then drops to another trough; in this region the solid phases are the α- and β-modifications of solid solutions of the 2 binary compds. Finally, there is an almost planar surface up to the $SrCl_3$ - $BaCl_2$ side, where the solid phase is a series of solid solutions of the chlorides. As a result of the relatively small heat of reaction of 4.6 kcal., and because of the stable complex compds. formed in this system, the important relationships are not along the diagonals but are in sections divided by the line connecting the 2 binary compds.

CA 44, 9761 d

The Configurational Free Energy of Binary Solid Solutions of Alkali Halides
V. Hovi
Soc. Sci. Fennica Commentationes Phys. - Math. 15,
No. 15, 1 - 8 (1950) (inEnglish)

An expression is derived in accordance with the principles of modern statistical thermodynamics for the configurational free energy of binary solid solutions of alkali halides in which only local order appears; the formulas for a numerical evaluation of the expression are given.

CA 44, 9823 a

The Electrolysis of Fused Salts I. Electromotive Force Observed in the Salt-Metal Systems
Hiroski Nozaki
J. Electrochem. Soc. Japan 16, 31 - 3 (1948)

The emf observed in some metal-salt systems enclosed in a Pt crucible under atmosphere or reduced pressures are: 1.65 v. at 675° for $Al-AlF_3$, 1.68 v. at 630° for Al-cryolite, and 1.67 v. at 725° for Al-NaF. The short-circuit current is 100 ma. in the 1st system when an Al rod 25 mm. in length and 20 mm. in diameter and a Pt crucible of 45 mm. depth and 40 mm. in diameter are used. In the 2nd system the corresponding current is very small. In the 3rd system metallic Na is produced at both electrodes.

II. Consideration of the appearance of the electromotive force in the salt-metal system and its relation to electrolysis, Ibid 33-6

The emf observed in the 1st system above can be explained by the solution of a new Al compd. which is assumed to have a lower valence, e.g., $Al_2F_6 + Al \rightleftharpoons 6\ AlF$. The main parts of the emf. of the 2nd and the 3rd systems are probably due to the same reaction in addition to exchange reaction as $Na_3AlF_6 + Al \rightleftharpoons 3\ Na + Al_2F_6$ and $2\ NaF + Al \rightleftharpoons 3\ Na + Na_3AlF_6$. These conclusions are also supported by the unpublished thermodynamic calcns. of N's collaborators. The results obtained from the Na cryolite and $NaAl_2F_6$ systems also coincide with the above explanation.

III. Electrolysis of aluminum and sodium fluorides. Ibid. 60-2

Current voltage curves in the electrolysis of fused salts were detd. at about 1000° in a graphite crucible with the molten metal at the bottom as the cathode and a Pt wire in the fused salt as the anode. The inside wall of the crucible was covered completely with a MgO lining to prevent the wall from acting as the cathode. In the system with the Al cathode and cryolite the current was very small, increased rapidly from 1.63 v. approaching a const. value, and again increased linearly from 5.5 v. It was concluded that the 1st discontinuity was due to the decompn. of the $AlCl_3 \cdot m\ Al$ dissolved in the fused salt as assumed above, while the 2nd was due to the decompn. of cryolite. In the system $Na_3AlF_6 + Al_2F_6$ (mol. ratio 8:2) and $Na_3AlF_6 + 6\ NaF$

(mol. ratio 7:3) the 1st discontinuities were at 3.6-7 and 2.8 v, resp. In the system of NaF with a Na cathode the 1st discontinuity of the 1st run was not clear, probably because of the solution of the Na formed in NaF, while the 2nd indicated the decompn. of NaF at about 4.0 v., corresponding to the theoretical value of 4.2 v. In the 2nd run in the same system, a finite current was observed at 0 v. from the existence of Na already formed in the fused NaF.

CA 44, 9852 e

Intermediate Uranium Fluoride Compds.:
α-UF_5, β- UF_5, U_2F_9, and U_4F_{17}
P. A. Agron, et al
U. S. Atomic Energy Comm. MDDC-1588,
8 pp (Jan. 16, 1948)

The occurrence of two allotropic forms of UF_5 was established by means of x-ray diffraction and chem. analysis. Chem. and x-ray analysis showed that a black fluoride originally designated "Black UF_4" was U_2F_9, and proved the existence of U_4F_{17}. The conditions of prepn. and properties of the compds. are outlined.

CA 44, 10549 d

Electrical Conductivity of Aluminum Electrolysis
Baths With a Molten Cryolite Base
A. Vayna (Industria Nazle. Alluminio, Mori, Italy)
Alluminio <u>19</u>, 215-24 (1950)

A modification of the cell of Jaeger and Kapma (CA 15, 2772) was used to measure the cond. of molten binary solutions of cryolite with Al_2O_3, NaF, CaF_2, and AlF_3, resp., at several temperatures near 1000°, and of ternary solutions of cryolite and Al_2O_3 with each of the other 3 compds. at 980° and 1000°. Alk. baths (excess NaF) have the highest and acid baths (excess AlF_3) the lowest cond.; conds. of neutral baths and of those containing CaF_2 are intermediate. Addition of Al_2O_3 lowers the cond. of all baths, perhaps because it raises their viscosity (Alluminio 19, 133 (1950)). The data, presented graphically, are discussed with reference to heat production and autoregulation in com. Al production.

CA 44, 10560 e

The Vapor Pressure of Plutonium Halides
T. E. Phipps, G. W. Sears, et al (Argonne)
J. Chem. Phys. 18, 713-23 (1950) - see CA 44, 8274 c

CA 45, 430 a

The Energy of Formation of Aluminum (I and II) Halides
F. Irmann (Eidg. Tech. Hochschule, Zurich, Switz.)
Helv. Chim. Acta 33, 1449-57 (1950) (in German)

Heats of formation ΔH_{298} of cryst. AlX and AlX_2 (X = F, Cl, Br, I) were calculated by means of the Born-Haber cycle. Lattice energies were calculated from the Born equation and were corrected by a small term obtained from similar compds. for which accurate ΔH_{298} values are known. A similar cycle was used to calculate heats of formation and of dissocn. into atoms for gaseous AlX. Rough estimates were made of the heats of formation of gaseous AlX_2. The values of ΔH_{298} (kcal/mole) for the crystal and for the gas, resp., are: AlF, - 103, -50; AlCl, -50, -5, AlBr, -36, 12; AlI, -19, 33; AlF_2. -184, -114; $AlCl_2$, -80, -30; $AlBr_2$, -58, -8; AlI_2, -27, 23. The heats of dissocn. (kcal/mole) are: AlF, 148; AlCl, 109; AlBr, 90; AlI, 68. For the monohalides, the uncertainties in ΔH_{298} are estimated to be ± 10 and ± 5 kcal/mole for crystal and vapor, resp. Values for the dihalides are less certain. The values are used to discuss the relative stabilities; the cryst. monohalides are only slightly less stable than the trihalides, but the cryst. dihalides are definitely less stable. Gaseous mono- and dihalides are both less stable than the trihalides, but the cryst. dihalides are both less stable than the trihalides. A rough statistical calcn. of entropies for gaseous AlX and AlX_3 made no change in the trend. About 50 references.

CA 45, 434 d

Measurements of the Absolute Values of the
Cross-sections for Ionization of Uranium
Tetrachloride and Hexafluoride by Electrons
W. E. Berkey, E. H. S. Burhop, J. D. Craggs,
J. Keene, and H. S. W. Massey
Nat'l. Nuclear Energy Ser., Div. I, 5, 127-44

For 100-v. electrons the ionization cross-section of UCl_4 is about 5×10^{-15} sq. cm., approx. ten times the value for argon. No value could be quoted for UF_6 because of extreme variations in results.

Ionization and Dissocn. of Uranium Tetrachloride
and Hexafluoride by Electron Impact
E. H. S. Burhop, H. S. W. Massey, and C. Watt,
Ibid 145-65

The relative intensities of the ions UCl_n^+, UCl_n^{++}, Cl^+, Cl^-, UF_n^+, UF_n^{++}, UF_n^-, F^+, F^- produced by electron impact are studied. Electron energy, current d, and pressure were varied. Appearance potentials were measured for all these ions.

CA 45, 476 i

The Large Fused-electrolyte Cells for the
Production of Aluminum
L. Ferrand
J. four elec. 59, 114-17 (1950)

Detailed discussion.

CA 45, 489 b

Nonvolatile Inorganic Fluorides
H. J. Emeleus (Cambridge Univ., Engl.)
Fluorine Chemistry (Academic Press, Inc.,
New York) 1, 1-76 (1950)
Volatile inorg. fluorides, Anton B. Burg (U. South
Calif., Los Angeles) 77-123
Halogen fluorides. H. S. Booth (Western Reserve Univ.,
Cleveland, O) 189-200

CA 45, 923 f

Anomalous Mixed Crystals Between β-$NaYF_4$ and YF_3
F. Hund (Tech. Hochschule Stuttgart, Neckarhausen, Ger.)
Z. anorg. Chem. 263, 102-11 (1950); Cf. CA 44, 5750 g

YCl_3 solution was added to NaF solution to give $\chi\ \beta\ NaYF_4 \cdot y\ YF_3$ ($\chi + y = 1; \chi = 0.9910$ to 0.4170). Debye-Scherrer patterns show that the lattice const. a_w increases from 5.44 A to 5.52 A as y increases, but that the structure retains its symmetry and there are no marked intensity changes. Both observed and calcd. ds. and intensities agree if the model used has a fixed cation lattice, and the extra F ions are put in interstitial holes, but there is little correlation for a model with fixed anion lattice and cation holes. The space group is F_m3_m, and for a YF_3-rich crystal the atoms are in the following positions: 1.18 Na + 2.82 Y statistically distributed in 000, 0 1/2 1/2, 1/2 0 1/2, 1/2 1/2 0; 1.64 F statistically distributed in 1/2 1/2 1/2, 1/2 00, 0 1/2 0, 0 0 1/2; and 8 F in 1/4 1/4 1/4, 1/4 3/4 3/4, 3/4 1/4 3/4, 3/4 3/4 3/4 1/4, 3/4 3/4 3/4, 3/4 1/4 1/4, 1/4 3/4 1/4, 1/4 1/4 3/4.

CA 45, 967 g

The Fluorides of Niobium, Tantalum, Tungsten
and Rhenium
H. J. Emeleus and V. Gutmann (Univ. Chem. Lab.,
Cambridge, Engl.)
J. Chem. Soc. 1950, 2115-18; cf. CA 44, 5242 g

Attempts were made to prep. the lower fluorides of these elements from the metals and from other lower halides by reaction with HF. A lower chloride of Nb (cf. Sue, CA 33, 8132-9) reacted above 500° and Nb powder reacted at

250-300° to give NbF_5. Nb previously heated in H at 250° gave mainly NbF_5 but also an unidentified blue film, possibly the lower fluoride of Ruff and Schiller (CA 6, 839). Ta or Ta preheated in H gave a mixture of nonvolatile TaF_3 (10%) and volatile TaF_5 (90%) at 300°. WBr_2, prepd. from WBr_5 and H, gave partial reaction at 550° to undetd. products and at 600° gave WF_6 and W; metallic W was unattacked up to 700°. Re also did not react, and $ReCl_3$ at 350° gave Re and possibly a little ReF_6. WF_2 and ReF_2 may form, but are unstable at these temperatures.

CA 45, 1414 f

Thermodynamic Properties and Equilibrium at High Temperatures of the Compds. of Plutonium
L. Brewer, L. Bromley, P. W. Gilles, and N. L. Lofgren
(Univ. of Calif., Berkeley)
Nat'l. Nuclear Energy Ser. Div. IV, 14B, Transuranium Elements, Pt. II, 861-86 (1949)

Values of the thermodynamic data for Pu compds. are given, including m.p., b.p., and vapor-pressure data. Also given are: the consts. for the free energy of vaporization equation together with heat and entropy of vaporization at the b.p., values of the free-energy function, $(\Delta F - \Delta H_{298})/T$, and ΔH_{298}, the heat of formation, and the heat, free energy, and entropy of formation for the aq. ions. Values given are often estimates detd. by analogy with U and rare earth metals. The high temperature chemistry of the compds. is discussed. The equil. concns. of halogen or halide in Pu and halogen systems at 3 different pressures; namely, 1, 10^{-3}, and 10^{-6} atm. are presented.

CA 45, 1836 a

The Crystal Modifications of Lead Fluoride
Ya. Sauka (Latvian State Univ.)
J. Gen. Chem. U.S.S.R. 19, 1453-7 (1949)
(Engl. Translation) See CA 44, 896 i

CA 45, 1890 c

Dehydration of Alkali Metal Acid Fluorides
Robert C. McHarness and Anthony F. Benning (to the U.S. of America as represented by the Atomic Energy Comm.)
U. S., 2,527,320, October 24, 1950

Correction of Patent No. (see CA 45, 52 a)

CA 45, 2278 b

Revised Dielectric Parameters of Alkali and
Halide Ions
Shepard Roberts (G. E. Research Lab.,
Schenectady, N. Y.)
Phys. Rev. 81, 161 (1951); cf. CA 44, 392 d, 2811 f.

The ionic parameters, nuclear charge, nuclear compliance, electronic compliance, dielec. polarizability, and optical polarizability are tabulated for Li, Na, K, Rb, Cs, F, Cl, Br and I.

CA 45, 2380 d

Metallurgical Reactions of Fluorides
Herbert H. Kellogg (Columbia Univ.)
J. Metals 191, Trans., 137-41 (1951)

Graphs representing the standard free-energy of formation as a function of temperature for fluorides of Cl, Se, Te, C, S, As, Ag, H, Pb, Cd, U, B, Mn, Si, Al, Mg, K, Na, Ba, Ca, and Li are presented, along with estimated values for the standard free-energy of formation of Au, Hg, Cu, Co, Bi, Sb, Fe, Ni, Sn, Zn, Cr, Ti, Zr, and Be fluorides. A few of the many possible uses of these data in metallurgical calculations are discussed, including the fluorination of oxides, sulfides, and chlorides, and the reduction of metal fluorides.

CA 45, 3740 h

Lining for Fused Salt Electrolysis Cells
Adam I. S. Duncan, J. G. Moore, and Imperial
Chem. Industries Ltd.
Brit., 647,313, December 13, 1950

In cells for the electrolysis of fused salts or salt mixtures, a lining is provided for the protection of the refractory wall of the cell from attack by Cl, Na_2O, etc. A satisfactory lining or shield is made of mild steel. The lining prevents contact of the fused electrolyte with the refractory wall and thus eliminates contamination of the electrolyte.

CA 45, 4993 b

Precision Lattice Constants and Coefficients of
Thermal Expansion of PbF_2
Ya. Sauka (Riga State Univ.)
Zhur. Fiz. Khim. 25, 41-8 (1951)

By means of Straumanis' asym. method (CA 43, 8859 a) lattice consts. of single crystals of PbF_2 are detd. At 18°, $a = 5.92732 + 0.00001$ A. for the cubic modification (I) and $a = 3.89098 \pm 0.00003$; $b = 6.42689 \pm 0.00002$ $c = 7.63574 \pm 0.00018$ A. for the orthorhombic variety (II). From detns.

at 3 different temperatures, the expansion coeffs. are calcd.: $\alpha = 28.8 \times 10^{-6}$, $\beta = 86.4 \times 10^{-6}$, for I and $\alpha_1 = 31.9 \times 10^{-6}$, $\alpha_2 = 37.1 \times 10^{-6}$, $\alpha_3 = 13.6 \times 10^{-6}$, $\beta = 82.6 \times 10^{-6}$ for II.

CA 45, 5014 b

Thermodynamic Functions of Al_4C_3, Si, SiO_2, SiC, AlF_3 and Na_3AlF_6

L. I. Ivanova
Zhur. Obshchei Khim. (J. Gen. Chem.) 21, 444-52 (1951)

The thermodynamic functions were calcd. from heat capacities, partly taken from the literature, partly calcd. by Debye's formula. Selected data of Cp, $H_T - H_o$, $S_T - S_o$ and $-(F_T - F_o)$ are: For 1/4 AlF_3, at 100, 500, 1000, 1300°K.; 3.1, 114, 1.52, 0.5; 5.2, 1915, 8.41, 2290; 7.4, 5029, 12.67, 7611; 8.6, 7229, 14.77, 11972. For 1/10 Na_3AlF_6 at 100, 500, 1000, 1300°K.; 3.00, 112, 1.50, 38; 6.13, 2122, 9.11, 2433; 7.29, 5524, 13.81, 8286; 7.41 7728, 15.73, 12721.

CA 45, 6476 e

An Example of a Particular Solidification Diagram in a Reciprocal System of Fused Salts

Andre Chretin, Pierre Silber, and Mohammad Ishaque
Compt. rend. 232, 1217-18 (1951)

Curves of cooling were plotted for the system KCl + NaF $\rightleftharpoons$ NaCl + KF. Five solid phases with 3 series of mixed crystals were found. KCl and NaF crystallize separately, forming a stable couple. The diagram shows a eutectic for KCl, KF, and NaF at 582° with 49% F and 90.5% K. Another equil. corresponds to a temp. min. (at 612° with 50.5% K and 9.25% F) of crystn. of the solid soln. NaCl-KCl with the addn. of NaF.

CA 45, 6483 e

Study of Ionic Crystals under Electron Bombardment

D. E. McLennan (Univ. Toronto)
Can. J. Phys. 29, 122-8 (1951)

Alkali halide crystals bombarded within an electron microscope show a generalized photographic effect. In macro-crystals (0.2-0.002 cm.) equil. F-center formation slowly reversible after bombardment ceases, and stable entrapped metal colloids in the crystal lattice were observed. Ionization pulses were noted only during bombardment. In micro-crystals (10-0.01 μ) electron-diffraction techniques showed the presence of metal, oxide, or carbonate after bombardment of halide. A postulated sequence of events under bombardment includes ionization, capture of Cl^- electron to produce Cl^o, migration of Cl^o to exterior of crystal and disintegration of crystal from center out.

CA 45, 6485 a

Electronic Structure of the F-Center in Alkali
Halide Crystals
Toshinosuke Muto
Rept. Inst. Sci. and Technol. Univ. Tokyo 1, 140-5 (1947);
cf. C.A. 44, 8775i

Two perturbation methods for solving the Schrodinger equation for an electron captured in the F-center are suggested; the 1st method, which corresponds to the at. wave function approximation, is based on the assumption that the potential due to the surrounding ions in the crystal lattice is approximated by the periodic static potential due to perfect lattice (that part due to the missing neg. ion is subtracted). The 2nd one, which corresponds to the mol.wave function approximation, is based on the assumption that the potential is approximated by the sum of that due to the nearest ions and that due to the other ions.

CA 45, 6485 b

Theory of the F-Absorption Band in Alkali Halide Crystals
Toshinosuke Muto
Rept. Inst. Sci. and Technol. Univ. Tokyo 2, 37-42 (1948);
cf. preceding abstr.

Theoretical. At sufficiently higher temps. than the Debye characteristic temp. of the NaCl crystal, the F-absorption max. shifts to the longer-wave-length side linearly with rising temp., and at sufficiently lower temps. more slight dependence on temp. is to be observed. The breadth of the absorption band increases with rising temp. unsymmetrically on both sides of the band center.

CA 45, 6485 c

Theory of the Kerr Effect in Colored Alkali
Halide (Preliminary Report)
Mitsukuni Watanabe
Rept. Inst. Sci. and Technol. Univ. Tokyo 2, 139-40 (1948)

The Mott-Tibbs model for F-centers in alkali halide crystals (Tibbs, C.A. 34, 1907-1) suggests that the Kerr const. in colored alkali halide crystals becomes infinite at the wave length corresponding to the energy difference between 1s-2p, or 1s-2s levels.

CA 45, 6515 b

Electrolytic Cleaning of Metals
Hugh G. Webster (to J. H. Shoemaker)
U. S., 2,547,510, Apr. 3, 1951

A bath for the electrolytic cleaning of oxide and scale from ferrous metals consists of NaOH 85, NaCl 10, Na aluminate 1, NaCN 2, and NaF 4 parts.

CA 45, 6525 g

New Compounds Containing Active Fluorine
Hans Bode (Chem. Staatsinst., Hamburg, Ger.)
Naturwissenschaften 37, 477 (1950)

Reaction of F_2 with halides of K, Rb, and Cs gives, not fluorides, but MF_2 for K and Rb and MF_3 for Rb (?) and Cs as intermediary products. The MF_2 compounds are optically isotropic and cubic. CsF_3 is anisotropic and probably rhombic. The compds. liberate I from KI solns.; they color free $NiCl_2$ red with formation of $M_2(NiF_6)$; they are white and hygroscopic. By reaction of F_2 with mixed alkali halides, compds. such as $KF_3 \cdot RbF_3$ and Rb_7SbF_{24} (in the presence of Sb_2O_3) are formed.

CA 45, 6535 c

Fluorine and Fluorocarbons
G. W. Busch. R. C. Carter, and F. E. McKenna (Univ. of Chicago)
Natl. Nuclear Energy Ser., Div. VIII, 1, Anal. Chem. Manhatten Project 226-48 (1950)

The chemistry of F is reviewed with particular regard to properties that can be used for detg. the element. Many F compds. can be decompd. by heating with powd. silica $+$ H_2SO_4 or $HClO_4$. The H_2SiF_6 formed distils off and is thus removed from the mineral. To avoid the action of F or HF on the container, special Pt app. is required of which 4 illustrations are shown. Fusion with Na_2CO_3 gives water-sol. NaF. UF_4 can be dissolved in a mixt. of H_3BO_3 and HCl, $AlCl_3 + HCl$, $H_3BO_3 + H_2SO_4$, or $HCl + HNO_3$ ....

CA 45, 6833 f

Fluorine-Resistant Lubricant
John F. Gall (to Penn. Salt Manufg. Co.)
U. S., 2,548,471, Apr. 10, 1951

A fluid mixt. of 1-7 moles of HF to 1 mole of KF possesses good lubricating properties and is inert to gaseous or liquid F. The compn. may be used from 0 to 300°. Smaller proportions of HF are sufficient at higher operating temps.

CA 45, 6931 f

X-Ray Luminescence Spectra of Alkali Halides
Aparesh Chatterjee (Calcutta Univ.)
Indian J. Phys. 24, 265-70 (1950)

Spectrograms covering the range of 2750-7000 A. are shown for X-ray-excited crystals of NaF, NaCl, NaBr, KBr, KI, KBr + TlCl (Mech. mixt.) and KBr + Tl (solid soln.). Other alkali halides showed little or no glow when irradiated; however, all showed a characteristic color change. The emission bands were not characteristic of any impurities present, and hence represent lattice emission. The importance of lattice-emission spectra in elucidating the electronic energy states of solids is discussed.

CA 45, 6989 b

Aluminum Welding Fluxes
Mike A. Miller and Warren E. Haupin (to Aluminum Co. of America)
U. S., 2,522,104, May 8, 1951

Improved arc stabilization, fluxing action, and slag removal were obtained with new flux compns. of nonhygroscopic salts with the following typical analysis: NaCl 33, KCl 34, LiF 15, AlF_3 10.5, NaF 4.5, Ca or Sr sulfate 3%. In coating the welding rod, the bare Al rod is heated to 1020°F. before dipping into the flux bath, which varies from 1110 to 1200°F. In U. S., 2,552,105, the flux compn. contained NaCl 33, KCl 33, LiF 15, AlF_3 7.5, MgF_2 8 and Ca or Sr sulfate 3.5%. In U. S., 2,552,106, the flux compn. contained NaCl 30, KCl 33.5, LiF 14, AlF_3 7, MgF_2 9, NaF_3, and Ca or Sr sulfate 3.5%. Cf. C.A. 44, 6380i.

CA 45, 7852 c

Distribution of the Thorium Isotope U X_1 Between
Lanthanum Fluoride Crystals, and its Saturated
Solutions in 3 and 12% Nitric Acid at 100°
V. G. Khlopin and M. S. Merkulova
Doklady Akad. Nauk S.S.S.R. 65, 861-4 (1949) cf. CA 44, 6241 b

The system UX_1 $(Th)F_4$-LaF_3 is particularly interesting because it is analogous to the system YF_3-CaF_2 in the formation of "anomalous mixed phases" (cf. CA 24, 1005). The distribution equil. is detd. from both sides by approach from an active satd. soln. with inactive crystals and from an inactive soln. with active crystals. The equil. is established in 48 hrs., but even after 8 hrs. the av. of the coeffs. $K_{(D)}$ (the ratio of the enrichment and impoverishing coeffs.) for both types of reactions is detd. with sufficient accuracy. With decreasing concn. of the Th isotope in the soln., $K_{(D)}$ continuously decreases to zero. This is the same phenomenon that was observed in systems of an inorg. host crystal with an org. foreign substance included (cf. CA 35, 3870-7). The low limit of miscibility characterizes the cryst. soln. in such a case as a pseudo- (anomalous) mixed-phase pehnomenon.

CA 45, 7857 i

Thermodynamics of Fluorine-Chlorine Exchange Reactions - Systems NaF-NaCl, BaF_2-$BaCl_2$, NiF_2-$NiCl_2$, and PbClF-$PbCl_2$
G. C. Hood and M. M. Woyski (Univ. of Wisconsin, Madison)
J. Am. Chem. Soc. 73, 2738-41 (1951)

The metal fluorides were prepared by reaction of anhyd. HF with the corresponding chlorides. Analysis of the kinetic data permitted calcn. of free energies for the exchange reactions. Thus, an evaluation was made of the thermodynamic fluorinating ability of each fluoride. In decreasing order of ability to fluorinate, these were found to be BaF_2, NaF, PbClF, NiF_2 and HF.

CA 45, 7863 i

The Nonreversible, Reciprocal, "Two-ridge" System of the Fluorides and Chlorides of Barium and Potassium
E. I. Banashek and A. G. Bergman
Doklady Akad. Nauk S.S.S.R. 57, 905-6 (1947); Chem. Zentr. (Russian zone Ed.) 1949, I, 2; cf. CA 44, 8217 h

A study made of the 4 binary systems belonging to the quaternary system: Ba - K - Cl - F verified the results of Ponomareff (CA 9, 1435), Plato (CA 2, 502, 3019), and Gemsky (CA 8, 2536). The visual polythermal method was used for the investigation. Two diagonal and 23 interior lines (of intersection) form the square liquidus diagram of the reciprocal system. The pure salts are represented at the corners of the square. The most sharply defined, stable line of the system is the K_2Cl_2-BaF_2 line. The next in order of stability is the K_2Cl_2-$BaF_2 \cdot BaCl_2$ line. The BaF_2 region occupies 50.12% of the field; next is the $BaF_2 \cdot BaCl_2$ region (28.13%). These two fields are characterized on the space model by two sharply defined ridges (space folds). There are 4 eutectics at 575° (BaF_2, K_2F_2, K_2Cl_2), 616, 625, and 728°. The last 3 contain no K_2F_2. The nonreversible, reciprocal system of the diagonal type is characterized by the formation of the compd. $BaF_2 \cdot BaCl_2$, which does not affect the direction and displacement of the displacement reactions. This is also true of the chlorides, which occupy only 0.75% of the liquidus field.

CA 45, 8315 i

A Quantum-Mechanical Treatment of the Lithium Fluoride Crystal
G. C. Benson and G. Wyllie (Bristol Univ., Engl.)
Proc. Phys. Soc. (London) 64A, 276-82 (1951)

A simplified quantum-mech. model for the LiF crystal is described. The lattice parameter, cohesive energy, and compressiblity are calcd. by use of 3 different choices of wave function for the F^- ion in the crystal; these are (1) the Hartree wave functions for the free ion F^-, (2) wave functions orthogonalized to the 1s-orbitals of the 6 nearest neighbor Li ions, (3) functions similar to 2 but based on wave functions for the free ion, that have been contracted to give agreement with the diamagnetism of F^-. The results obtained in (1) are in fair agreement with the empirical values. Large discrepancies are observed when the more complete wave functions (2) are used; this indicates that the Hartree wave functions for the free ion are too diffuse. Results of (3), which agree well with expt., substantiate this interpretation. It is assumed that the metal and halogen ions are arranged in the usual cubic lattice array and that the structure is completely ionic. Purely central forces act between ions, and the force between two ions that are not nearest neighbors is considered to be the ordinary electrostatic term. Only uniform lattice deformations are allowed, and the energy assocd. with the thermal vibration of the ions is not considered. Repulsion between the closed shells of the halogen ions is probably significant in most Li halides. An exam. of the ratios of the radii of the various halogen ions to that of the Li^+ ion indicates that only in the case of F is there some justification for neglecting this effect.

CA 45, 8339 d

Equilibrium "Liquid-Solid" in the Ternary System Formed by the Fluorides of Na, K and Ca
Pierre Silber and Mohammad Ishaque
Compt. rend. 232, 1485-7 (1951); cf. CA 45, 6476 e

The study by thermal analysis (curves of cooling) shows for CaF_2-Na_2F_2 a eutectic (a) at 810° (51% Na_2F_2); for Na_2F_2-K_2F_2, two series of mixed crystals with a eutectic (b) at 722° (61% K_2F_2); for K_2F_2-CaF_2, a double salt $CaF_2 \cdot KF$, after fusion at 1068° forms a eutectic with each salt (c) 26.7% CaF_2 at 782° and (d) 76.9% CaF_2 at 1060°. Four solid phases appear: for CaF_2, a double salt $KF \cdot CaF_2$ and two series of mixed crystals $NaF \cdot KF$: series I rich in NaF and series II rich in KF. The corresponding areas in the plot are bounded by 5 lines for the 2 solids which det. 2 points; (e) at 682°, 14% CaF_2, 50% K_2F_2 and 36% Na_2F_2; and (f) at 772°, 34% CaF_2, 19% K_2F_2, and 47% Na_2F_2.

CA 45, 8368 f

Sodium^{20} from the Gamma-Ray Bombardment of
Sodium Fluoride
R. K. Sheline (Univ. of Chicago)
Phys. Rev. 82, 954 (1951)

Alverez has reported (CA 45, 956f) the reactions $Ne^{20}(p,n)Na^{20}$; $Na^{20} \dashrightarrow \beta^{+} + Ne^{20*}$; Ne^{20} has an alpha-decay. By using 76 m.e.v. betatron gamma-rays, the reaction Na^{23} (γ,3n) - Na^{20} was obtained. The $\beta+$ half-life is 0.23 ± 0.08 sec. The end point of the β^{+} spectrum lies in the range 3.5-7.3 m.e.v.

CA 45, 9978 a

Thermal Expansion of Crystals. IV. Silver Chloride,
Lithium Fluoride, and Magnesium Oxide
S. S. Sharma (Indian Inst. Sci., Bangalore)
Proc. Indian Acad. Sci. 32A, 268-74 (1950); cf. CA 45, 7842e

Coeffs. of linear expansion are given for the compds.: AgCl to 325°, $\alpha_t = 0.0_{4}3136 - 0.0_{7}1588t \pm 0.0_{9}2038t^2$; LiF to 380°, $\alpha_t = 0.0_{4}3376 + 0.0_{7}2054t \pm 0.0_{10}4885t^2$; MgO to 710°, $\alpha_t = 0.0_{4}1098 + 0.0_{8}5865 + 0.0_{11}1052t^2$. Gruneisen's consts. calcd. for AgCl above room temp. and for LiF from -222° to 400° vary markedly with temp.

CA 45, 10024 d

Silicate Models. II. The System Sodium Fluoride-Beryllium
Fluoride and its Relations to the System Calcium Oxide-Silica.
Erich Thilo and Hansjurgen Schroder (Humboldt Univ., Berlin)
Z. physik. Chem. 197, 39-62 (1951); cf. C.A. 44, 1316g

The system NaF-BeF_2 was studied by thermal analysis to a BeF_2 content of 61 mole %; only solid solns. exist above this compn. The results are completely analogous to those for the CaO-SiO_2 system. The temps. in °K. of almost all invariant points in the fluoride system when multiplied by 2.82 are converted to the corresponding points in the silicate system. The definite compds. found and their m.ps. are: NaF 990°, Na_2BeF_4 578°, $NaBeF_3$ 372°, $Na_3Be_2F_7$ 348° (incongruent). The eutectic NaF-Na_2BeF_4 occurs at 31 mole % BeF_2 and m. 560°; $Na_3Be_2F_7$-$NaBeF_3$ at 44.3% and m. 340°. In the subsystem NaF-Na_2BeF_4 there is formed by a solid-state reaction Na_3BeF_5. The alpha and beta modifications of Na_2BeF_4 were definitely identified; 3 addnl. modifications were established with high probability, and the beta and alpha modifications of $NaBeF_3$ were detected. The various transition temps. were detd. Incidental results show that the thermal decompn. of $(NH_4)_2BeF_4$ occurs in 2 steps; the intermediate product NH_4BeF_3, stable between 230 and 270°, has a characteristic x-ray diagram.

CA 46, 837 c

Surface Tension of the Cryolitic Molten Baths
A. Vajna (Lab. ric. ind. nazl. allum, Mori, Italy)
Alluminio 20, 29-38 (1951); cf. C.A. 45, 5043 e

The baths contg. CaF_2 have a surface tension greater than the alk. baths and these greater than the acid baths. The neutral baths are intermediate. The obtained results of the surface and interface tensions of the phases in contact (solid-liquid-gas, liquid-liquid, and liquid-liquid-solid) are used to explain some peculiar phenomena happening in the electrolytic industrial cells; chiefly the anodic effect.

CA 46, 1222 g

Potassium Titanium Fluoride
Henry C. Kawecki and Edwin J. Bielecki (to Beryllium Cor.)
U. S., 2,568,341, Sept. 18, 1951

The process is described for the production of high-purity Na_2TiF_6, K_2TiF_6, and $(NH_4)_2TiF_6$ from Fe-bearing titaniferous raw materials, ilmenite ores, or a slag concentrate. The raw material is digested with sufficient HF (60% com. grade) in water soln. to form a soln. contg. TiF_4 and FeF_2, and the insolubles are sepd. A salt of the alkali whose fluotitanate is desired is added to the soln. at 70°, with excess HF. The alkali salt should have an anion (chloride or nitrate) which will form a ferrous salt more sol. than $FeSO_4$. The desired fluotitanate is crystd. out of the soln. to which 5% H_2SO_4 has been added for each 50% HF by wt., to produce large crystals. After decantation, the crystals are filtered or centrifuged.

CA 46, 1336 g

The Theory of Electrolytic Solutions. II. Integral Heat of Dilution of Electrolyte.
Tatsuro Watari (Tokyo Inst. Technol).
J. Electrochem. Soc. Japan 19, 189-92 (1951); cf. CA 45, 3222i, 8328b

By taking into account the undissocd. mol. $M^{+}A^{-}$ and its monohydrate $M^{+}(H_2O)A^{-}$, the integral heat of uni-univalent electrolytes is calcd., and applied to LiCl, KF, and NaCl.

GENERAL INFORMATION CONCERING FLUORIDES

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