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**SOLUBILITY AND STABILITY OF STRUCTURAL METAL DIFLUORIDES
 IN MOLTEN FLUORIDE MIXTURES**

C. M. Blood

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ABSTRACT

Studies of the corrosion of nickel alloys by molten fluorides of interest as nuclear reactor fuel-solvents led to the determination of equilibrium quotients for the reduction by hydrogen of dissolved impurities, NiF_2 , FeF_2 , and CrF_2 , and also to the determination of the solubilities of NiF_2 and FeF_2 in the molten fluorides. This information is useful for practical purposes (the removal of Ni and Fe impurities from molten fluorides) and also is a source of fundamental information regarding the solution behavior of the molten fluorides and the chemical properties of the impurities.

Equilibrium quotients are reported for NiF_2 at 550 to 625°C in NaF-ZrF_4 melts having an NaF concentration of 53 and 60 mole %; for NiF_2 at 600°C in NaF-ZrF_4 having an NaF concentration of 43, 48, and 56 mole %; for NiF_2 at 500 to 600°C in LiF-BeF_2 (62 mole % LiF); for FeF_2 at 600 to 800°C in NaF-ZrF_4 (53 mole % NaF) and in LiF-BeF_2 (62 mole % LiF); and for CrF_2 at 750 to 850°C in NaF-ZrF_4 (53 mole % NaF) and in LiF-BeF_2 (62 mole % LiF).

Solubilities are reported for NiF_2 at 550 to 625°C in NaF-ZrF_4 (53 mole % NaF); for NiF_2 at 600°C in NaF-ZrF_4 having an NaF

concentration of 43, 48, 56, and 60 mole %; for NiF_2 at 475 to 600°C in $\text{LiF}-\text{BeF}_2$ (62 mole % LiF); and for FeF_2 at 500 and 550°C in $\text{LiF}-\text{BeF}_2$ (62 mole % LiF). In $\text{LiF}-\text{BeF}_2$ (62 mole % LiF) the saturating phases were crystalline NiF_2 , FeF_2 , and CrF_2 . In the $\text{NaF}-\text{ZrF}_4$ solvents, the saturating phases were $\text{NaF}\cdot\text{NiF}_2\cdot 2\text{ZrF}_4$, $\text{NaF}\cdot\text{FeF}_2\cdot 2\text{ZrF}_4$ and $\text{NaF}\cdot\text{CrF}_2\cdot 2\text{ZrF}_4$, and the apparent solubility depended on the amount of solute added to the molten mixtures.

For NiF_2 and FeF_2 in the $\text{LiF}-\text{BeF}_2$ solvent, a combination of the equilibrium quotients and solubilities will yield experimental equilibrium constants which suggest revisions of some thermochemical quantities and estimates. Better activity coefficients for NiF_2 , FeF_2 , and CrF_2 can be expected when the calculations have been completed.

INTRODUCTION

Studies of the corrosion of nickel alloys by molten fluorides, which were of interest as nuclear reactor-fuel solvents, revealed that NiF_2 , FeF_2 and CrF_2 were corrosion products which dissolved in the melt.

Purification procedures for the molten fluorides involved the use of HF to remove oxides and sulfur compounds which were found in the component fluoride salts used for the mixtures. When purification was carried out in nickel apparatus, the HF could form NiF_2 from the container and FeF_2 from compounds of iron carried in the component salts. Both NiF_2 and FeF_2 were corrosive impurities, since they could be displaced by chromium

from the alloy containers into which the solvents were transferred for use.

When hydrogen was used to remove the reducible impurities from the solvents, it was observed that NiF_2 was much more readily reduced than might be expected on the basis of free energy values tabulated in the thermochemical literature. This led to the determination of equilibrium quotients for the reduction by hydrogen at 500 to 850°C of dissolved NiF_2 , FeF_2 , and CrF_2 in the fluoride solvents for the purpose of obtaining respective activity coefficients for the solutes. The solvents used in this investigation were NaF-ZrF_4 mixtures covering a range of compositions and a mixture of LiF-BeF_2 (62 mole % LiF).

Solubilities of NiF_2 and FeF_2 were determined in order to ensure that the measured values of the equilibrium quotients were determined within the solubility limits. The intrinsic value of the solubilities as data on phase behavior from which activity coefficients could be obtained was of particular interest where saturating phases for the respective metal fluorides were observed to be the pure crystalline NiF_2 , FeF_2 , and CrF_2 in molten LiF-BeF_2 (62 mole % LiF).

This report of tabular and graphic data for equilibrium quotients and solubilities, including the identity of the saturating phases, will serve as the source for a number of projected publications on these studies.

EXPERIMENTAL

Materials

Solvents

The solvents were prepared from reagent grade LiF , BeF_2 , NaF , and sublimed ZrF_4 . They were purified by treatment with H_2 and HF , which removed oxide, detectable S (<5 ppm), and nearly all structural-metal cations (<50 ppm Cr). The purified solvents were transferred in the molten state to the experimental apparatus through a nickel filter of 0.0004-in. porosity.

Solutes

Pure NiF_2 and FeF_2 were prepared from reagent grade NiCl_2 (cobalt free) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. After dehydration at 100°C , the solid chlorides were treated at 400°C in a nickel pot with anhydrous HF gas till chloride was undetectable by bubbling the effluent gas through an aqueous solution of AgNO_3 . Excess HF was removed by flushing the system with helium.

Pure CrF_2 was made by the reaction of molten SnF_2 with chromium metal at 1100°C for 2 hr. The tin precipitated from the melt, leaving a layer of CrF_2 .

The solutes so prepared were >98% pure, based on the cation-to-fluorine ratio as determined by wet analysis, and contained only spectroscopically detectable traces of other metallic elements.

Protective Atmosphere

Helium containing less than 5 ppm oxygen provided an inert atmosphere over the liquid during sampling and solute additions.

To prevent hydrolysis of the molten salts, the helium was passed through magnesium perchlorate and a dry-ice cold trap to remove the small quantities of H_2O that might be present.

Gases

Mixtures of hydrogen and helium were made up in cylinder-tank quantities. Helium under pressure was added to the mixing cylinder containing small amounts of hydrogen. The partial pressure of hydrogen (about 3.0 to 9.0 %) was determined by pressure-volume measurements with a gas burette before and after oxidation of the hydrogen with heated copper oxide. The small amounts of oxygen present, if any, in the mixture were removed by passage through a platinum catalyst (Dexo unit), and, subsequently, water was removed in the same manner as that used for drying the protective atmosphere before entry into the apparatus.

Commercial cylinder hydrogen was used. It was treated the same as the mixtures of hydrogen and helium for the removal of oxygen and water.

Anhydrous HF obtained in cylinders contained less than 0.1% of gases insoluble in the standardized KOH solutions used for titrating the HF. The HF was used without further purification.

Apparatus

A schematic diagram of the equilibration apparatus used is shown in Fig. 1. The reactor consisted of a 4-in.-diam cylindrical can about 15 in. high. It was closed at the top by a flange and flange plate. A thermocouple well, a 3/8-in.-diam gas-inlet tube

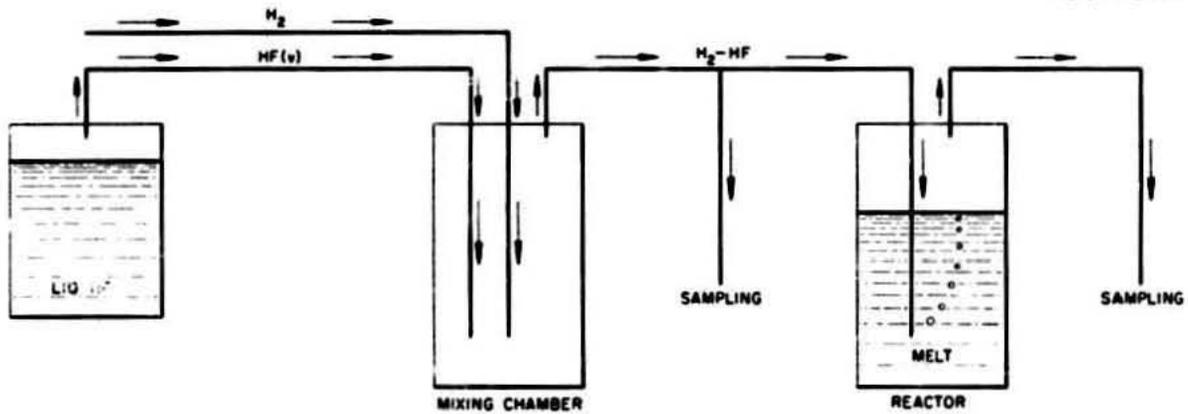


Fig. 1. Flow Diagram of Equilibration Apparatus.

reaching nearly to the bottom of the can, a 6-in length of 1-in. diam pipe, and a 3/8-in. diam gas-outlet tube were welded through the flange plate. The 1-in.-diam pipe, which served as a port through which samples of the melt could be taken and additions made, was closed by a threaded cap seated on a Teflon gasket.

For experiments with NiF_2 , the equilibration pot, thermocouple well, gas-inlet tube, and baffle system were fabricated from grade A nickel. For experiments with FeF_2 , these parts were of mild steel. For experiments with CrF_2 , a chromium-plated nickel reactor was used, with the exception that the baffle system was eliminated.

The reactor was heated by a 5-in.-diam tube furnace equipped with a temperature controller.

The gas-mixing chamber consisted of a 4-in.-diam cylindrical nickel can about 7 in. high, closed at the top similar to the

reactor. Two 1/4-in.-diam nickel inlet tubes reaching nearly to the bottom of the can, and one 1/4-in.-diam outlet tube were welded through the flange plate. One of the inlet tubes supplied the HF flow, and the other supplied the hydrogen or hydrogen-helium flow. The temperature of the mixing chamber was $\sim 400^{\circ}\text{C}$, and mixing was accomplished by convection of the gases.

The flow rate of the gases to the mixing chamber could be adjusted to a constant rate by pressure regulators and suitable orifices. In the case of HF, small cylinders (6 lb.) of anhydrous liquid HF were thermostatically controlled to $\pm 0.1^{\circ}\text{C}$ at desired temperatures between 16 and 35°C . The flow rate of HF gas from the thermostat was controlled by passage through heated copper tubing (100°C) containing a number of orifices made of sintered nickel of 0.0004-in. porosity.

The various pieces of apparatus were connected by copper and nickel tubing and Swagelok fittings; flexible tubing of fluorothene or Teflon was used in low-temperature regions of the apparatus.

Filters through which samples of the molten mixture were drawn consisted of sintered copper (0.0004-in. pore size) welded as porous caps on lengths of 3/8-in.-diam tubing. Helium was passed through the filter sticks as they were inserted through the loading port into the melt. Samples of the melt were drawn by reducing the gas pressure within the filter sticks.

Procedure

The equilibrium reduction by hydrogen of dissolved metal fluorides MF_2 yields equilibrium quotients K_N that are proportional

to the ratio of the square of the partial pressure of HF, p_{HF} , over the partial pressure of hydrogen, p_{H_2} :

$$K_N \sim \frac{(p_{\text{HF}})^2}{p_{\text{H}_2}} .$$

The method used for equilibration consisted of the continuous passage of a gaseous mixture of HF and hydrogen of a known and constant HF concentration through the molten solution at a given temperature (500 to 850°K) and at a total pressure of approximately 1 atm until the concentration of the MF_2 attained a value that remained constant for several days. Equilibrium concentrations of MF_2 were measured for various quantities of the solutes.

In the case of NiF_2 , equilibrium concentrations were measured for small concentrations to the approximate saturation limits at 500 and 550°C in LiF-BeF_2 (62 mole % LiF). In order to accommodate the relatively noble tendency of Ni^0 , the low partial pressures of hydrogen required for the equilibrium gas concentrations were obtained by diluting the hydrogen with helium.

For CrF_2 , equilibrium concentrations at 750 to 850°C were very difficult to attain in any reasonable length of time (about three weeks or more). For this case, equilibrium was approached for both the oxidizing and the reducing mixtures of HF and hydrogen. These oxidizing and reducing mixtures of HF and hydrogen were controlled to within 50% of the equilibrium concentrations of HF. This method of attaining equilibrium concentrations of CrF_2 appeared to be satisfactory since the average equilibrium quotient

obtained checked those for a number of nearly equilibrium concentrations of this solute. The effect of employing this method for CrF_2 causes the precision of equilibrium quotients to be 2 to 3 times less than those for NiF_2 and FeF_2 .

Generally, filtered samples of the equilibrating molten solution were taken periodically in order to follow the MF_2 concentrations to a constant value for the corresponding equal influent and effluent partial pressures of HF and hydrogen. To ensure that equilibrium had been attained, sampling of the equilibrating solution was continued for several more days at the same partial pressures of HF and hydrogen before changing equilibrium conditions.

The filtered samples obtained with a copper filtering device were withdrawn from the melt under a helium cover; the solidified sample was removed, ground, and chemically analyzed for its nickel, iron, or chromium content.

A standardized aqueous solution of KOH was used to titrate the HF from the influent and effluent gas streams, and the residual volumes of either the hydrogen or the mixture of helium and hydrogen were accurately metered. The partial pressures of HF in the gas streams were defined by acidimetric titration of the excess KOH. The partial pressure of hydrogen in the residual gas mixtures of known hydrogen concentration was determined by difference between the partial pressure of the HF and the measured total pressure.

In the case of NiF_2 and FeF_2 , the residence time of the equilibrating gas bubbles in the molten solution was increased

sixfold by the use of a system of baffle plates.

The determination of solubilities for NiF_2 and FeF_2 in molten fluoride solutions generally involved equilibration in the presence of excess solute in a helium atmosphere at a given temperature. Filtered samples of the supernatant were analyzed for the amount of cation present. Solubility determinations were sometimes carried out in the same solution along with the equilibrium measurements. In particular, independent solubility experiments were conducted for NiF_2 and for FeF_2 in LiF-BeF_2 (62 mole % LiF).

Temperatures of the molten solution for both equilibrium and solubility experiments were recorded continuously and measured to $\pm 2^\circ\text{C}$ by Chromel-Alumel thermocouples which were checked against a standard Pt vs Pt -- 10% Rh thermocouple and potentiometer.

RESULTS AND DISCUSSION

Equilibrium Quotients

The equilibrium reduction experiments between 500 and 850°C were originally designed to obtain activity coefficients based on the present thermochemical values for the solid and the supercooled-liquid solutes as reference state.

For the reaction



where M^0 is the metal (Ni^0 , Fe^0 , or Cr^0) and MF_2 is the corresponding fluoride, the equilibrium constant K_a becomes

$$K_a = \frac{(a_{\text{HF}})^2 (a_{\text{M}^0})}{(a_{\text{H}_2}) (a_{\text{MF}_2})} \quad (2)$$

where a represents the activity of the designated reactants and products. The term a_{M^0} was defined as unity for Ni^0 and Fe^0 where the reaction vessel was constructed of the respective metals. In the case of Cr^0 , a_{M^0} was also defined as unity, where the reaction vessel was constructed of chromium-plated nickel and an excess of chromium metal aggregate was added to the molten solution. The activities of HF and hydrogen were measured as respective partial pressures since both gases are expected to behave ideally at temperatures above 500°C . The term a_{MF_2} was defined as

$$a_{\text{MF}_2} = N_{\text{MF}_2} \gamma_{\text{MF}_2} \quad (3)$$

where N is the mole fraction of the MF_2 in solution, based on a three-component system comprised of the MF_2 and the simple end members of the solvent, and γ is the activity coefficient. For concentrations of a dissolved MF_2 up to saturation, Eq. (2), by substitution, becomes

$$K_a = \frac{(p_{\text{HF}})^2}{(p_{\text{H}_2}) (N_{\text{MF}_2}) (\gamma_{\text{MF}_2})} = K_N K_\gamma \quad (4)$$

where

$$K_N = \frac{(p_{\text{HF}})^2}{(p_{\text{H}_2}) (N_{\text{MF}_2})} \quad (5)$$

is the experimental equilibrium quotient expressed in atmospheres and

$$K_\gamma = \frac{1}{\gamma_{\text{MF}_2}} \quad (6)$$

is the activity coefficient quotient. Activity coefficients for the reaction based on either the solid or supercooled liquid as reference state can be obtained from Eq. (4) as follows:

$$\gamma_{MF_2} = \frac{K_N}{K_a} \quad (7)$$

where K_a is the equilibrium constant for the respective standard state.

The average values of the equilibrium quotients for NiF_2 dissolved in various solvents and at designated temperatures are listed in Table 1. The tabulated precisions are the arithmetic mean deviations and have a range of 3 to 9%. The temperature dependencies of the K_N values for NiF_2 in NaF-ZrF₄ (53 mole % NaF) and Li-BeF₂ (62 mole % LiF) are shown in Fig. 2, and the temperature dependency of the K_N values for NiF_2 in NaF-ZrF₄ (60 mole % NaF) is shown in Fig. 3. Table 1 and Figs. 2 and 3 also show the effect of decreasing the NaF concentration of the NaF-ZrF₄ solvents on the K_N values at 600°C for NiF_2 . The K_N values decrease fivefold (from 2.59×10^4 to 0.455×10^4) for the corresponding decrease in the NaF concentrations from 60 mole % to 43 mole %.

The effect of NiF_2 concentration on the K_N values for NaF-ZrF₄ solvents and the LiF-BeF₂ solvent shown in Figs. 4, 5, 6, 7, and 8 indicate that K_N is independent of the NiF_2 concentration range from dilute to saturated solutions. In particular, detailed studies of the K_N values were made near the saturation limits of

Table 1. Equilibrium Quotients for NiF_2 in Molten Fluoride Solutions

Solvent	T ($^{\circ}\text{C}$)	$K_N^* \times 10^{-4}$ (atm)	Number of Determinations
NaF-ZrF_4 (53 mole % NaF)	625	2.19 ± 0.20	24
	600	1.53 ± 0.07	16
	575	1.10 ± 0.06	43
	550	0.757 ± 0.035	19
NaF-ZrF_4	(43 mole % NaF) 600	0.455 ± 0.014	10
	(48 mole % NaF) 600	0.916 ± 0.042	16
	(56 mole % NaF) 600	1.85 ± 0.11	22
NaF-ZrF_4 (60 mole % NaF)	625	3.72 ± 0.12	9
	600	2.59 ± 0.07	21
	575	1.92	1
LiF-BeF_2 (62 mole % LiF)	600	1.73 ± 0.12	22
	550	0.990 ± 0.057	54
	500	0.504 ± 0.046	96

* $K_N = \frac{(p_{\text{HF}})^2}{(p_{\text{H}_2}) N_{\text{NiF}_2}}$; the precision of K_N is the arithmetic mean deviation.

NiF_2 in NaF-ZrF_4 (53 mole % NaF) at 550 $^{\circ}\text{C}$, and in LiF-BeF_2 (62 mole % LiF) at 500 and 550 $^{\circ}\text{C}$.

The equilibrium quotients for FeF_2 dissolved in NaF-ZrF_4 (53 mole % NaF) and LiF-BeF_2 (62 mole % LiF) are listed in Table 2. The arithmetic mean deviations have a range of 3 to 8%. The

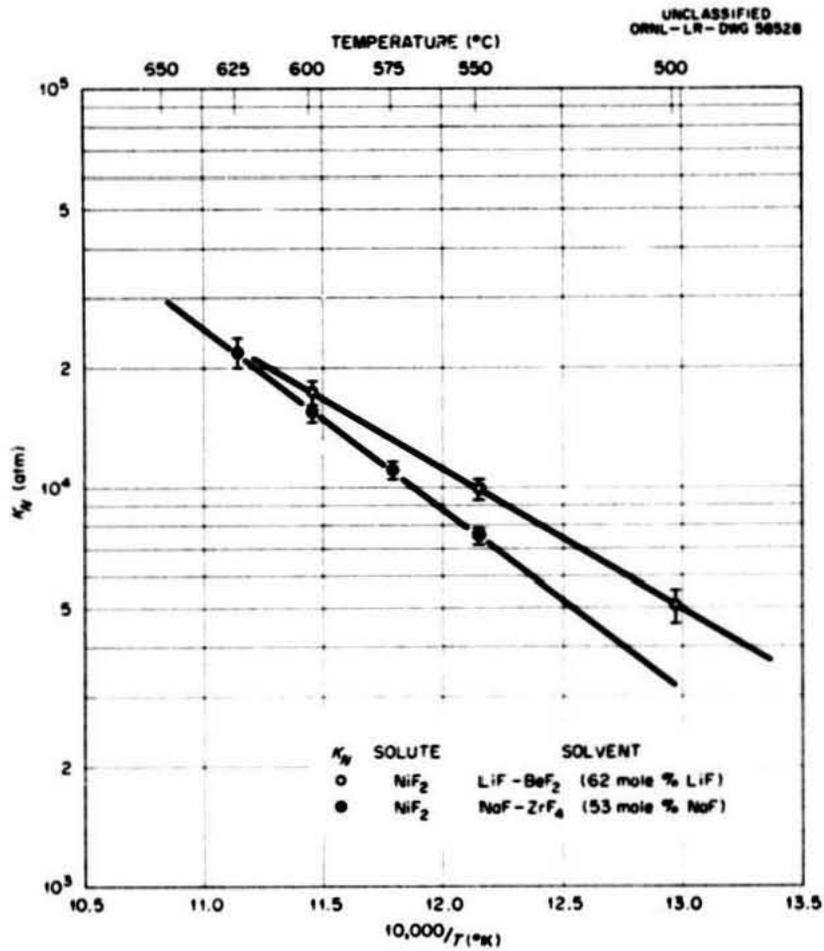


Fig. 2. Effect of Temperature on Equilibrium Quotient, $K_N = (p_{HF})^2 / N_{NiF_2} (p_{H_2})$.

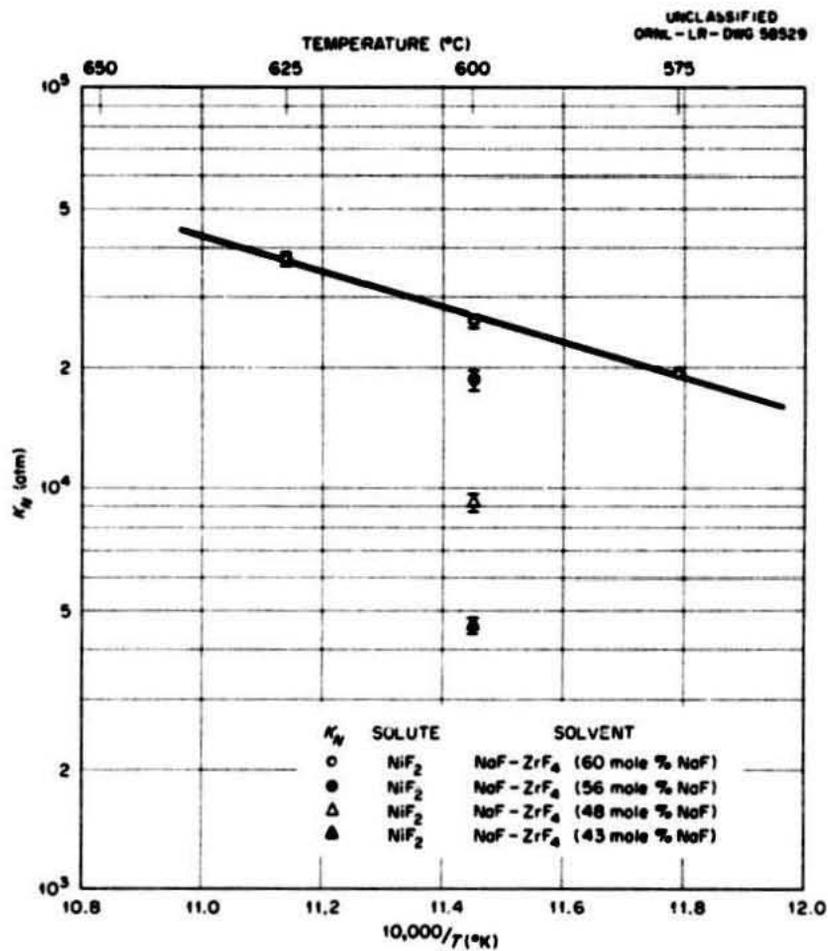


Fig. 3. Effect of Temperature on Equilibrium Quotient, $K_N = (p_{HF})^2 / N_{NiF_2} (p_{H_2})$.

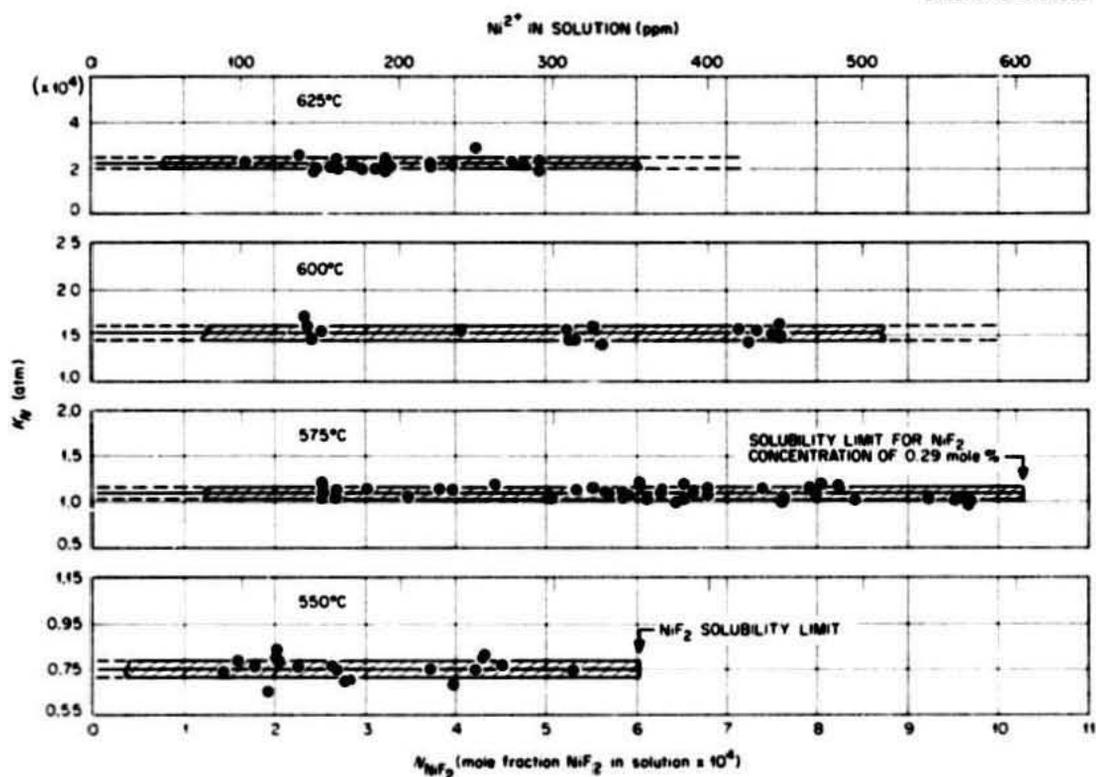


Fig. 4. Equilibrium Quotients for the Reduction by Hydrogen of NiF_2 in $NaF-ZrF_4$ (53 mole % NaF).

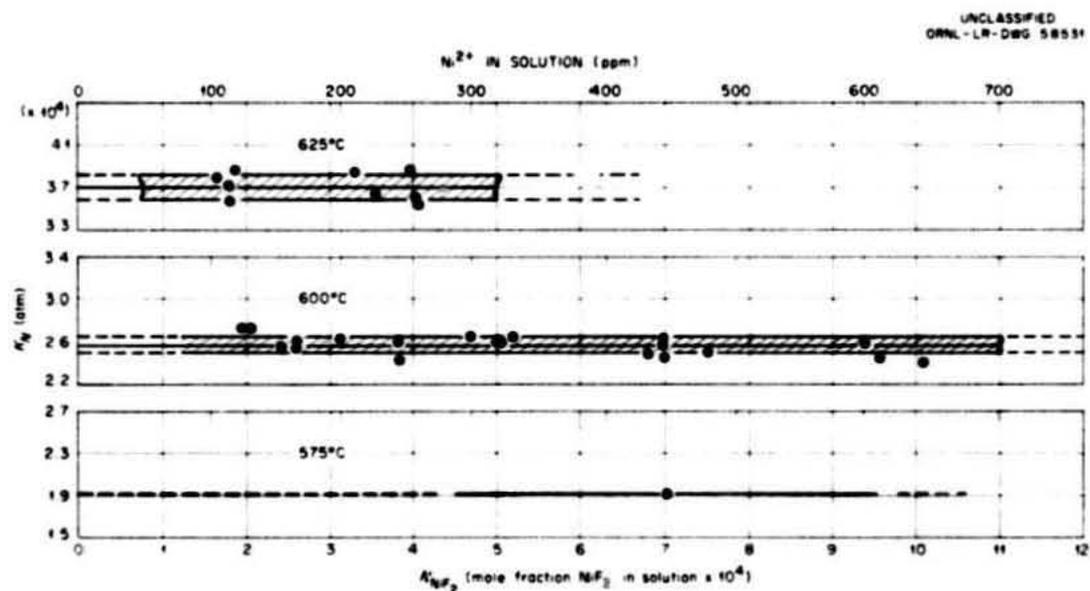


Fig. 5. Equilibrium Quotients for the Reduction by Hydrogen of NiF_2 in $NaF-ZrF_4$ (60 mole % NaF).

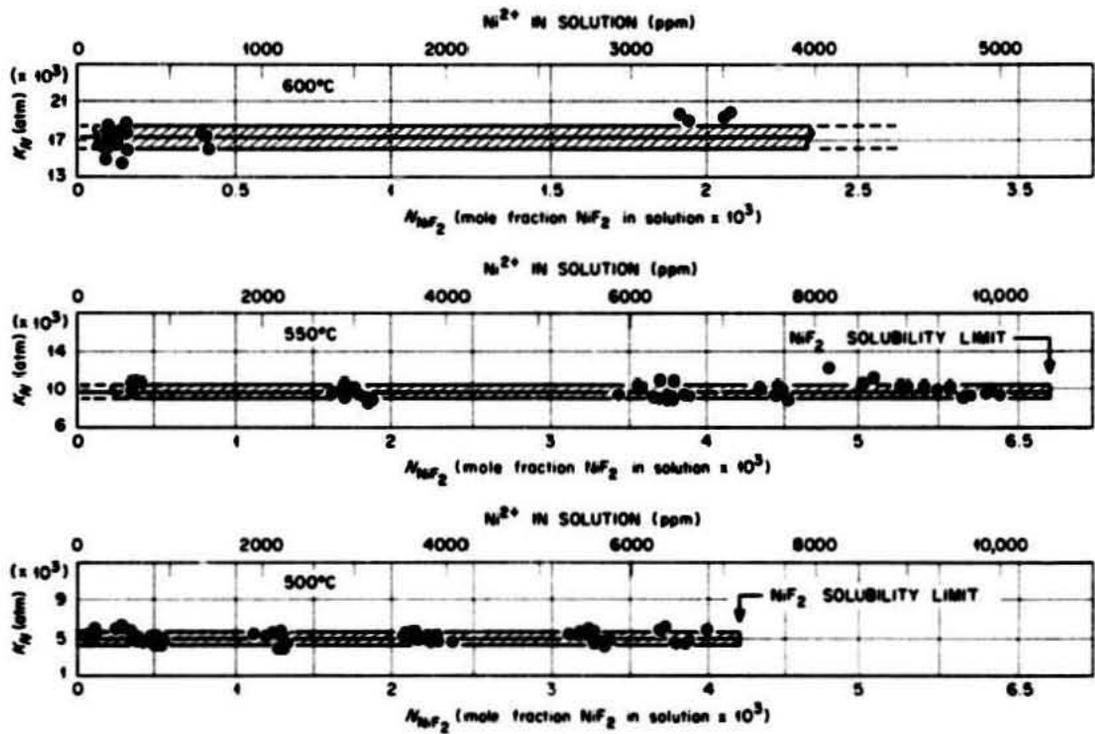


Fig. 6. Equilibrium Quotients for the Reduction by Hydrogen of NiF_2 in $LiF-BeF_2$ (62 mole % LiF).

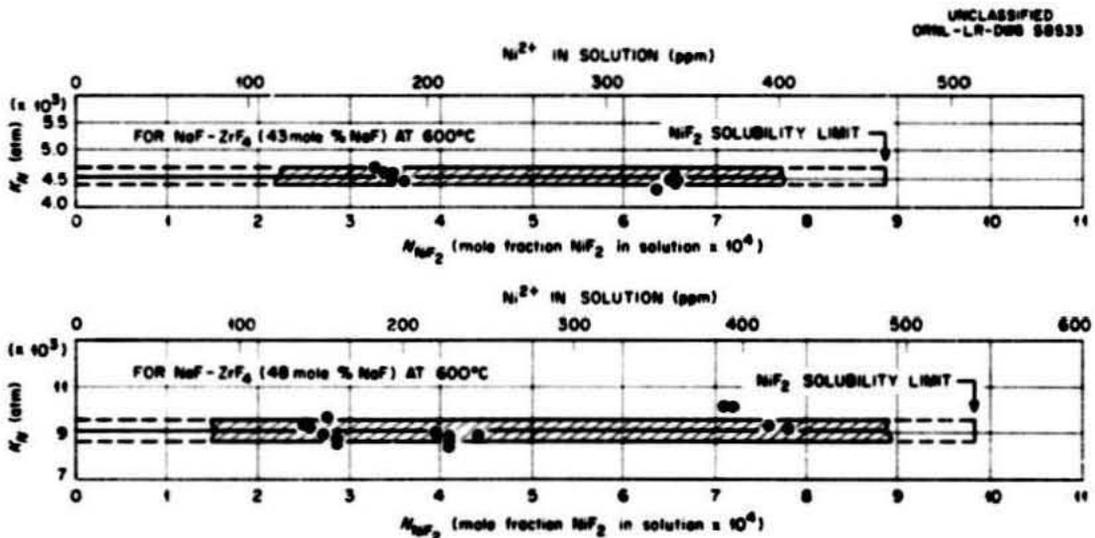


Fig. 7. Equilibrium Quotients for the Reduction by Hydrogen of NiF_2 in $NaF-ZrF_4$ Solutions.

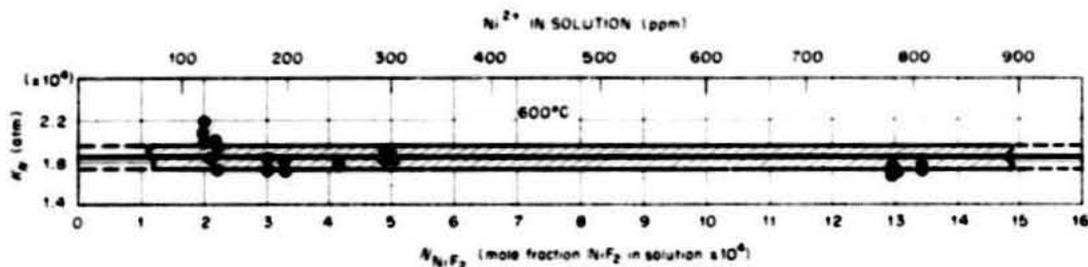


Fig. 8. Equilibrium Quotients for the Reduction by Hydrogen of NiF_2 in NaF-ZrF_4 (56 mole % NiF_2).

Table 2. Equilibrium Quotients for FeF_2 in Molten Fluoride Solutions

Solvent	T(°C)	K_N^* (atm)	Number of Determinations
NaF-ZrF_4 (53 mole % NaF)	800	2.54 ± 0.20	21
	700	0.63 ± 0.03	20
	600	0.096 ± 0.007	12
LiF-BeF_2 (62 mole % LiF)	800	1.88 ± 0.11	4
	700	0.528 ± 0.023	33
	600	0.133 ± 0.004	8

$K_N^* = \frac{(P_{\text{HF}})^2}{(P_{\text{H}_2}) N_{\text{FeF}_2}}$; the precision of K_N is the arithmetic mean deviation.

temperature dependencies of the K_N values for both solvents are shown in Fig. 9. The effect of FeF_2 concentration on the K_N values for both solvents, shown in Figs. 10 and 11, respectively, indicates that K_N is independent of the solute concentration range studied.

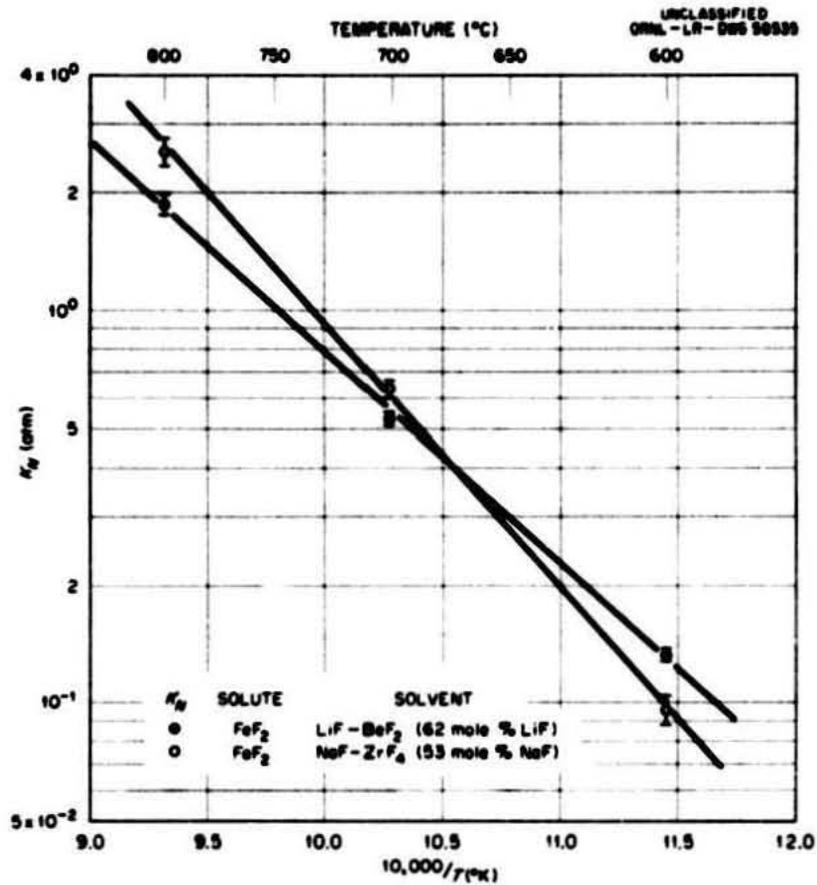


Fig. 9. Effect of Temperature on Equilibrium Quotient, $K_N = (p_{\text{HF}})^2 / N_{\text{FeF}_2} (p_{\text{H}_2})$.

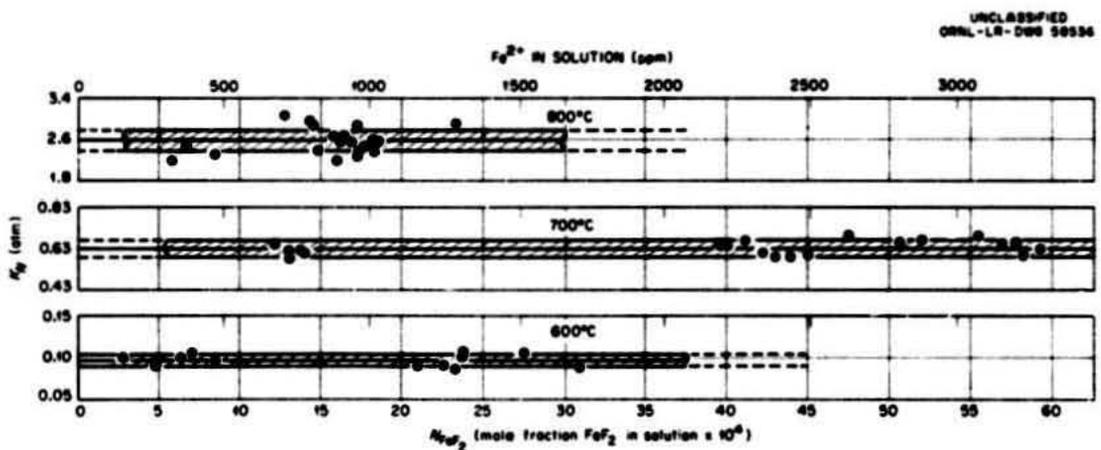


Fig. 10. Equilibrium Quotients for the Reduction by Hydrogen of FeF_2 in $\text{NaF} - \text{ZrF}_4$ (53 mole % NaF).

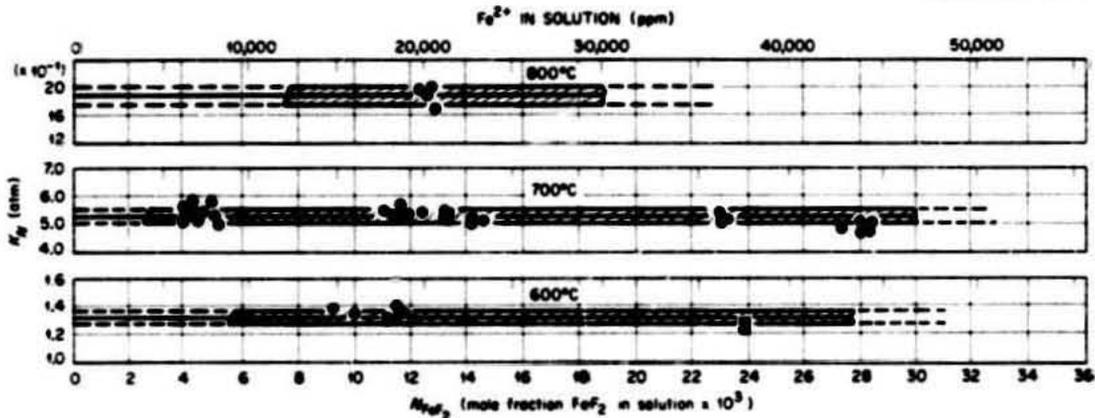


Fig. 11. Equilibrium Quotients for the Reduction by Hydrogen of FeF_2 in LiF-BeF_2 (62 mole% LiF).

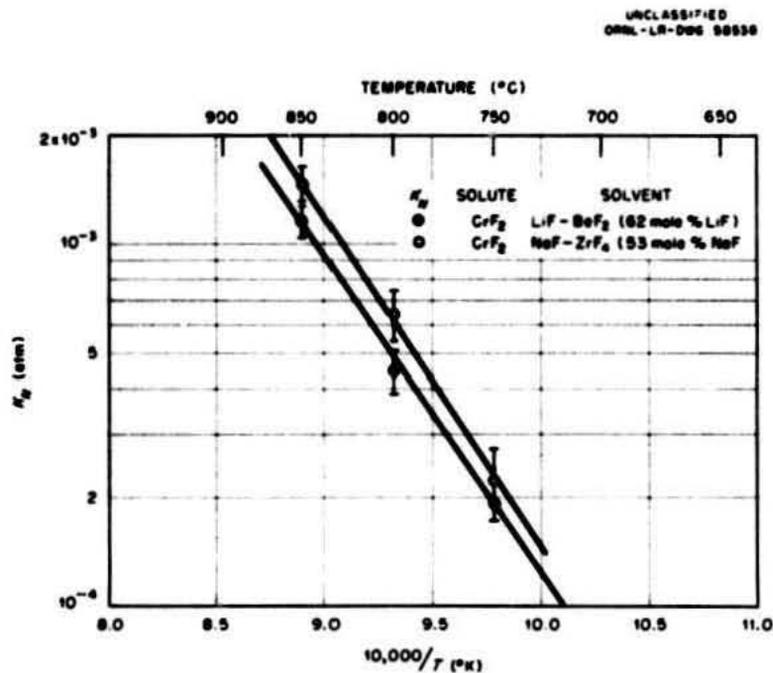
The equilibrium quotients for CrF_2 dissolved in NaF-ZrF_4 (53 mole % NaF) and LiF-BeF_2 (62 mole % LiF) are listed in Table 3. The arithmetic mean deviations have a range of 12 to 24%. The precision is 2 to 3 times less than that for NiF_2 or FeF_2 because of the experimental technique of approaching equilibrium from oxidizing or reducing mixtures of HF and hydrogen. The temperature dependencies of the K_N values for both solvents are shown in Fig. 12. The effect of CrF_2 concentration on the K_N values for both solvents shown in Figs. 13 and 14, respectively, indicate that K_N is independent of the solute concentration range studied.

The experimental equilibrium data from which the average K_N values in Tables 1, 2, and 3 were calculated are listed in Tables A through H, and J and K, in the Appendix. For a definition of the terms see "Equilibrium Quotients" in "Results and Discussion" section.

Table 3. Equilibrium Quotients for CrF_2 in Molten Fluoride Solutions

Solvent	T (°C)	$K_N^* \times 10^3$ (atm)	Number of Determinations
NaF-ZrF ₄ (53 mole % NaF)	850	1.45 ± 0.17	46
	800	0.635 ± 0.102	38
	750	0.221 ± 0.052	75
LiF-BeF ₂ (62 mole % LiF)	850	1.19 ± 0.15	34
	800	0.442 ± 0.059	49
	750	0.192 ± 0.022	35

$K_N^* = \frac{(P_{\text{HF}})^2}{(P_{\text{H}_2}) N_{\text{CrF}_2}}$; the precision of K_N is the arithmetic mean deviation.

Fig. 12. Effect of Temperature on Equilibrium Quotient, $K_N = \frac{(P_{\text{HF}})^2}{N_{\text{CrF}_2} (P_{\text{H}_2})}$.

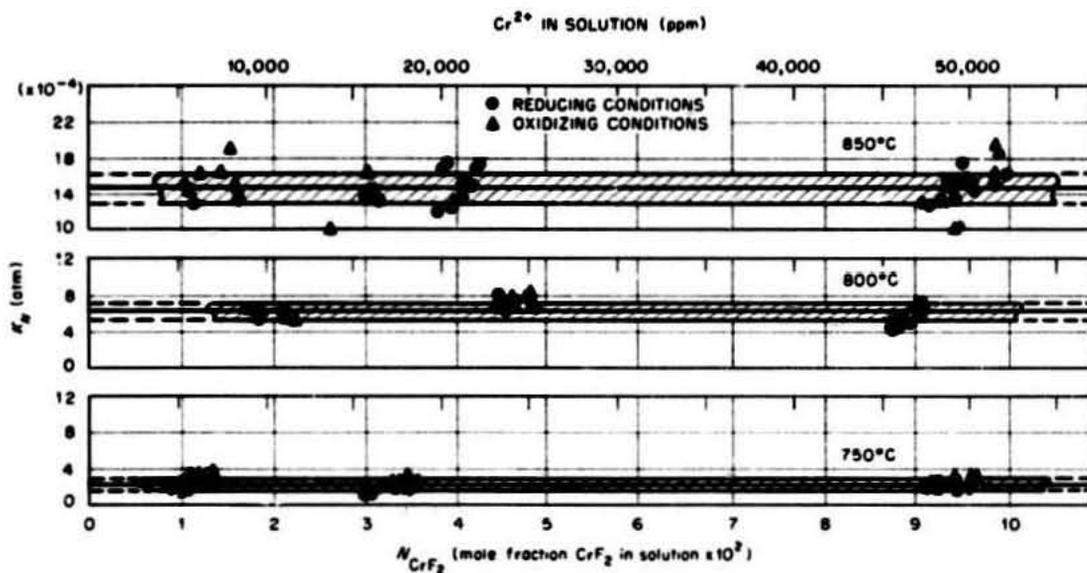
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Fig. 13. Equilibrium Quotients for the Reduction by Hydrogen of CrF_2 in NaF-ZrF_4 (53 mole % NaF).

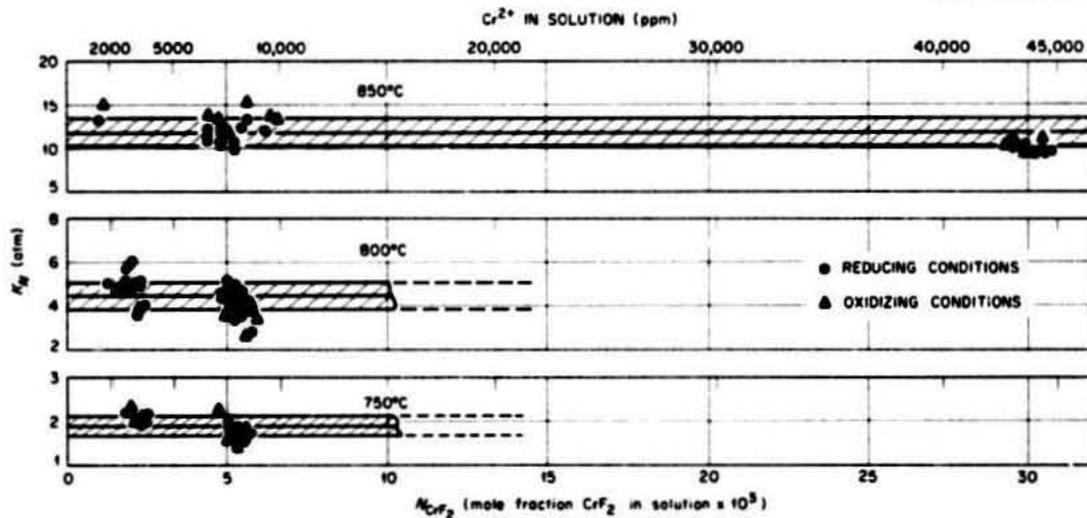
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Fig. 14. Equilibrium Quotients for the Reduction by Hydrogen of CrF_2 in LiF-BaF_2 (62 mole % LiF).

Solubilities

Determinations¹ of the solubility of NiF_2 at 600°C in NaF-ZrF_4 (53 mole % NaF) shown in Fig. 15 demonstrated that the apparent saturation limit depended on the amount of NiF_2 added. This apparent increase in solubility with increasing solute concentration was due to the formation of a complex compound, identified as $\text{NaF}\cdot\text{NiF}_2\cdot 2\text{ZrF}_4$, which altered the solvent composition as it precipitated. This altered solvent had a greater capacity for NiF_2 than the original solvent had. Similar complex compounds were identified for FeF_2 and CrF_2 in the NaF-ZrF_4 solvents.

The solubilities of NiF_2 in various NaF-ZrF_4 solvents at 600°C are listed in Table 4 and shown in Fig. 16. It was observed that the saturation limits increase with increasing NaF concentrations of the solvent.

The solubilities of NiF_2 in NaF-ZrF_4 (53 mole % NaF) for the solute concentration of 0.29 mole % are given in Table 5.

Independent solubility experiments in connection with the equilibrium reduction of FeF_2 in LiF-BeF_2 (62 mole % LiF) revealed the presence of crystalline FeF_2 in equilibrated samples. This information suggested that in this solvent NiF_2 , FeF_2 , and CrF_2 might be equilibrium saturating phases. This was verified by solubility measurements over a range of excess solute additions for NiF_2 and FeF_2 , and by special preparations in the case of CrF_2 . The saturating phases for the solutes were identified as

1. J. D. Redman, ORNL-2106 (deleted version), p. 100.

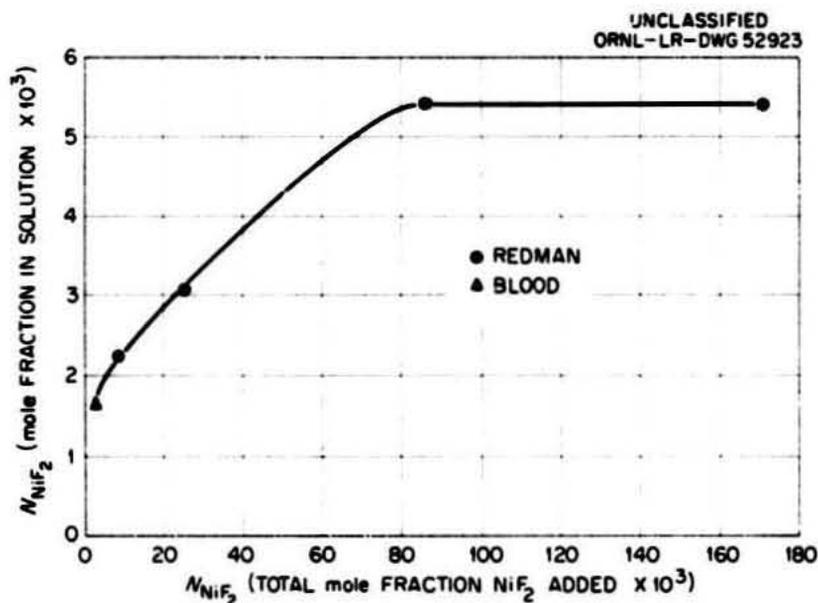


Fig. 15. Effect of Solute Concentration on Solubility of NiF₂ in NaF-ZrF₄ (53 mole % NaF) at 600°C. Data determined by Redman and Blood.

Table 4. Solubilities* of NiF₂ in NaF-ZrF₄ Solvents at 600°C

Mole % NaF	Ni ²⁺ (ppm)	$N_{NiF_2} \times 10^4$
43	460	8.89 ± 0.10
48	515	9.40 ± 0.27
53	980	16.70 ± 0.33
56	1380	22.82 ± 0.46
60	2195	34.44 ± 0.16

*Saturation concentrations were measured in solutions containing less than a twofold excess of NiF₂, and therefore represent a close approach to the liquidus for NaF·NiF₂·2ZrF₄.

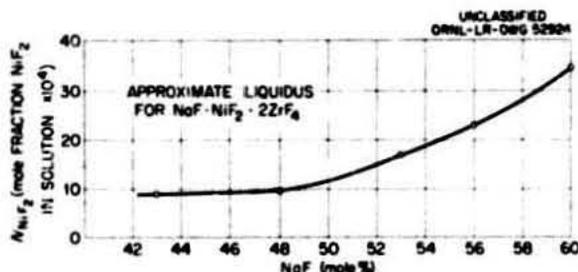


Fig. 16. NiF_2 Concentrations for Saturated Solutions in NaF-ZrF_4 at 600°C .

Table 5. Solubilities of NiF_2 in NaF-ZrF_4 (53 mole % NaF) for NiF_2 Concentration of 0.29 mole %

Temperature ($^\circ\text{C}$)	Ni^{2+} (ppm)	$N_{\text{NiF}_2} \times 10^3$
550	355	$0.60 \pm .02$
575	605	$1.01 \pm .03$
625	1435	$2.59 \pm .08$
650	1755	$2.99 \pm .09^*$
700	1700	$2.90 \pm .09^*$

* Unsaturated solution.

crystalline NiF_2 , FeF_2 , and CrF_2 , by petrographic and x-ray examination.

The solubilities of NiF_2 and FeF_2 in LiF-BeF_2 (62 mole % LiF) are listed in Table 6, and the temperature dependencies are shown in Fig. 17.

The analyses for NiF_2 and FeF_2 concentration resulted in an arithmetic mean deviation of 2 to 3%. The uncertainty of

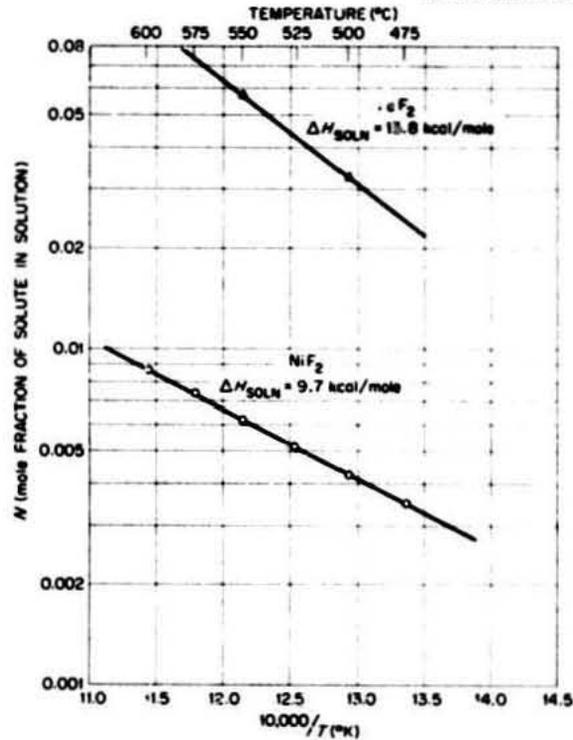
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Fig. 17. Solubility of NiF_2 and FeF_2 in LiF-BeF_2 (62 mole % LiF).

Table 6. Solubilities of NiF_2 and FeF_2 in LiF-BeF_2 (62 mole % LiF)

Solute	Total Solute Added ($N \times 10^3$)	$N^{\text{Sat'n}} \times 10^3$ Found in Filtrate					
		475°C	500°C	525°C	550°C	575°C	600°C
NiF_2	5.87	3.29	4.09	5.10			
NiF_2	11.82	3.52	4.28	5.21	6.28	7.48	8.84
NiF_2	24.16	3.57	4.28	5.12	6.10	7.20	8.37
NiF_2	37.08	3.57	4.29	5.17	6.17	7.30	8.57
NiF_2 (av)		3.49 ± 0.10	4.23 ± 0.08	5.15 ± 0.04	6.18 ± 0.06	7.33 ± 0.10	8.59 ± 0.16
FeF_2	67.5		32.4 ± 0.65		56.2 ± 0.29		

* N = mole fraction of the solute in the mixture, calculated on the basis of a three-component system comprised of MF_2 and the simple end members of the solvent.

$\pm 2^\circ\text{C}$ in temperature corresponds to a solubility difference of 2.4%. The combined deviations result in an estimated error of 4% or less.

CONCLUSIONS

1. The original intent of the equilibrium reduction experiments was to obtain activity coefficients based on the solid and supercooled liquid as the reference states for NiF_2 , FeF_2 , and CrF_2 . This objective was accomplished and was furthered by the results of the NiF_2 and FeF_2 solubility experiments which showed that the saturating phases were crystalline NiF_2 and FeF_2 in the LiF-BeF_2 (62 mole % LiF) solutions.
2. For combinations of the equilibrium quotients at saturation and the respective solubility in the LiF-BeF_2 solvent, it follows from eqs. (3) and (4) that

$$K_{a(s)} = \frac{(P_{\text{HF}})^2}{P_{\text{H}_2}} = K_N N_{\text{MF}_2(\text{sat}'n)} \quad (8)$$

where $K_{a(s)}$ is the equilibrium constant for the reaction, $\text{MF}_2 + \text{H}_2 \rightleftharpoons \text{M}^0 + 2\text{HF}$, based on the particular solid MF_2 .

3. Preliminary thermochemical calculations for the solubility of NiF_2 and FeF_2 showed that the solutes exhibit nearly ideal behavior in the LiF-BeF_2 solutions and suggested revisions of estimates of some thermochemical quantities for the solutes. Activity coefficients can be obtained directly from the solubilities in this case.

4. The experimental equilibrium constants obtained from eq. (8) will yield revised values for the free energy functions of formation for NiF_2 and possibly for FeF_2 .
5. Better values for activity coefficients of NiF_2 , FeF_2 , and CrF_2 in the solvents studied can be expected when calculations based on equilibrium quotients and solubilities reported here have been completed.

ACKNOWLEDGEMENTS

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The many helpful suggestions of F. F. Blankenship, W. R. Grimes, R. F. Newton, and G. M. Watson are also acknowledged.

Appendix

Table A

Equilibrium Data for the Reaction $\text{NiF}_2 + \text{H}_2 = \text{Ni}^0 + 2\text{HF}$
in NaF-ZrF₄ (53 mole % NaF)

	$N_{\text{NiF}_2} \times 10^4$	$K_N \times 10^{-3}$
At 550°C:	4.567	7.70
	4.345	8.26
	4.345	7.99
	4.175	7.45
	4.090	6.78
	2.641	7.60
	2.863	7.07
	2.726	7.49
	2.812	7.03
	1.619	7.86
	2.045	7.81
	1.789	7.64
	1.960	6.61
	1.448	7.42
	2.045	8.09
	2.045	8.43
	2.300	7.67
3.749	7.51	
5.334	7.44	
	<hr/>	
		$\text{Av} = 7.57 \pm 0.35$
	$N_{\text{NiF}_2} \times 10^4$	$K_N \times 10^{-4}$
At 575°C:	2.556	1.16
	2.556	1.05
	2.556	1.13
	2.726	1.07
	5.538	1.14
	5.879	1.09
	5.794	1.08
	6.134	1.03
	7.668	1.05
	7.668	1.04
	7.412	1.16
	8.009	1.08
	8.452	1.02
	9.628	1.02
	9.713	1.01
9.713	0.993	
9.542	1.00	
9.253	1.02	
6.560	1.18	

Table A - Continued

	$N_{NiF_2} \times 10^4$	$K_N \times 10^{-4}$
At 575°C - Contd.	6.816	1.14
	6.816	1.07
	6.049	1.22
	6.305	1.12
	5.708	1.11
	5.708	1.11
	6.475	0.980
	5.879	1.07
	5.368	1.13
	4.430	1.21
	5.078	1.03
	4.004	1.13
	3.834	1.15
	3.493	1.07
	3.067	1.15
	2.556	1.19
	2.726	1.13
	6.646	1.09
	6.305	1.14
	6.526	1.03
	8.264	1.16
	8.060	1.19
	7.924	1.16
	8.264	1.16

$$A_v = 1.10 \pm 0.06$$

At 600°C:

5.248	1.56
5.282	1.45
5.623	1.40
5.334	1.43
2.556	1.54
2.334	1.70
2.386	1.60
2.437	1.47
4.090	1.55
5.538	1.59
7.157	1.55
7.583	1.62
7.327	1.56
7.498	1.50
7.242	1.42
7.583	1.48

$$A_v = 1.53 \pm 0.07$$

Table A - Continued

	$N_{NiF_2} \times 10^4$	$K_N \times 10^{-6}$
At 625°C:	4.942	2.28
	4.601	2.50
	4.260	2.92
	4.771	2.21
	4.686	2.31
	3.749	2.06
	3.749	2.04
	4.942	1.91
	4.004	2.10
	3.238	2.42
	3.238	2.37
	3.323	2.13
	2.897	2.15
	3.238	2.04
	2.692	2.39
	3.238	1.94
	3.152	1.95
	2.300	2.58
	2.982	1.95
	2.641	2.04
	2.726	1.95
	2.471	2.00
	2.471	1.93
	1.704	2.31
		$A_v = 2.19 \pm 0.20$

Table B

Equilibrium Data at 600°C for the Reaction $\text{NiF}_2 + \text{H}_2 \rightleftharpoons \text{Ni}^0 + 2\text{HF}$
 in NaF-ZrF_6 (43 mole % NaF)

$N_{\text{NiF}} \times 10^4$	$K_N \times 10^{-3}$
6.569	4.41
6.376	4.26
6.569	4.52
6.569	4.48
6.569	4.48
3.478	4.98
3.478	4.58
3.671	4.43
3.284	4.74
3.381	4.61
	$\text{Av} = 4.55 \pm 0.14$

Table C

Equilibrium Data at 600°C for the Reaction $\text{NiF}_2 + \text{H}_2 \rightleftharpoons \text{Ni}^0 + 2\text{HF}$
 in NaF-ZrF₄ (48 mole % NaF)

$N_{\text{NiF}_2} \times 10^4$	$K_N \times 10^{-3}$
4.380	8.94
4.106	8.67
3.978	9.03
4.106	8.41
4.106	8.74
2.884	8.53
2.884	8.61
2.701	8.98
2.555	9.40
2.738	9.91
2.555	9.18
2.555	9.40
7.209	10.11
7.118	10.16
7.629	9.35
7.811	9.14
	Av = 9.16 ± 0.42

Table D

Equilibrium Data at 600°C for the Reaction $\text{NiF}_2 + \text{H}_2 \rightleftharpoons \text{Ni}^0 + 2\text{HF}$
 in NaF-ZrF₄ (56 mole % NaF)

$N_{\text{NiF}_2} \times 10^4$	$K_N \times 10^{-4}$
2.150	2.08
2.034	2.22
2.266	1.95
1.985	2.10
2.034	2.00
2.117	1.84
2.233	1.72
3.308	1.72
3.060	1.85
3.027	1.82
3.060	1.74
3.027	1.77
4.135	1.81
4.879	1.89
4.879	1.85
4.962	1.91
5.045	1.84
13.45	1.77
13.40	1.73
13.07	1.71
12.98	1.78
12.95	1.68
	$\overline{Av} = 1.85 \pm 0.11$

Table E

Equilibrium Data for the Reaction $\text{NiF}_2 + \text{H}_2 \rightleftharpoons \text{Ni}^0 + 2\text{HF}$
 in NaF-ZrF_4 (60 mole % NaF)

	$N_{\text{NiF}_2} \times 10^4$	$K_N \times 10^{-6}$
At 575°C:	7.029	1.92
At 600°C:	10.12	2.41
	9.414	2.59
	9.571	2.46
	7.029	2.47
	6.825	2.51
	6.982	2.59
	7.061	2.65
	7.531	2.52
	5.021	2.61
	3.844	2.44
	2.589	2.56
	2.432	2.56
	2.589	2.62
	1.961	2.75
	2.087	2.75
	4.707	2.67
	5.099	2.62
	5.178	2.67
	3.844	2.62
	3.138	2.64
	5.068	2.60
		$\overline{A_v} = 2.59 \pm 0.07$
At 625°C:	4.032	3.60
	3.970	3.87
	4.079	3.53
	3.295	3.86
	3.530	3.66
	1.647	3.80
	1.804	3.56
	1.804	3.72
	1.883	3.87
		$\overline{A_v} = 3.72 \pm 0.12$

Table F
 Equilibrium Data for the Reaction $\text{NiF}_2 + \text{H}_2 \rightleftharpoons \text{Ni}^0 + 2\text{HF}$
 in $\text{LiF}-\text{BeF}_2$ (62 mole % LiF)

	$N_{\text{NiF}_2} \times 10^4$	$K_N \times 10^{-3}$
At 500°C	0.8678	5.71
	0.9545	6.03
	0.9545	6.12
	0.9545	5.77
	0.9835	6.02
	0.9545	5.77
	1.001	5.67
	1.215	5.39
	1.157	4.97
	1.128	5.03
	1.128	4.96
	1.012	5.61
	2.459	6.04
	2.632	6.29
	3.008	6.18
	3.066	5.30
	3.355	5.65
	3.616	4.85
	3.789	5.09
	3.934	4.81
	4.050	4.45
	4.078	4.47
	5.178	4.11
	5.235	4.22
	5.235	4.13
	5.120	4.11
	4.975	4.49
	5.091	4.46
	4.674	4.91
	4.512	5.03
	4.744	4.39
	4.541	4.96
	4.975	5.25
	4.744	4.78
	4.744	4.49
	4.964	4.36
5.438	4.87	
5.496	4.33	
10.96	5.31	
11.88	5.07	
12.34	5.17	
12.45	5.34	

Table F - Continued

	$N_{NiF_2} \times 10^4$	$K_N \times 10^{-3}$
At 500°C - Contd.	12.55	5.26
	12.46	5.23
	12.35	5.38
	12.64	5.47
	12.73	5.12
	13.13	5.13
	12.78	5.35
	13.36	4.49
	13.10	4.60
	13.02	4.26
	13.04	4.01
	12.61	4.00
	20.75	5.09
	20.84	5.38
	21.08	5.49
	21.25	5.44
	21.40	5.31
	22.74	5.23
	22.62	5.12
	21.45	4.91
	21.86	4.79
	22.88	4.66
	22.50	4.53
	22.79	4.79
	22.94	4.76
	22.59	4.97
	22.21	5.17
	21.38	5.72
	21.09	5.59
	21.09	5.54
	23.78	4.65
	31.11	5.31
	32.14	5.33
	31.94	5.47
	32.70	5.44
	32.54	5.71
	32.88	5.23
	32.46	5.29
	32.72	5.00
	32.70	4.67
	32.58	4.85
	33.06	4.25
	32.72	4.59
	33.12	4.33

Table F - Continued

	$N_{NiF_2} \times 10^4$	$K_N \times 10^{-3}$
At 500°C - Contd.	33.28	4.75
	33.75	4.59
	33.66	4.55
	33.47	4.71
	39.98	5.79
	38.57	4.16
	37.98	4.32
	38.84	4.57
	36.95	5.87
	37.02	5.84
		$\overline{Av} = 5.04 \pm 0.46$
	$N_{NiF_2} \times 10^3$	$K_N \times 10^{-3}$
At 550°C:	3.45	9.57
	3.72	10.88
	3.78	10.92
	3.79	9.19
	3.71	9.17
	3.91	9.46
	3.77	9.26
	3.75	8.80
	3.74	9.34
	3.73	9.06
	3.57	10.25
	3.61	10.14
	3.87	9.30
	3.67	9.09
	3.685	9.08
	1.685	10.43
	1.68	10.02
	1.68	9.99
	1.80	9.36
	1.83	9.24
	1.83	9.67
	1.78	9.78
	1.87	8.84
	1.875	8.98
	1.63	9.86
	1.71	10.05
	1.70	10.04
	1.70	9.66
	1.71	9.13
	0.37	9.81
	0.34	10.04
	0.34	11.00

Table F - Continued

	$N_{NiF_2} \times 10^3$	$K_N \times 10^{-3}$
At 550°C - Contd.	0.35	10.20
	0.375	10.95
	0.38	10.98
	4.37	10.39
	4.81	12.32
	4.55	8.95
	4.48	10.28
	4.48	9.37
	4.51	9.92
	5.04	10.46
	5.02	10.51
	5.26	10.54
	5.10	11.24
	5.41	10.20
	5.50	10.04
	5.30	10.60
	5.58	10.27
	5.67	9.11
	5.71	9.50
	5.80	9.62
5.89	9.66	
5.82	9.85	
		$\overline{Av} = 9.90 \pm 0.57$
	$N_{NiF_2} \times 10^4$	$K_N \times 10^{-4}$
At 600°C:	1.418	1.45
	1.261	1.76
	1.273	1.69
	1.273	1.66
	0.897	1.62
	0.897	1.46
	0.897	1.59
	0.955	1.85
	0.926	1.66
	0.949	1.76
	1.504	1.83
	1.504	1.88
	1.620	1.55
	1.620	1.76
	3.963	1.76
	4.125	1.71
	4.165	1.61
4.107	1.73	

Table F - Continued

	$N_{\text{NiF}_2} \times 10^4$	$K_N \times 10^{-4}$
At 600°C - Contd.	19.15	1.98
	19.50	1.92
	20.74	1.99
	20.54	1.94
		$\text{Av} = 1.73 \pm 0.12$

Table G
Equilibrium Data for the Reaction $\text{FeF}_2 + \text{H}_2 \rightleftharpoons \text{Fe}^0 + 2\text{HF}$
in NaF-ZrF₄ (53 mole % NaF)

	$N_{\text{FeF}_2} \times 10^4$	K_N
At 600°C:	30.95	0.086
	27.50	0.102
	23.30	0.086
	23.70	0.102
	23.80	0.104
	22.50	0.091
	21.05	0.088
	2.70	0.102
	6.30	0.100
	4.70	0.088
	6.95	0.105
	8.55	0.096
		<u>0.096</u>
		Av = 0.096 ± 0.007
At 700°C:	47.50	0.68
	50.70	0.66
	52.00	0.66
	55.40	0.68
	57.00	0.65
	57.80	0.65
	59.30	0.63
	58.30	0.59
	40.10	0.64
	45.55	0.59
	43.85	0.58
	39.50	0.64
	41.30	0.66
	42.20	0.59
	43.15	0.58
	13.70	0.61
	13.03	0.58
	13.03	0.62
	13.95	0.61
	12.15	0.64
		<u>0.63</u>
		Av = 0.63 ± 0.03
At 800°C:	8.500	2.32
	6.650	2.47
	6.050	2.20

Table G - Continued

	$N_{FeF_2} \times 10^6$	K_N
At 800°C - Contd.	16.10	2.20
	14.90	2.38
	23.40	2.86
	17.25	2.28
	17.70	2.44
	17.40	2.40
	18.35	2.41
	17.20	2.83
	18.20	2.56
	18.55	2.55
	14.20	2.95
	12.85	3.07
	14.60	2.86
	15.80	2.71
	16.90	2.58
	16.45	2.73
	16.20	2.55
	18.25	2.42
		<hr/>
		$A_v = 2.54 \pm 0.20$

Table H
Equilibrium Data for the Reaction $\text{FeF}_2 + \text{H}_2 = \text{Fe}^0 + 2\text{HF}$
in LiF-BeF₂ (62 mole % LiF)

	$N_{\text{FeF}_2} \times 10^3$	K_N	
At 600°C:	9.19	0.138	
	9.99	0.135	
	11.16	0.132	
	11.59	0.134	
	11.47	0.141	
	11.72	0.133	
	23.92	0.123	
	23.91	0.128	
			<hr style="width: 100%; border: 0.5px solid black;"/>
			$A_v = 0.133 \pm 0.004$
At 700°C:	27.33	0.487	
	28.07	0.470	
	28.31	0.481	
	27.94	0.506	
	28.40	0.497	
	23.03	0.510	
	23.03	0.516	
	23.22	0.519	
	22.93	0.528	
	11.32	0.535	
	11.10	0.549	
	11.60	0.532	
	11.92	0.530	
	11.60	0.572	
	12.42	0.547	
	13.27	0.538	
	13.20	0.549	
	13.13	0.537	
	13.27	0.541	
	14.15	0.504	
	14.15	0.506	
	14.53	0.511	
	5.12	0.501	
	4.57	0.551	
4.40	0.502		
4.08	0.529		
3.95	0.507		
3.87	0.564		
4.09	0.565		

Table H - Continued

	$N_{\text{FeF}_2} \times 10^3$	K_H
At 700°C:	3.96	0.553
	4.18	0.589
	5.01	0.535
	4.80	0.582
		$A_v = 0.528 \pm 0.023$
At 800°C:	12.85	1.68
	12.56	1.84
	12.28	1.95
	12.68	2.03
		$A_v = 1.88 \pm 0.11$

Table J
 Equilibrium Data for the Reaction $\text{CrF}_2 + \text{H}_2 \rightleftharpoons \text{Cr}^0 + 2 \text{HF}$
 in NaF-ZrF_4 (53 mole % NaF)

	$N_{\text{CrF}_2} \times 10^2$	$K_N \times 10^4$	Reaction* Direction
At 750°C:	9.139	1.97	R
	9.177	2.71	O
	9.234	2.09	O
	9.234	2.85	O
	9.253	2.48	O
	9.215	2.28	O
	9.253	2.02	R
	9.424	3.03	O
	9.444	1.94	R
	9.444	2.26	~ even
	9.500	2.60	O
	9.556	2.46	O
	9.481	2.06	R
	9.556	2.03	R
	9.633	3.23	O
	9.709	2.31	R
	9.595	2.47	R
	9.880	3.15	O
	3.073	1.30	R
	3.073	1.37	R
	3.092	1.34	O
	3.131	1.52	R
	3.131	1.17	R
	3.131	1.48	R
	3.092	1.40	R
	3.131	1.25	R
	3.131	1.40	R
	3.092	1.28	R
	3.131	1.66	O
	3.131	1.36	R
	3.111	1.29	R
	3.131	1.19	R
	3.150	1.16	R
	3.111	1.35	R
	3.131	1.71	O
	3.323	2.43	O
	3.419	1.85	R
	3.381	1.54	R
	3.419	2.03	O
	3.381	1.87	R
	3.438	2.22	O
	3.400	1.96	O

Table J Continued

	$N_{CrF_2} \times 10^2$	$K_N \times 10^4$	Reaction* Direction
At 750°C - Contd.	3.438	1.90	O
	3.438	2.40	O
	3.458	2.05	O
	3.438	2.14	O
	3.496	2.09	O
	3.516	1.93	R
	3.592	2.55	O
	3.534	2.44	O
	3.553	2.04	O
	0.9531	1.80	O
	0.9433	1.69	R
	1.065	2.47	R
	1.085	2.33	R
	1.046	2.24	R
	1.046	2.27	R
	1.065	2.32	R
	0.988	2.60	R
	1.027	2.82	R
	1.046	2.30	R
	1.065	2.09	R
	1.085	2.39	O
	1.104	3.07	O
	1.085	2.96	O
	1.142	2.51	R
	1.065	3.26	O
	1.104	2.65	R
	1.162	3.08	O
	1.220	3.49	O
	1.259	3.58	O
	1.259	2.93	R
	1.278	3.49	O
	1.316	3.26	O
	1.394	3.35	R
		$Av = 2.21 \pm 0.52$	
At 800°C	1.742	6.62	R
	1.857	5.33	R
	1.886	6.67	O
	2.128	6.70	O
	2.283	5.23	O
	2.166	5.64	O

Table J - Continued

	$N_{CrF_2} \times 10^2$	$K_N \times 10^4$	Reaction* Direction
At 800°C - Contd.	8.797	5.18	R
	8.835	5.21	R
	8.759	4.70	R
	8.835	4.89	R
	8.816	4.85	R
	8.816	4.25	R
	8.797	4.66	R
	8.778	5.15	O
	8.853	5.37	R
	8.835	5.22	O
	8.949	5.14	R
	8.892	5.63	O
	9.044	6.37	O
	9.083	6.89	O
	9.083	5.88	O
	9.063	6.82	O
	4.573	6.39	R
	4.630	8.06	O
	4.650	7.76	O
	4.688	6.56	R
	4.515	8.18	R
	4.515	7.01	R
	4.592	7.17	R
	4.611	6.52	R
	4.592	7.14	R
	4.650	7.84	R
	4.630	7.59	R
	4.669	7.45	R
	4.842	7.51	R
	4.823	8.52	O
	4.803	7.77	O
	4.880	7.25	R
		$A_v = 6.35 \pm 1.02$	
	$N_{CrF_2} \times 10^2$	$K_N \times 10^3$	Reaction* Direction
At 850°C	9.481	0.97	R
	9.424	0.99	O
	9.272	1.27	O
	9.139	1.23	R
	9.083	1.24	R
	9.424	1.34	O
	9.253	1.32	O
	9.291	1.38	O
	9.424	1.51	O
	9.348	1.50	R
	9.367	1.46	R

Table J - Continued

	$N_{CrF_2} \times 10^2$	$K_N \times 10^3$	Reaction* Direction
At 850°C - Contd.	9.728	1.47	R
	9.860	1.49	O
	9.842	1.61	O
	9.994	1.60	R
	9.728	1.41	R
	9.520	1.55	R
	9.500	1.69	R
	9.860	1.88	O
	9.899	1.84	O
	2.630	1.00	O
	3.035	1.37	O
	3.035	1.62	O
	3.053	1.39	O
	3.111	1.42	O
	3.188	1.31	R
	3.870	1.66	R
	3.912	1.72	R
	3.818	1.19	R
	3.959	1.21	R
	4.035	1.33	R
	4.093	1.48	R
	4.073	1.35	R
	4.073	1.52	O
	4.247	1.70	O
	4.227	1.51	R
	4.267	1.74	R
	1.075	1.41	O
	1.142	1.26	R
	1.027	1.50	O
	1.181	1.59	O
	1.433	1.64	O
	1.529	1.89	O
	1.570	1.48	O
	1.626	1.32	R
	1.626	1.38	R
		$\overline{Av} = 1.45 \pm 0.17$	

* R - Reducing Conditions
O - Oxidizing Conditions

Table K
Equilibrium Data for the Reaction $\text{CrF}_2 + \text{H}_2 \rightleftharpoons \text{Cr}^0 + 2\text{HF}$
in LiF-EeF₂ (62 mole % LiF)

	$N_{\text{CrF}_2} \times 10^3$	$K_N \times 10^4$	Reaction* Direction
At 750°C	4.81	2.30	O
	5.06	1.55	O
	5.04	1.92	R
	5.03	2.07	R
	5.07	1.81	~ even
	5.23	1.87	R
	5.26	1.45	O
	5.24	1.77	O
	5.19	1.74	O
	5.19	1.62	O
	5.26	1.89	R
	5.28	1.73	O
	5.59	1.55	R
	5.23	1.85	R
	5.21	1.96	R
	5.22	1.96	R
	5.19	1.52	O
	5.68	1.65	O
	5.60	1.75	R
	5.60	1.90	O
	5.76	1.88	O
	5.56	1.53	R
	5.16	1.74	R
	2.01	2.67	O
	2.03	2.56	R
	2.10	2.24	O
	2.03	2.21	~ even
	2.03	2.22	R
	2.14	2.06	O
	2.28	1.94	R
	2.32	1.88	R
	2.35	1.93	R
	2.38	2.20	O
	2.41	2.30	O
	2.47	2.04	O
		<u>Av = 1.92 ± 0.22</u>	
At 800°C	5.38	3.54	R
	5.11	3.90	R
	5.39	4.12	O
	5.52	2.61	O

Table K - Continued

	$N_{CrF_2} \times 10^3$	$K_N \times 10^4$	Reaction* Direction
At 800°C - Contd.	5.73	3.83	O
	5.62	2.78	R
	5.90	3.37	O
	5.68	4.07	O
	5.52	3.76	O
	5.52	4.03	~ even
	5.52	4.19	R
	5.27	4.51	R
	5.19	4.58	O
	5.30	3.76	R
	5.35	5.10	R
	5.33	4.60	R
	5.17	4.78	R
	5.11	4.71	R
	5.03	4.01	R
	5.12	4.94	R
	4.94	3.48	O
	4.90	4.60	R
	4.86	4.33	R
	4.96	5.17	R
	4.95	4.67	R
	5.13	3.35	R
	4.82	3.68	R
	4.78	4.53	R
	5.04	4.41	O
	5.05	4.77	O
	4.86	4.51	O
	4.91	4.59	O
	5.19	4.52	R
	2.35	3.96	R
	1.94	4.75	R
	2.17	3.98	O
	2.23	3.56	R
	2.10	5.06	R
	2.37	4.93	R
	2.39	3.96	R
	2.19	5.04	R
	2.33	6.08	R
	1.31	5.07	R
	1.53	4.84	O
	1.66	4.78	R
	1.73	5.03	R
	1.78	5.74	R
	1.82	5.84	R
	1.89	6.06	R

$$\bar{A}_v = 4.42 \pm 0.59$$

Table K - Continued

	$N_{CrF_2} \times 10^3$	$K_N \times 10^3$	Reaction* Direction
At 850°C	5.38	1.23	~ even
	5.22	1.07	R
	5.16	1.00	R
	4.79	1.03	R
	4.37	1.61	R
	4.38	1.23	R
	4.36	1.39	O
	4.40	1.10	R
	4.71	1.18	R
	4.74	1.27	O
	4.71	1.09	R
	4.73	1.26	R
	4.72	1.38	~ even
	5.07	1.20	O
	5.62	1.34	R
	5.61	1.54	O
	6.15	1.23	O
	6.37	1.42	O
	6.57	1.36	O
	1.02	1.34	R
	1.12	1.53	O
	30.44	1.02	O
	29.72	1.00	O
	29.80	1.02	R
	29.87	1.06	R
	29.45	1.16	R
	29.38	1.04	R
	29.80	1.00	R
	29.38	1.10	O
	29.58	1.10	O
	30.59	1.14	O
	30.67	0.97	R
	30.51	0.98	R
	30.16	0.97	O
	$A_v = 1.19 \pm 0.15$		

* R = Reducing Conditions
O = Oxidizing Conditions