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ANP CHEMISTRY SECTION PROGRESS REPORTPhase EquilibriaThe System NaF-ZrF₄-UF₆

Na₂UF₆ has been successfully used as the uranium bearing compound to be added to a fluoride solvent to bring a reactor to criticality in known controlled increments. However, because of its relatively high melting point, (665°C), some effort has been made to locate a lower melting substitute. One such mixture, previously described,¹ is a ternary peritectic composition at the junction of the Na₂ZrF₄-Na₃ (Zr, U) F₇-Na₇ (Zr, U)₆F₃₁ phase fields and is apparently located at or near the composition NaF-ZrF₄ - UF₆ (63.5-18.0-18.5 mole %). This mixture showed only a single break on the cooling curves at 607°C, which is about 50°C lower than the melting point of Na₂UF₆. The calculated uranium content of the above mixture is 1.44 grams/cm³ at 700°C as compared to 2.75 grams/cm³ for Na₂UF₆ at the same temperature.

RbF-ZrF₄ System

Visual observation experiments have recently shown that the eutectic between Rb₂ZrF₆ and Rb₅Zr₄F₂₁ lies near 42 mole % ZrF₄ at about 410°C. Results of quenching experiments had previously indicated that the eutectic was near 38 mole % ZrF₄ at 375°C. It now seems apparent that 375°C is the lowered rapid inversion temperature instead of the eutectic temperature. In the region from 37 to 44.5 mole % ZrF₄ Rb₂ZrF₆ appears optically like quench growth at all temperatures above the lowered inversion temperature. This accounts for the misinterpretation of the quenching data.

Petrographic examinations of a series of quenches at 48.3 mole % ZrF₄ established that Rb₅Zr₄F₂₁ is the primary phase, the liquidus is about 396°C, and the solidus is about 390°C. Thus, the eutectic between Rb₅Zr₄F₂₁ and RbZrF₅ is near 48.5 mole % ZrF₄ at 390°C.

Examinations of slowly cooled preparations have shown the existence of a yet unidentified compound containing more than 50 mole % ZrF₄. Thermal analysis indicates a eutectic at about 55 mole % ZrF₄.

A revised diagram is shown in Figure 1.

1. ANP Chemistry Section Progress Report for Period Ending December 19, 1955, CF 55-12-109.

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~~SECRET~~The System RbF-UF₄

An early interpretation of thermal analysis data,¹ of the system RbF-UF₄ inferred that the system contained the compounds:

- (1) 3RbF·UF₄, congruent
- (2) 2RbF·UF₄, incongruent
- (3) RbF·UF₄, incongruent
- (4) RbF·2UF₄, incongruent
- (5) RbF·3UF₄, incongruent
- (6) RbF·6UF₄, incongruent

Recent investigations have been made on the system in conjunction with work on the RbF-NaF-ZrF₄ system. It is now believed that the compound list for the system contains:

- (1) 3RbF·UF₄, congruent, m.p. 995°C
- (2) 2RbF·UF₄, incongruent
- (3) 7RbF·6UF₄, incongruent
- (4) RbF·UF₄, congruent, m.p. 725°C
- (5) RbF·2UF₄, incongruent
- (6) RbF·4UF₄, incongruent

The System NaF-RbF-ZrF₄-UF₄

The system NaF-RbF-ZrF₄-UF₄ provides a potential fuel for circulating fuel reactors. A search is underway for a quaternary eutectic near the region of minimum liquidus temperature of the NaF-RbF-ZrF₄ solvent, i.e., 398°C at 8NaF-53 RbF-39 ZrF₄ (mole %).

Phase equilibrium studies indicate that mixtures whose solvent compositions lie on the low ZrF₄ side of the boundary curve in the region 35-40 ZrF₄ (mole %) and 0-15 NaF (mole %) will have RbF·UF₄ as the primary uranium containing phase. In those mixtures above this boundary line RbF·4UF₄ will be the primary uranium containing phase, and uranium will also be contained in solid solution with 4RbF·4ZrF₄. It can be inferred from thermal analysis data that a region between these primary phase fields and containing 6-15 NaF (mole %) will provide a 7 mole % UF₄ fuel with a melting point of approximately 545°C.

The System RbF-CeF₃

An incomplete study of this system indicates the existence of two or more compounds; one of these is believed to be Rb₃CeF₆ melting congruently at about 745°C. The RbF-Rb₃CeF₆ eutectic

1. ANP Quar. Prog. Rep. June 10, 1951, ANP-65, p. 87.

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contains approximately 15 mole % CeF_3 and melts at $660^\circ\text{C} \pm 5^\circ$. The data obtained to date with mixtures containing $33\text{-}1/3$ to 60 mole % CeF_3 cannot be interpreted unequivocally but the solidus temperature appears to be $615^\circ\text{C} \pm 5^\circ$ for mixtures containing 42.5 to 55 mole % CeF_3 . The cooling curves show thermal effects with compositions in this region ranging from about 500 to 580°C which are undoubtedly due to solid transformations and probably account for the fact that the slowly cooled mixtures contain extremely small crystals that are not readily amenable to microscopic identification.

The System RbF-CaF_2

Thermal analysis data obtained with mixtures containing 10 to 35 mole % CaF_2 indicate the existence of a eutectic, probably containing less than 10 mole % CaF_2 , having a melting point of $760^\circ\text{C} \pm 5^\circ$. Petrographic examination of slowly cooled melts showed the presence of an isotropic crystalline phase having a refractive index near 1.410. This phase has not been definitely identified but by analogy from the KF-CaF_2 system in which the compound KCaF_3 was reported,¹ the compound is expected to be RbCaF_3 . Examination of the solid samples was hampered by the hygroscopic nature of RbF .

The System RbF-BeF_2

Continuing studies of this system have demonstrated the existence of the compound RbBe_2F_5 in addition to the compound at 25, $33\text{-}1/3$ and 50 mole % BeF_2 previously reported.² Thus it appears that phase relationships in this system are almost completely analogous to those in the system KF-BeF_2 .³ Thermal data did not clearly demonstrate melting relations of the RbBe_2F_5 compound but quenching studies of this compound indicated that it probably melts congruently at about 465°C . Since this composition did not quench to a glass, quenching studies with other compositions in this region of the diagram are planned. Although the viscosity of mixtures in the low-melting part of this system is undoubtedly too high to be of practical importance, it was found that the viscosity of a 50-50 (mole %) mixture was significantly less than that of the comparable KF-BeF_2 mixture.⁴

1. P. W. Silber and Ishaque, *Comp. rend.* 232, 1485 (1951).
2. ANP Chemistry Section Progress Reports, CF-56-1-55, CF-56-1-101 CF-56-2-9.
3. ANP Quar. Prog. Rep. Dec. 10, 1955, QRNL-2012.
4. S. I. Cohen, personal communication.

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The System NaF-RbF-BeF₂

Preliminary studies of this system included thermal analysis of compositions on the joins NaF-RbBeF₃, NaF-Rb₂BeF₄ and NaF-Rb₃BeF₅, supplemented by examination of the slowly cooled melts. The data obtained to date indicates that the NaF-Rb₂BeF₄ join comprises a quasi-binary system having a eutectic containing approximately 43 mole % NaF and 19 mole % BeF₂ melting at 655°C $\pm$ 5°. Study of the other joins is incomplete but the 1:1:1 composition (molar ratio) that was found to be a compound composition in the NaF-KF-BeF₂ contained two crystalline phases that are as yet unidentified. The liquidus temperature of this mixture (565°C) is sufficiently low for it to be of interest as a possible fuel carrier if the addition of UF₄ effects a significant lowering of the liquidus temperature. The NaF-Rb₃BeF₅ join is believed to be a quasi-binary with a eutectic containing about 45 mole % NaF and 14 mole % BeF₂ melting at 640°C $\pm$ 5°.

The System NaF-LiF-BeF₂

Quenching studies on the NaF-LiF-BeF₂ system have been continued. The phase which was believed to be a ternary compound and which has appeared in mixtures in the region between Na₂BeF₄ and the composition NaF-LiF-BeF₂ has now been identified by high temperature X-ray diffraction as a polymorph of Na₂BeF₄. This phase, which is stable above 320°C, had not been reported in previous investigations of the NaF-BeF₂ system,^{1,2} and had not been found in quenched samples of NaF-BeF₂ mixtures examined in this laboratory. Its inversion is too rapid for it to be quenched in the binary system, but it is stabilized by addition of LiF with which it undoubtedly forms a limited solid solution.

An unidentified phase which has an X-ray diffraction pattern related to one presented by Jahn³ for a phase he believed to be Na₃LiBe₂F₈ has been found in samples equilibrated and quenched from below 320°C. Samples of the composition corresponding to Na₃LiBe₂F₈ contained Na₂LiBe₂F₇ as well as the phase in question. It is possible that it is LiF·5NaF·3BeF₂ since the X-ray diffraction pattern of samples of this composition which had been equilibrated below 320°C gave no indication of the presence of any of the other phases of the system. It is not yet known whether it is a sub-solidus compound or melts incongruently to Na₂BeF₄ and liquid.

1. Roy, Roy and Osborn, J. Am. Ceram. Soc., 36 (6)185 (1953).
2. Thilo and Schroeder, Z. Physik. Chem., 197, 39 (1951).
3. Jahn, Zeit. f. anorg. u. allgem. chem., 277, 17 (1954).

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The eutectic on the quasi-binary join $\text{LiF-Na}_2\text{LiBe}_2\text{F}_7$ has been established at 37 BeF_2 -26 LiF -37 NaF (mole %) and 340°C by quenches on both sides. Examinations of quenched samples on the join $\text{Na}_2\text{LiBe}_2\text{F}_7\text{-Na}_2\text{BeF}_4$ show this to be a quasi-binary system with a eutectic at 38.5 BeF_2 -16.5 LiF -45 NaF (mole %) and 343°C . Experiments are under way to determine the ternary eutectics in the three "compatibility" triangles, $\text{LiF-Na}_2\text{LiBe}_2\text{F}_7\text{-Na}_2\text{BeF}_4$, $\text{Na}_2\text{LiBe}_2\text{F}_7\text{-NaBeF}_3\text{-Na}_2\text{BeF}_4$ and $\text{LiF-NaF-Na}_2\text{BeF}_4$.

The System Flinak- UF_4

Previously reported liquidus temperatures of Flinak (NaF-KF-LiF , 11.5-42.0-46.5 mole %)- UF_4 mixtures¹ indicated that the liquidus temperature of mixtures containing approximately 4 mole % UF_4 increases quite rapidly with increasing UF_4 concentration. In connection with the preparation of an enriched uranium mixture for radiation damage studies, it became necessary to determine liquidus temperatures of mixtures with higher concentrations of UF_4 as quickly as possible. Visual observation of mixtures containing 5.0, 7.5 and 10 mole % UF_4 gave liquidus temperatures of 550, 570 and 595°C , respectively. The visual observation data for the 10 mole % UF_4 mixture checked quite well with earlier thermal analysis data. It appears from these data that the liquidus temperature of Flinak- UF_4 mixtures in the 0-10 mole % UF_4 range is not as strongly dependent upon UF_4 concentration as the earlier visual observation-filtration data¹ had indicated. The liquidus curve obtained from visual observation data extrapolates to a minimum at approximately 1.1 mole % UF_4 which has a liquidus temperature, determined by thermal analysis, of 452°C .

The System LiF-CsF

Recent availability of pure CsF prompted a re-examination of the LiF-CsF system which is of interest because an incongruently melting compound is formed as in the case of the LiF-RbF system. The melting point of the material used in the recent investigation was found to be $700^\circ\text{C} \pm 5^\circ$ which agrees with recently published values of 705°C ² and 703°C ³. The thermal analysis data shown in Figure 2 includes some data from the earlier studies. The compound, believed to have the composition $\text{LiF}\cdot\text{CsF}$, is easily recognized under the microscope because it is birefringent whereas both LiF and CsF are isotropic. However, for reasons that are as yet unknown, the mixtures examined to date did not give sharply defined peaks for the compound on X-ray diffraction patterns.

1. R. J. Sheil, ANP Quar. Prog. Rep. Dec. 10, 1954, ORNL-1816.
2. Schmitz-Dumont, et al., Z. anorg. Chem. 252, 329 (1953).
3. M. A. Bredig, H. R. Bronstein and Wm. T. Smith, Jr., J. Am. Chem. Soc. 77, 1454 (1955).

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The System $\text{UF}_4\text{-UO}_2$

A limited investigation of this system is being conducted to supplement information available in the literature.¹ The freezing point of UF_4 was redetermined as the starting point in this investigation. The value obtained (1034°C) is in excellent agreement with the published value¹ of 1036°C . Cooling curves with $\text{UF}_4\text{-UO}_2$ mixtures containing approximately 2 to 10 weight % UO_2 gave variable results due to undercooling. The highest liquidus temperature obtained with a mixture containing 2.2 wt. % UO_2 was 1019°C . These experiments are being continued in an effort to obtain more reproducible data. Petrographic and X-ray diffraction examination of the slowly-cooled melts showed no evidence of solid solution or compound formation between UF_4 and UO_2 but the possibility of solid solutions at elevated temperatures followed by ex-solution at lower temperatures is not ruled out by the available data.

An interesting phenomenon connected with these experiments was the effect of the oxide content of the mixtures on their ability to penetrate graphite. Mixtures containing 2% or less UO_2 did not penetrate ordinary graphite at temperatures up to 1100° while mixtures containing 4% or more UO_2 penetrated both ordinary and high density graphite at the same temperatures. It is not clear whether this is a wetting effect or whether chemical attack on the graphite occurs.

The System LiF-NiF_2

Data on the mixture LiF-NiF_2 (90-10 mole %) were reported in a previous progress report.² Thermal analysis data obtained with other mixtures in this system containing 20, 30, 40 and 50 mole % NiF_2 are difficult to interpret. Solid phase studies of slowly cooled melts indicate that there is a cubic compound probably containing 25 mole % NiF_2 . The 80-20 mole % mixtures contained only the compound and LiF having a higher index than that of the pure material. LiF was not observed in the 70-30 or 60-40 mixtures but well-crystallized NiF_2 was found suggesting that it may be the primary phase at these compositions. Liquidus temperatures of melts in this system (minimum about 805°C) are too high to be of interest for electro-chemical studies.

1. A. D. Ryon and L. P. Twichell, H-5.3852, July 25, 1947.

2. ANP Chemistry Section Progress Report for Period Ending January 30, 1956, CF-56-2-9.

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The System ZnF_2 - ZnO

A review of earlier attempts to determine the melting point of pure ZnF_2 showed that a wide range of liquidus temperatures was obtained, from 885 to 940°C, and that a second break appeared on the cooling curves at temperatures at or near 845°C. Since ZnO was found in all of the samples that were examined, it seemed probable that the variation in liquidus temperature and the lower thermal effect were due to the presence of this impurity. Confirmation of this was obtained recently with oxide-free ZnF_2 prepared by $\text{NH}_4\text{F}\cdot\text{HF}$ treatment of ZnF_2 previously dried in an HF atmosphere. Only one thermal effect was noted at 940°C $\pm$ 5°C on cooling curves. Because of the large discrepancy between this value for the melting point and those reported in the literature, 872°C¹ and 875°C $\pm$ 3°C², the slowly cooled ZnF_2 was subjected to rigorous examination by means of chemical and spectrographic analysis, petrographic and X-ray examination including a high precision determination of cell parameters. Since all the data obtained indicated that our material was pure ZnF_2 , the melting points reported in the literature are believed to be erroneous. Data obtained with mixtures containing 5, 10, 15 and 20 mole % ZnO showed that the eutectic melting at 850°C $\pm$ 5°C contains approximately 21.5 mole % ZnO . Only the pure components were found in the slowly cooled mixtures, indicating that solid solution does not occur, at least at room temperature.

Study of Eutectic Mixtures by Zone Melting

In the current zone melting studies, initiated to aid cooling curve determinations of eutectic mixtures, 30" long stainless steel tubes were filled to a depth of 15" with the molten material. The tubes were pulled twice upward through the hot zone of the furnace, kept at 800°C, at a speed of 1" per hour. The furnace was kept at an inclined position (45°).

Three compositions of the NaF-KF-ZrF_4 system were subjected to zone melting. Analysis of the solidified melt revealed that the expected ternary composition was not reached in any of the tubes, but only approached it. Further refining of the techniques will be necessary.

1. N. A. Pushin and A. V. Baskow, Z. anorg. Chem., 81, 359 (1913).
2. H. M. Haendler, W. L. Patterson, Jr. and W. J. Bernard, J. Am. Chem. Soc. 74, 3167 (1952).

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Chemical EquilibriaEffect of Total Pressure on the Rate of Reduction of KF by UF₃ in NaF-LiF-KF Eutectic at 750°C.

In spite of an unfavorable standard free energy change of more than 30 kcal. per gram atom of potassium for the reaction $UF_3 + KF \rightarrow UF_4 + K$, potassium vapor is evolved from a solution of UF₃ in molten NaF-LiF-KF eutectic. That this reaction should proceed at a noticeable rate is additional evidence of the strong complexing of UF₄ in fluoride melts. Thus the same complexing by fluoride ions which renders UF₄ solutions much less corrosive than might have been expected also contributes materially to the relatively rapid deterioration of UF₃ solutions. The kinetics of the change of UF₃ to UF₄ in a mixture containing KF is complicated by two competing reactions: first, the evolution of K from KF, and second, disproportionation to produce an alloy of uranium with the container wall according to the reaction $4UF_3 \rightarrow 3UF_4 + U^0$ (alloy). For most melts, particularly those that do not contain any cations as easily reducible as K⁺, or in which there are no excess F⁻ ions for complexing UF₄, the second reaction predominates. An example of a potentially valuable aircraft reactor fuel in which the first reaction becomes manifest is the solution of UF₃ in the LiF-NaF-KF (46.5-11.5-42.0 mole %) eutectic. To gain a rough idea of the rate of attrition of UF₃ in this solvent under various conditions, samples have been taken for analysis from open copper crucibles held at constant temperature in a helium atmosphere.

Previous reports^{1,2} have given the effect of total pressure at 650°C where there was a very marked acceleration in the rate of reaction, as measured by the amount of UF₃ remaining after two hours at helium pressures below 50 mm, in contrast to virtually no dependence on pressure above 50 mm. The results at 750°C are now available. When the total pressure was maintained above the critical value of 130 mm, 10 wt % of U³⁺ or 47% of the original amount was found after two hours in a solution that originally contained 21.4 wt. % U³⁺. This compares with 12.4 wt. % or 58% of the original amount remaining at 650°. The difference is probably due to a more rapid evolution of K at the higher temperature. While the effect of temperature on the competing reactions cannot be resolved with certainty, the disproportionation, although initially rapid, would be expected to slow

1. B. H. Clampitt, ANP Quarterly Progress Report December 10, 1955, ORNL - 2012.
2. ANP Chemistry Section Progress Report for Period Ending November 7, 1955, CF-55-11-41.

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down to a very slow rate controlled by the diffusion of U^O into the copper container wall long before the two hour period elapsed. Hence an approximately constant amount of UF_4 , enough to correspond to saturation of the wall surface with U^O , would be formed by the disproportionation reaction at each temperature. On the other hand, the evolution of K appears to reach a near-equilibrium steady state, and to proceed at a rate controlled by vaporization of potassium vapor from a solution of potassium in salt. This inference is based primarily on the assumption that the sharp break in the rate as a function of pressure occurs at the "bubble point" pressure for the solution. This pressure is 130 mm at 750° as compared to 50 mm at $650^\circ C$.

The vapor pressure of pure potassium at $650^\circ C$ is 240 mm, and at $750^\circ C$ is 750 mm; thus the steady state activity of K is approximately 0.2 at each temperature and hence the solution is not saturated. The absence of a phase with a brilliant blue-green color, previously reported¹ as a result of equilibration of alkali metal and alkali halide, further attests to the absence of a liquid potassium phase.

At pressures lower than the bubble point pressure, the slow rate corresponding to the near-equilibrium, steady state is greatly exceeded due to the rapid evolution of K and the amount of UF_3 remaining unconverted to UF_4 in two hours is roughly proportional to the pressure. By making some very approximate assumptions it is possible to estimate that about 35% of the UF_3 was converted by disproportionation at each temperature, but the conversion by reduction of KF increased from about 7% at $650^\circ C$ to about 18% at $750^\circ C$.

For the steady state condition, the apparent heat of activation is 18 kcal if the rates are considered proportional to the steady state potassium pressure at the two temperatures. This is in good agreement with the 20 kcal heat of vaporization of potassium, particularly since 18 kcal applies to solutions in which the activity of potassium is only 0.2.

It is interesting to note that since the UF_3/UF_4 ratio does not change markedly with temperature, and the near equilibrium steady state activity of potassium does not change from the value 0.2, the equilibrium constant for the reaction is independent of temperature. This means that the heat of reaction is very small in spite of the large positive standard free energy for the reaction. Evidently a large negative heat of complexing is involved, and the reaction is

1. ANP Chemistry Section Progress Report for Period Ending December 19, 1955, CF-55-12-109.

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better represented by the equation:

On the assumption that the activity coefficients of KF and UF_3 are of the order of unity the relation

$$K_a = 1 - \frac{F^0}{RT} = \frac{(a_{UF_4})(a_K)}{(a_{UF_3})(a_{KF})} = \frac{(X_X UF_4)(0.2)}{(.02)(0.4)} = 1^{-16}$$

gives an order of 10^{-7} for the activity coefficient of UF_4 in the NaF-LiF-KF eutectic. This compares with 10^{-1} from a similar calculation based on the reaction $2UF_4 + Fe^0 \rightarrow 2UF_3 + FeF_2$ in the same solvent, and also in an $NaZrF_5$ solvent in which UF_4 must compete with ZrF_4 for fluoride ions. Thus the outstanding mystery regarding these experiments is how UF_3 can reduce KF to produce K at an activity of 0.2. It should be remembered that K at unit activity will reduce not only UF_4 , but also UF_3 .

On the basis of these results, the NaF-LiF-KF type of melts for which the beneficial effects of UF_3 are most needed are the melts with which UF_3 is least compatible. This is a consequence of the extremely small activity coefficient for UF_4 in the presence of the large excess of fluoride ions, and the correspondingly high activity of U^0 required by the disproportionation equilibration to balance the low UF_4 activity.

Colors of Alkali Metals Saturated with Alkali Halides

The following observations have been made on the blue-green colors of the metal layers² in two phase condensed systems comprised of an alkali metal and an alkali halide at temperatures above $400^\circ C$.

1. It is definitely the metal phase, rather than the salt phase which processes the brilliantly colored luster. Dr. Max Bredig has pointed out that the vapor of alkali metals appears colored, and that the color attributed to the metal may be a consequence of viewing it through a layer of vapor. This possibility cannot be completely ruled out, but it appears more likely that both the vapor and the salt treated metal are colored.

1. J. D. Redman, ANP Quarterly Progress Report December 10, 1954, ORNL-1771, p. 62.
2. ANP Chemistry Section Progress Report for Period Ending December 19, 1955, CF-55-12-109.

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2. Except in the case of lithium metal, the color does not depend on composition. In other words, sodium and potassium develop the same colors, and do so regardless of which alkali halide is used with them (even LiF or LiBr).
3. Lithium metal does not become colored at temperatures below the point at which it becomes self luminous.
4. The color depends on the temperature, changing from green at 500°C to deeper blue at higher temperatures (>600°C).
5. Whether the salt phase is liquid or solid does not make any difference.
6. A few milligrams of salt are sufficient to color 20 grams of metal. However, a definite minimum amount of salt is required, and smaller amounts have no effect. The minimum required to cause color does not appear to correlate with solubility.
7. The color corresponding to a given temperature is either present or absent. There is no gradual transition from the normal silver color to the blue-green luster.
8. The salt phase in equilibrium with the molten alkali metal becomes darker at higher temperatures, but does not become brilliantly colored.
9. The metal colors do not appear to be related to F-centers in the solid alkali halide, nor to Mollwo's alkali halide melts which had been exposed to alkali metal vapors¹.
10. From these observations, it appears that the blue-green (metal fogs or "pyrosols" which have been noted during electrolysis of alkali halide were probably due to a colored metal phase, rather than to subhalides or to diffraction by colloids.

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1. Mollwo, Erich. Akad. Wissench. bottingen, Nachrichten Math. Physikal. Klasse., Fachgruppe II, Neue Folge, Vol I, No 18, p 203-7 (1935).

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~~SECRET~~Reaction of UF_4 with Cr and Fe in LiF-ZrF_4

The reaction of UF_4 with Cr^0 has been studied at 600 and 800°C using LiF-ZrF_4 (52-48 mole %) as reaction medium. The results obtained for this system using 12.0 wt % UF_4 (3.9 mole %) are given in Table I.

Table I

Data for the Reaction of UF_4 with Cr^0 in Molten LiF-ZrF_4 (52-48 mole%)
at 600 and 800°C.

Conditions of Equilibration		Present in Filtrate		
Temp (°C)	Time (hr)	Total U (wt%)	Total Cr^1 (ppm)	Total Ni (ppm)
600	3	9.9	2550	30
600	3	9.7	3000	75
600	5	10.0	2980	70
600	5	9.4	3060	45
600	12	9.6	2910	30
600	12	9.6	3060	35
800	3	10.1	3820	55
800	3	9.2	3830	30
800	5	8.9	4070	35
800	5	8.6	4040	45
800	12	9.5	3780	60
800	12	9.5	3830	50

1. Blank of 250 ppm of Cr at 800°C.

The data given in Table I show that the equilibrium concentrations of Cr are relatively high in this solvent and that the reaction is temperature dependent. The corresponding Cr values using NaF-ZrF_4 (53-47 mole %) as reaction medium are 1700 and 2100 ppm at 600 and 800°C, respectively. Assuming that chromium is divalent equilibrium constants calculated from mole fractions are 7×10^{-4} and 3×10^{-3} at 600 and 800°C, respectively for the LiF-ZrF_4 case compared to 1×10^{-4} and 3×10^{-4} at 600 and 800°C, respectively in the NaF-ZrF_4 mixture.

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The results of similar studies on the reaction of UF_4 with Fe^0 are given in Table II.

Table II

Data for the Reaction of UF_4 with Fe^0 in Molten LiF-ZrF_4 (52-48 mole%)
at 600 and 800°C.

<u>Conditions of Equilibration</u>		<u>Present in Filtrate</u>		
<u>Temp</u> <u>(°C)</u>	<u>Time</u> <u>(hr)</u>	<u>Total</u> <u>U</u> <u>(wt%)</u>	<u>Total</u> <u>Fe^I</u> <u>(ppm)</u>	<u>Total</u> <u>Ni</u> <u>(ppm)</u>
600	3	9.1	460	30
600	3	10.0	550	35
600	5	9.7	460	40
600	5	9.9	520	65
800	3	9.8	360	15
800	3	9.6	390	20
800	5	9.6	400	35
800	5	9.5	350	35

1. Blank of 100 ppm of Fe at 800°C.

The iron values reported in Table II are in agreement with the results found for other solvents studied. For example, values of 490 and 390 ppm at 600 and 800°C, respectively, were found in NaF-ZrF_4 (53-47 mole %). The iron values apparently are not greatly influenced by varying the reaction medium and in nearly all cases are somewhat higher at 600 than at 800°C.

Reaction of UF_4 with Cr and Fe in NaF-ZrF_4

Filtration studies on the reaction of UF_4 with Cr^0 and Fe^0 have been carried out at 600 and 800°C in nickel using NaF-ZrF_4 (50-41 mole %) as reaction medium. Results obtained for these systems using 11.4 wt% UF_4 (3.7 mole %) are given in Table III.

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Table III

Data for the Reaction of UF_4 with Cr^0 and Fe^0 in Molten NaF-ZrF_4
 (59-41 Mole %) at 600 and 800°C.

Conditions of Equilibration			Present in Filtrate			
Temp (°C)	Time (hr)	Metal	Total U (wt%)	Total Cr ^(a) (ppm)	Total Fe ^(b) (ppm)	Total Ni (ppm)
600	3	Cr	8.9	710	---	65
600	3	Cr	8.7	1010	---	95
600	5	Cr	9.4	1060	---	70
600	5	Cr	8.8	970	---	95
600	5	Cr	8.6	1030	---	35
800	3	Cr	9.9	1000	---	90
800	3	Cr	8.7	950	---	45
800	5	Cr	9.6	1190	---	60
800	5	Cr	10.4	1080	---	70
600	3	Fe	8.5	---	510	35
600	3	Fe	8.6	---	630	40
600	5	Fe	8.6	---	370	60
600	5	Fe	8.5	---	600	70
800	3	Fe	8.9	---	680	70
800	3	Fe	8.6	---	290	65
800	3	Fe	9.2	---	460	70
800	3	Fe	9.2	---	440	75
800	5	Fe	9.3	---	465	100
800	5	Fe	8.8	---	280	35

(a) Blanks of 270 ppm of Cr at 800°C.

(b) Blanks of 140 ppm of Fe at 800°C.

The chromium concentrations reported in Table III are considerably lower than those found in the other NaF-ZrF_4 mixtures and also indicate that the temperature coefficient of the $\text{UF}_4\text{-Cr}^0$ system is small when 59-41 NaF-ZrF_4 is used as reaction medium. The chromium values expressed in ppm found in other NaF-ZrF_4 mixtures

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at 600 and 800°C respectively are: 50-50 mole % -2250 and 2550, 53-47 mole % -1700 and 2100. The other ZrF₄ containing solvent studied, LiF-NaF-ZrF₄ (55-22-23 mole %) yielded 500 and 650 ppm of chromium at 600 and 800°C, respectively.

The iron concentrations given in Table III are approximately the same as found when either NaF-ZrF₄ (50-50 mole %) or NaF-ZrF₄ (53-47 mole %) is used as reaction medium. The temperature effect appears to be slight although a slight decrease in iron concentration with increasing temperature is indicated. A similar temperature effect occurs when the other two NaF-ZrF₄ mixtures are used as solvents.

Reaction of UF₄ with V in Various Solvents

Earlier studies¹ on the reaction of UF₄ with V⁰ at 600 and 800°C using NaF-LiF-KF (11.5 - 46.5 - 42.0 mole %) as the reaction medium gave vanadium concentrations of approximately 25 ppm at both temperatures. Data also have been presented² for this system using LiF-NaF-ZrF₄ (55-22-23 mole %) as the reaction medium which indicated that vanadium concentrations of approximately 800 ppm prevailed at both 600 and 800°C. Unreported data indicate that the reaction of UF₄ with V⁰ also occurs to a significant extent at 600 and 800°C when NaF-ZrF₄ (50-50 mole %) serves as the reaction medium. From the foregoing results it was concluded that UF₄ is stable in contact with V⁰ when the NaF-LiF-KF mixture is used as solvent whereas in ZrF₄ containing solvents UF₄ is unstable in contact with V⁰. These conclusions were of considerable interest since in virtually all other cases studied the metals are more stable toward UF₄ in ZrF₄ containing melts than in the NaF-LiF-KF mixture. Further studies by Analytical have shown the low vanadium values reported for the NaF-LiF-KF melts are in gross error and on the basis of recent results it is evident that UF₄ undergoes a significant reaction with V⁰ in all of the solvents studied. It is planned to repeat the studies on the UF₄-V⁰ system in the several reaction media.

1. ~~ANP Chemistry Section Progress Report for Period Ending September 12, 1955, CF-55-9-60.~~
2. ~~ANP Chemistry Section Progress Report for Period Ending January 16, 1956, CF-56-1-101.~~

Diffusion of Sodium Vapor

Two experiments have been run in an attempt to determine whether or not the movement of sodium from an area at 500°F to cooler surfaces is significant. In the first run about 5 g of sodium was loaded into a glass tube 1/2" in diameter and 36" long, the lower 5" of the tube heated to 500°F and the remainder of the tube air cooled. The tube contained helium at a pressure of one atmosphere above the molten sodium. After 42 days the tube was sectioned and analyzed for sodium. The only section of the tube which contained any significant amount of sodium was the section immediately above the heater. A 1" length at this point had approximately 5 mg of sodium on the surface whereas the other sections above this carried less than 0.1 mg. The temperature of the section which showed the highest sodium content was approximately 300°F during the experiment. Tungsten wires (3 pairs) sealed into the tube at several different positions showed infinite resistance at all times. The second experiment was similar to the first except that the tube above the sodium was held at 250°F instead of air cooled. The results of this second experiment were comparable to the first except for a larger amount (28 mg) of sodium appearing on the section immediately above the 500°F area.

Filtration of NaK to Remove Oxides

Attempts to remove oxides from NaK by filtering through ultra fine sintered glass filters have proven unsuccessful because of the high pressure required to force NaK through this type filter. A metal still is being assembled at present and it is planned to use this apparatus for distilling NaK in a further attempt to remove the oxides.

Corrosion Studies

Diffusion Studies by Activation Analysis

Interface reaction of molten fluorides with the chromium component of Inconel results in the removal of the latter from the alloy. Then, subsequent migration of the chromium in the Inconel results in the formation of subsurface voids. A concentration gradient in chromium is thus established through the metal wall, causing a migration of the chromium from the higher-concentration area toward the chromium-depleted surface. The thickness of the layer impoverished in chromium is a function of the depth of the corrosive attack.

Experiments are underway utilizing activation analysis to study the diffusion of chromium in Inconel. A measure of the

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diffusion velocity of chromium in Inconel may be obtained by activation analysis measurements over a period of time.

As a standard on which to base future measurements a clean section of Inconel was activated in the X-10 graphite reactor. Three hours after removal from the reactor the radiation rate of a 12 gram section was 7 R/hr at 5 inches from the surface. This specimen was allowed to cool for several days to diminish the portion of the activity due to nickel. At the end of this time most of the activity was that of activated chromium and an autoradiograph showed a very homogeneous distribution of activity.

The aim of the current work is to establish whether diffusion studies are sensitive enough to follow the diffusion of chromium in the wall of a 1/2" o.d. tube. Two approaches are currently under investigation in conjunction with M. G. Leddicotte of the Activation Analysis Group: (a) Exposure of the irradiated sample to a photographic plate. The optical density of the plate is then determined as a function of distance from the periphery. In evaluating the data obtained, it is believed that results are inconclusive because of the limited resolution of the densitometer. (b) Measurement of the radioactivity in various portions of each sample. It is believed that by milling successively small amounts of metal from the inside of the tube, a series of samples can be obtained from increasing depths, as measured from the interface. The amount of the sample, the depth of each milling and a measurement of the amount of Cr^{51} (27.8d) radioactivity in each portion will be used to determine the degree of chromium diffusion.

Preliminary work has consisted of determining the radioactivity of the samples used for radioautograph analyses by means of a gamma-ray spectrometer. The gamma spectral analysis displayed a continuous record of the relationship between the counting rate and the gamma ray energy, allowing one to obtain the relative intensities of all the gamma-emitting radioelements in the sample. Results indicate that the Cr^{51} activity is somewhat more intense than the other radioelements in the sample, therefore, a measurement of the Cr^{51} intensity in each portion milled from the sample should be possible.

Current work by the Analytical Chemistry Division includes the design of suitable equipment for obtaining and retaining each layer milled from the specimen.

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Testing of Valve-Seat Materials

The General Electric Company silicones previously reported,¹ as surviving testing in NaK in surveys searching for possible valve-seat material have now been carefully examined. G. E. silicone No. 81578 was practically unharmed showing 5% stretch under tension, No. 81577 was next in resistance with 5-10% stretch under tension; third was No. 81576 which showed 10% stretch and was easily torn from the clamp holding it in place. It is of interest to note that in these three silicones, less attack was noted with increasing material density.

Of the samples that failed, some were attacked considerably more at the surface of the NaK, thus indicating possible harmful effects of oxides, while others were attacked relatively uniformly.

Fluoride Production Facilities

The large-scale fluoride processing facility was reactivated early in March using stainless-steel reactor cans containing copper liners. It will be recalled that failure of the nickel cans resulted in considerable loss of production time in the processing of fluoride mixes. During three weeks of operation in March some 2500 lbs of purified fluoride compositions were successfully prepared in the new cans. A large backlog of requests for special fluoride compositions was reduced to current requests.

The $ZrCl_4$ to ZrF_4 conversion facility has recently been shown to operate successfully. Analysis of the product from two runs indicated that good conversion is being obtained. Loss of material per run due to fine $ZrCl_4$ being swept into the gas lines has been reduced to some 20 lbs out of a 250 lb charge. Test batches of fuel compositions will be made using the recently converted ZrF_4 .

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January 30, 1956, CF-5612-9.

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