the data for n-pentane with an average deviation of 1.8 and 1.4 B.t.u. per pound. However, these methods are unsatisfactory for ethyl alcohol as indicated by average deviations of 10.8 B.t.u. per pound (32%) for correlation (*2*), and 10.7 B.t.u. per pound (31%) for correlation (*3*). The same correlations can be used to estimate the enthalpy deviations for the ethyl alcohol-hydrocarbon mixtures using a pseudocritical point concept. Here again, the errors are large when compared with the data of Tables I to IX. The average deviations range from 3 to 46%, depending upon the hydrocarbon content of the mixture. The conventional generalized correlations, while satisfactory for hydrocarbons, are not suitable for ethyl alcohol or its mixtures with benzene and pentane.

NOMENCLATURE

h = enthalpy correction applied to data points
H = enthalpy at any pressure, smoothed enthalpy data
L = latent heat of vaporization
T = absolute temperature
W = weight
x = mole fraction

Superscript

^{0} = datum state, 77° F.

Subscripts

c = critical property; calorimeter in Equation 1
f = formation or Freon 11
i = component in a mixture
m = mixture property or mixture
1 = inlet to the calorimeter
2 = outlet to the calorimeter or dimer

ACKNOWLEDGMENT

This work was conducted with the aid of fellowships from the Dow Chemical Co., the Du Pont Co., and Procter and Gamble Co. The assistance of Alden H. Emery, Jr., is also acknowledged.

LITERATURE CITED

(1) Edmister, W. C., *Petrol. Refiner* **37**, 195 (1958).
(2) Hougen, O. A., Watson, K. M., "Chemical Process Principles," Vol. **11**, Wiley, New York, 1947.
(3) Lydersen, A. L., Greenkorn, A. R., Hougen, O. A., "Generalized Properties of Pure Fluids," Engineering Experimental Station Rept. No. 4, University of Wisconsin, Madison, Wis., October 1955.
(4) McCracken, P. G., Smith, J. M., *A. I. Ch. E. Journal* **2**, 498 (1956).
(5) Organick, E. I., Studhalter, W. R., *Chem. Eng. Progr.* **44**, 847 (1948).
(6) Papini, G., Cuomo, S., *Antincendio (Rome)* **8**, 338 (1956).
(7) Schnaible, H. W., Van Ness, H. C., Smith, J. M., *A. I. Ch. E. Journal* **3**, 147 (1957).
(8) Smith, J. M., Reid, R. C., *Chem. Eng. Progr.* **47**, 415 (1951).
(9) Storvick, Truman, S., Ph. D. thesis, Purdue University, Lafayette, Ind., January 1959.

RECEIVED for review March 30, 1959. Accepted October 15, 1959.

Rare Earth and Yttrium Fluorides

Solubility Relations in Various Molten NaF-ZrF_4 and NaF-ZrF_4-UF_4 Solvents

W. T. WARD, R. A. STREHLOW, W. R. GRIMES and G. M. WATSON
Oak Ridge National Laboratory, Oak Ridge, Tenn.

AS PART of an extensive study of phase relations in molten fluoride mixtures, the solubilities of cerium, lanthanum, samarium, and yttium trifluorides (LaF_3, CeF_3, SmF_3, and YF_3) in various solvent compositions were determined. Inasmuch as the series of rare earths offers distinct regularity of properties in both elemental and combined states, it was hoped that these solubility measurements might allow some interesting comparisons to be made. In addition, because the rare earth trifluorides are known to form solid solutions, and the liquidus temperatures involved in these systems are high, equilibria might be reached rapidly enough to effect a rare earth extraction by a solid solvent.

The solubilities of some rare earth fluorides, (principally those of samarium, europium, and gadolinium) are also important in designing a nuclear reactor fueled with a molten fluoride mixture containing fissionable material. These three rare earths are expected to account for significantly more than half of the nuclear poisoning by nongasous elements. Consequently, information obtained in this work was expected to be pertinent to design of a poison depletion process and to give assurance that precipitation of these fission products will not hinder the operation of a reactor.

Because the fission products formed in greater yields include several of the rare earths, rare gases, alkaline earths, and the 4*d* transition elements (particularly elements Nos. 41-46), the selection of subjects for initial study was made after considering relative importance based on fission yield and thermal neutron cross sections of the various products. This report presents some of the data obtained in this laboratory on the solubility of LaF_3, CeF_3, SmF_3, and YF_3 in a sodium, zirconium, and uranium fluoride solvent consisting of 50 mole % NaF, 46 mole % ZrF_4 and 4 mole % UF_4. Two pseudo-ternary systems, LaF_3-CeF_3-solvent and CeF_3-SmF_3-solvent have also been studied, as have various other mixtures of fission products to determine their solubility relations. Several series of experiments were carried out using NaF-ZrF_4 solvents of other compositions so that some information relating to the shape of the liquidus surface in the NaF-ZrF_4-CeF_3 system could be obtained. In addition to delineating the allowable rare earth concen-

Table I. Solubilities of CeF_3 in Solvents of Various Compositions at Three Temperatures

Solvent Composition, Mole %[a]		Molecular Wt. Used for Solvent Mixture, G./Mole	Mole % CeF_3 at		
NaF	ZrF_4		550° C.	675° C.	800° C.
42	58	114.6	3.0	8.2	10.3
50	50	104.5	2.12	3.0	4.4
53	47	100.9	1.64	2.37	3.9
59	41	93.3	0.56	0.62	1.61
63	37	88.4	0.26	0.44	1.07
80.5	19.5	66.4	...	...	4.71

[a] ±0.5 mole %.

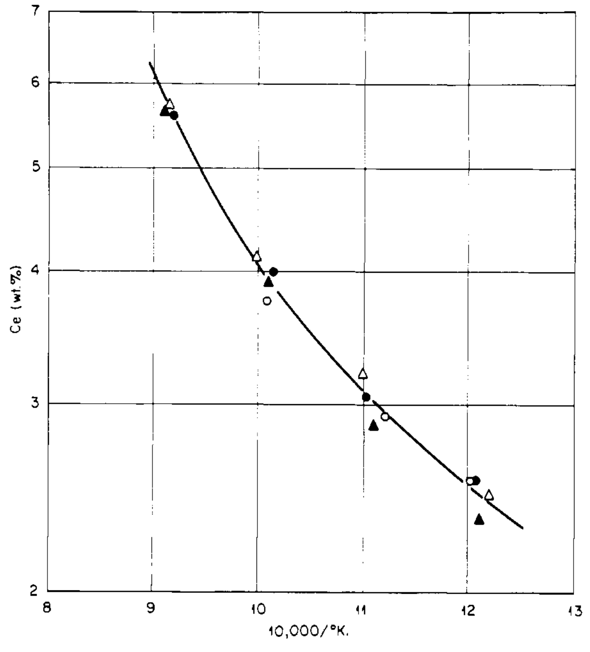

Figure 1. Solubility of CeF_3 in NaF-ZrF_4-UF_4 (50–46–4 mole %) as determined in four separate experiments

tration limits, the data may be useful in determining the feasibility of a poison-depletion technique based on an exchange of a low for a high cross-section material.

GENERAL PROCEDURE

Weighed quantities of the fission product fluoride and solvent were placed in a nickel reactor vessel. The salt mixture was heated under a dry helium atmosphere, and after melting was continuously stirred by bubbling helium. For an hour the temperature of the melt was maintained at 900° C. (about 400° C. higher than the melting point of the solvent), after which it was lowered in a stepwise manner to about 820°, 730°, 640°, and 550° C. A sample was obtained after an hour's equilibration at each temperature by withdrawing some of the liquid through a sintered-metal filter.

The filtrates from the initial determinations were analyzed using conventional chemical techniques. However, accurate analyses for the rare earths in presence of sodium, zirconium, and uranium were difficult to obtain using even the best of the standard analytical methods. Consequently, a method using radioactive tracers was developed and has proved to be very successful.

Oxide- and water-free solvent mixture was mixed with radioactively labeled fission product fluorides. These were prepared by mixing a few millicuries of the most suitable available radio-isotope in the form of an aqueous hydrochloric acid solution of the chloride with an aqueous solution of the same, but inert, fission product chloride. From the resulting solution, the fission product fluoride was precipitated with an aqueous hydrofluoric acid solution. This precipitate, after centrifuging, washing, and recentrifuging, was dried in a vacuum oven.

The required number of millicuries varied according to the amount of labeled fluoride to be made and the half-life of the isotope being used. Used in the experiments were: Ce^{141} (half-life, 32 days), La^{140} (40 hours), Sm^{153} (47 hours), and Y^{91} (58 days).

The reactor vessel, made of 1/4-inch thick nickel, had an internal diameter of 2 inches and was 17 inches long. A section of 1/2-inch nickel pipe was welded into the flanged top of the reactor to facilitate loading the chemical charge and to admit filter sticks. Other openings in the top accommodated a thermocouple well, a connection to a pressure gage, and a dip leg (a piece of 1/4-inch tubing extending to 1/4 inch above the reactor bottom) to admit helium.

Thin-walled nickel reactor liners were used in all of the experiments. Initially, liners holding about a kilogram of charge and having an outside diameter of 2 inches were used. Later, as the precision of the method became evident, a change weighing about 200 grams was contained in a 1-inch diameter liner having a flared top.

The reactor was mounted vertically in a 2700-watt electric furnace connected to a Micromax temperature controller. The thermocouple in the reactor was connected to a continuous recorder. Because a temperature gradient existed in the first experiments of the series, an auxiliary Variac-controlled Calrod heater was placed under the reactor vessel. The power input was adjusted to minimize the temperature inequality.

The filter sticks were constructed from sintered nickel or copper disks with nominal pore size of 0.0004 inch. The disks were welded into sections of 3/8-inch tubing about 1-1/4 inches long. The open end of the tubing was reduced in diameter and welded to a 22-inch length of 1/8-inch tubing. This was slipped through a Teflon gasket in a threaded cap which fit the 1/2-inch pipe in the top of the reactor. A piece of soft rubber tubing fit over the top of the filter stick and was arranged so that it could be connected to either a vacuum pump or the helium source.

FILTRATION TECHNIQUE AND ANALYSIS

The connected filter stick was flushed with helium for several minutes before it was put into the reactor. A small helium flow was maintained while it was being inserted in order to prevent the liquid from freezing in the filter disk. After the temperature of the filter stick reached that of the melt, the helium flow was stopped and a vacuum was

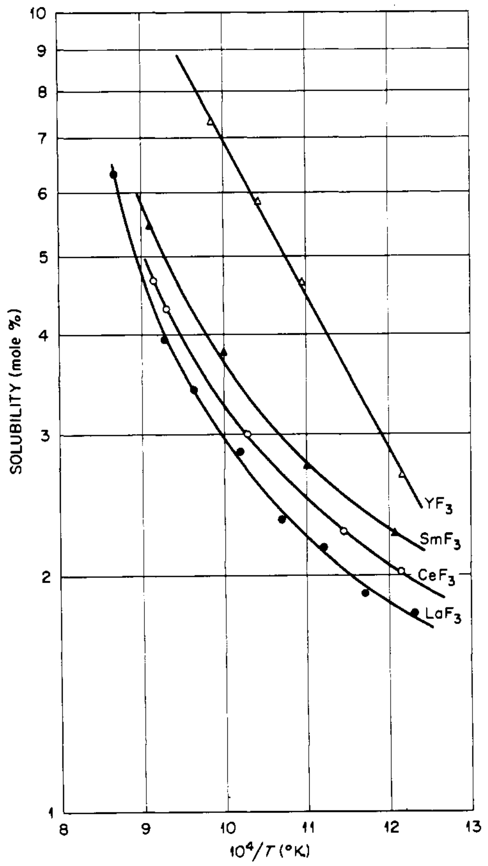

Figure 2. Solubility of LaF_3, CeF_3, SmF_3, and YF_3 in NaF-ZrF_4-UF_4 (50–46–4 mole %)

applied. The filtrate froze in the top region of the filter stick. After the filter stick was removed from the reactor and cooled, it was cut open and emptied. The 5- to 8-gram sample was then analyzed.

A set of standard samples made up for each batch of labeled material consisted of approximately 1 gram of the solvent plus varying amounts of tracer-containing fluoride salt, both accurately weighed. These standards were placed in cork-stoppered glass tubes which fit in a well counter. The four filtrates obtained at the successive temperatures in a run were separately ground up. Samples of each filtrate of approximately 1 gram, accurately weighed, were placed in similar tubes and counted with the standards and a blank containing only solvent. The reading of the blank was subtracted from the other readings to adjust for both background and the uranium counts. The count for each standard was plotted on an arithmetic scale against milligrams of labeled fluoride as weighed. After drawing a smooth curve through the points, it was possible to determine the number of milligrams of fission product fluoride present in the sample. This allowed the calculation of the weight per cent of fission product to be made.

The solubilities of two separately labeled fluorides were measured in three experiments. By selecting the pairs so that their half lives were sufficiently different, it was possible to determine simultaneously the weights of each of the fission products in the filtrates. This technique involves counting the filtrates several times and requires that the differences in decay rates be utilized in the determination.

For the series of experiments in the uranium-free solvent compositions, mixtures of NaF-ZrF_4 were used to which NaF or ZrF_4 was added. The solubility of CeF_3, was determined at four temperatures in each of five solvent compositions.

RESULTS

The solubility of CeF_3 in NaF-ZrF_4-UF_4 (50-46-4 mole %) was determined in several different experiments, either as the prime objective or as the first step in a mixed fission-product solubility experiment. The solubilities determined in four of these experiments are shown in Figure 1, where the logarithm of the solubilities in weight per cent of cerium are plotted against the reciprocal of the temperature. This illustrates the degree of scatter of the experimental points and the reproducibility of the experiments. The precision is approximately $\pm 5\%$.

The solubilities for LaF_3, SmF_3, and YF_3, (single experiments) are shown in Figure 2 with the curve of CeF_3 solubility which best fit all the data. The solubilities of these fluorides increase with decreasing atomic size of the trivalent positive ion.

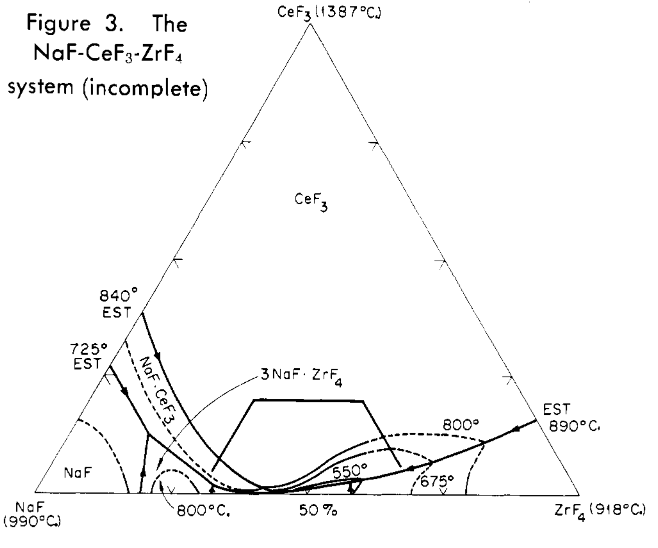

Figure 3. The NaF-CeF_3-ZrF_4 system (incomplete)

There is good indication based on petrographic observation that the precipitating phase for the solvent is the rare-earth fluoride, except for compositions containing less than about 42% ZrF_4, in which the precipitating phase is a 1 to 1 compound with NaF. The study of solubility as a function of composition yielded results which are listed in Table I and are shown as isotherms in a phase diagram of the system NaF-CeF_3-ZrF_4, Figures 3 and 4. This diagram, although incomplete, represents the phase relationships that are most probably correct. The binary system NaF-ZrF_4 is given by Barton and others (*1*). The values of the eutectic points in the NaF-CeF_3 system were estimated with the aid of C. J. Barton and information reported by Dergunov (*2*) for the NaF-LaF_3 system. Assuming that the CeF_3-ZrF_4 binary was an ideal eutectic system, the composition and eutectic temperature were calculated.

The solubility data shown in Tables II to XII relate to the solvent NaF-ZrF_4-UF_4 (50-46-4 mole %).

DISCUSSION

For elements which are so remarkably similar in their chemical behavior, the rare earth and yttrium fluorides exhibit surprising differences in their solubilities. The fluorides of lanthanum and samarium differ in solubility by more than 20%. The distinctly higher solubility of YF_3 is particularly noteworthy because the heat of fusion estimated for YF_3 is higher than those estimated earth fluorides (*3*). Qualitatively, the most striking difference exists between the solubility of YF_3 and the solubilities of the rare earth fluorides with respect to the linearity of the log *s vs.* $1/T$ plot of the YF_3. That the pronounced curvature of the solubility curves of the other fluorides studied is not due to solid solution or addition compound formation has been indicated by x-ray and petrographic identification of CeF_3 in both slowly cooled and quenched filtrate samples from the solubility studies with that compound. There is some indication, based on unpublished work at this laboratory, that the solubilities of CeF_3 and LaF_3 in other molten salt solvents do not show so pronounced a curvature over this temperature range; solvent interaction in the NaF-ZrF_4-UF_4 mixture is probably related to this aspect of the data.

For the three rare earth fluorides studied, an empirical correlation has been observed which should allow reasonable estimations of the solubilites of some other rare earth fluorides. Graphically interpolated solubilities of LaF_3, CeF_3, and SmF_3, are shown in Table XIII. Of the three tri-positively charged ions, lanthanum has the largest and samarium the smallest radius.

The solubility data are correlated with the ionic size data from Goldschmidt (*4*) in Figure 5 which shows the solubility points for the isotherms listed in Table XIII plotted against the radii of the positive ions. Two points for YF_3 lie in the range extrapolated from the rare earth solu-

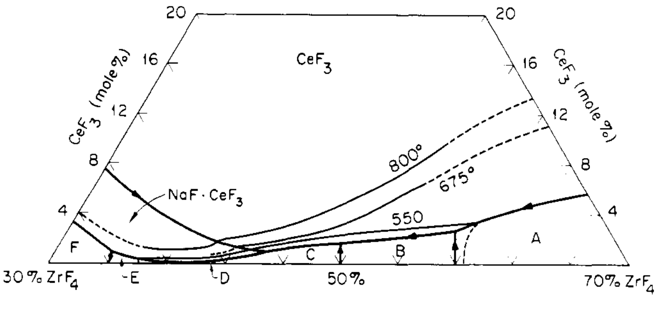

Figure 4. Detail of the system NaF-CeF_3-ZrF_4 (incomplete)

Probable NaF-ZrF primary phase fields

A. ZrF_4	C. $7NaF \cdot 6ZrF_4$	E. $5NaF \cdot 2ZrF_4$
B. $3NaF \cdot 4ZrF_4$	D. $2NaF \cdot ZrF_4$	F. $3NaF \cdot ZrF_4$

bilities with the others for YF_3 being higher. This correlation should be useful in predicting the solubilities of some other rare earth fluorides. The probable range of accuracy of these points is indicated on the graph as ±5%.

Solubilities of these fluorides individually are comfortably high for reactor operation. The studies of mixed rare earth fluoride solubilities had as a principal objective the determinations of solubility behavior under conditions more nearly approximating those found in an operating reactor. There exists the additional possibility of depleting the fuel of poisons such as gadolinium, samarium, and europium by exchange for cerium which is, from the standpoint of cross-section, relatively innocuous. Figures 6 and 7 show portions of the pseudo-ternary systems LaF_3-CeF_3-solvent and CeF_3-SmF_3-solvent. The points corresponding to liquidus points are taken from Tables X and XI. There is no profound difference between the total rare earth fluoride solubilities individually and mixed. The combined solubilities of the two rare earth fluorides are intermediate between the solubilities of the individual fluorides at the same temperature.

Figure 8 shows the additive nature of the solubility

Table II. Solubility of CeF_3[a]

	Temp., ° C.	Mole % CeF_3 in filtrate	Temp., ° C.	Mole % CeF_3 in filtrate
Initial charge, wt. % CeF_3	5.5		9.9	
	812	2.84[b]	812	4.57
	718	3.11[b]	712	3.22
	619	2.35	634	2.44
	559	2.05	556	2.05
Initial charge, wt. % CeF_3	8.7		8.5	
	820	4.68	825	4.60
	729	3.33	718	3.15
	638	2.57	628	2.30
	548	1.97	554	1.87

[a] This and Tables III to XII relate to the NaF-ZrF_4-UF_4 (50–46–4 mole %) solvent, M. W. = 110.48.

[b] Probably unsaturated.

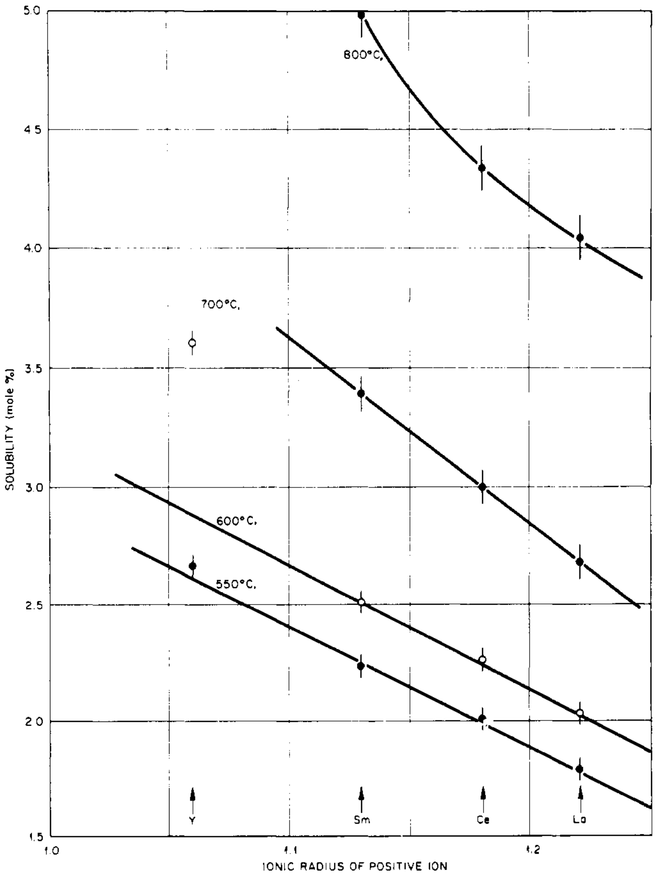

Figure 5. Relation between ionic size and solubility of trifluorides in NaF-ZrF_4-UF_4 (50–46–4 mole %)

Table III. Solubility of LaF_3

Initial charge, wt. % LaF_3	12.8		7.6	
	Temp., ° C.	Mole % LaF_3 in filtrate	Temp., ° C.	Mole % LaF_3 in filtrate
	877	6.33	...	...
	805	3.95	808	3.83
	764	3.41	...	...
	707	2.86	718	2.61
	662	2.35	...	...
	619	2.17	613	1.95
	582	1.89	...	...
	539	1.78	553	1.75

Table IV. Solubility of CeF_3 in Presence of LaF_3

Initial charge	5.1 Wt. % CeF_3 and 8.5 Wt. % LaF_3		4.8 Wt. % CeF_3 and 17 Wt. % LaF_3	
	Temp., ° C.	Wt. % CeF_3 in filtrate	Temp., ° C.	Wt. % CeF_3 in filtrate
	810	3.12	818	1.39
	708	1.70	718	1.01
	624	1.31	622	0.79
	563	1.14	568	0.69

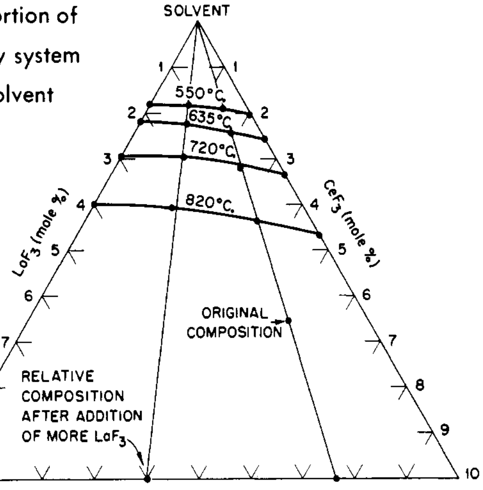

Figure 6. Portion of pseudo ternary system LaF_3-CeF_3-solvent

Table V. Time Required to Reach Equilibrium After Adding LaF_3 to Previously Equilibrated CeF_3-Solvent Mixture

	Temp., ° C.	Time after Melting, Hr.	Ce in Filtrate Wt. % CeF_3	Approx. Ce-La Content in Reactor, Wt. %
Before LaF_3 addition	559	...	3.57	5.5 CeF_3, no LaF_3
After LaF_3 addition	558	1.33	1.73	5.1 CeF_3, 8.5 LaF_3
	561	3.25	1.60	5.1 CeF_3, 8.5 LaF_3
	559	6.0	1.48	5.1 CeF_3, 8.5 LaF_3
	574	22.5	1.22	5.1 CeF_3, 8.5 LaF_3
	563	...[a]	1.14	5.1 CeF_3, 8.5 LaF_3

[a] After equilibrating at 800° C.

Table VI. Solubility of SmF_3

Initial charge, 13.0 Wt. % SmF_3

Temp., ° C.	Mole % SmF_3
823	5.46
728	3.80
636	2.74
556	2.26

derived from the CeF_3-LaF_3 mixed-tracer determination. The solid lines show the solubilities of CeF_3 and LaF_3 in equilibrium with solid CeF_3 and LaF_3 respectively. The points show the sums of the LaF_3 and CeF_3 solubilities from Table X. The combined solubilities are generally intermediate between those for the CeF_3 and LaF_3 and more nearly approximate the value of the predominant solute-constituent. This is clearly not the case for the YF_3-SmF_3-solvent system (cf. Table IX). In view of the data presented here and the reported dimorphic character of YF_3 (*5*), it may be surmised that YF_3-SmF_3 do not form extensive solid solutions.

The possibility of carrying out a poison depletion operation is based on a reaction of a type indicated in the following equation:

$$CeF_3\,(s) + LaF_3\,(d) \rightarrow LaF_3\,(ss) + CeF_3\,(d)$$

Where s = solid, d = dissolved, and ss = solid solution.

Table VII. Solubility of SmF_3 in Presence of CeF_3

Initial charge	12.8 Wt. % SmF_3 and 9.4 Wt. % CeF_3		13.5 Wt. % SmF_3 and 16.9 Wt. % CeF_3	
	Temp., ° C.	Wt. % SmF_3 in filtrate	Temp., ° C.	Wt. % SmF_3 in filtrate
	812	4.14	823	2.50
	723	3.16	728	2.07
	640	2.43	636	1.68
	556	2.08	553	1.42

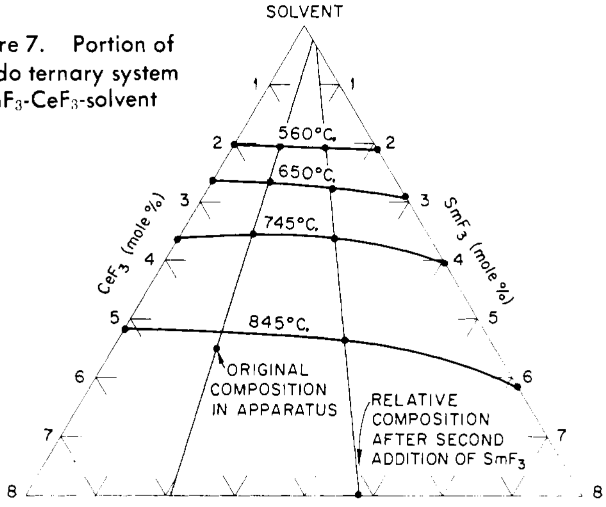

Figure 7. Portion of pseudo ternary system SmF_3-CeF_3-solvent

Table VIII. Solubility of YF_3

Initial charge, wt. % YF_3	12.48		17.1	
	Temp., ° C.	YF_3, mole %	Temp., ° C.	YF_3, mole %
	828	10.39[a]	839	13.97
	740	7.32	686	5.87
	639	4.65		
	549	2.67		

[a] Probably unsaturated.

Table IX. Solubilities of YF_3 and SmF_3

(Double tracer)

Composition in reactor	14.8 Wt. % YF_3 (12.51 mole %)	14.0 Wt. % SmF_3 (8.30 mole %)
Temp., ° C.	Mole % YF_3	Mole % SmF_3
830	7.88	4.23
736	4.88	2.42
642	3.30	1.55
551	2.34	1.08

Table X. Solubilities of CeF_3 and LaF_3

(Double tracer)

Composition in reactor	8.6 wt. % CeF_3, 2.7 wt. % LaF_3		8.0 wt. % CeF_3, 11.8 wt. % LaF_3	
	Mole % in filtrate			Mole % in filtrate	

Temp., ° C.	CeF_3	LaF_3	Temp., ° C.	CeF_3	LaF_3
814	3.33	1.03	816	1.54	2.55
726	2.47	0.78	723	1.23	1.78
636	1.82	0.57	632	0.93	1.31
553	1.43	0.41	553	0.76	1.10

Table XI. Solubilities of CeF_3 and SmF_3

(Double tracer)

Composition in reactor

6.68 wt. % CeF_3, 2.71 wt. % SmF_3			6.8 wt. % CeF_3, 9.0 wt. % SmF_3		
Temp., ° C.	Mole % in filtrate CeF_3	Mole % in filtrate SmF_3	Temp., ° C.	Mole % in filtrate CeF_3	Mole % in filtrate SmF_3
848	2.81	1.04	845	2.08	3.29
750	2.49	1.05	740	1.36	2.28
648	1.79	0.87	657	0.98	1.81
558	1.36	0.70	564	0.72	1.36

If CeF_3 and LaF_3 are distributed between liquid and solid solutions then the activity constant for the equilibrium is:

$$K_a = \frac{{}^{a}LaF_3\,(ss)\; {}^{a}CeF_3\,(d)}{{}^{a}CeF_3\,(ss)\; {}^{a}LaF_3\,(d)} =$$

$$K_\gamma\, \frac{{}^{N}LaF_3\,(ss)\; {}^{N}CeF_3\,(d)}{{}^{N}CeF_3\,(ss)\; {}^{N}LaF_3\,(d)} = K_\gamma K_N \qquad (1)$$

If $K\gamma$ is assumed to be constant, K_N would be constant because:

$$K_N = \frac{K_a}{K_\gamma} \qquad (2)$$

Experimental data concerning solubility of LaF_3 and CeF_3 are summarized in Table XIV and indicate that the following relations hold.

Table XII. Control Samples, Mixed Tracer Experiments

Control Sample No.	Amount Added (weighed out), Mg.		Calc. from Counting Data, Mg.		Error, %	
	CeF_3	LaF_3	CeF_3	LaF_3	CeF_3	LaF_3
1	6.9	27.4	7.0	27.5	+ 1.4	+ 0.4
2	13.9	14.1	14.0	14.0	+ 0.7	−0.7
3	19.2	39.2	18.8	37.8	−2.1	−3.6
4	31.2	32.3	30.5	32.6	−2.2	+ 0.9
5	60.4	28.8	61.0	27.2	+ 1.0	−5.6
		Average error,			1.5%	2.2%
	CeF_3	SmF_3	CeF_3	SmF_3	CeF_3	SmF_3
1	26.1	13.0	26.3	11.7	+ 0.8	−10.0
2	10.6	23.1	9.9	22.0	−6.6	−4.8
3	31.0	9.1	31.1	8.5	+ 0.3	−6.5
4	19.0	31.4	18.7	28.0	−1.6	−10.8
5	37.0	36.0	36.9	32.5	−0.3	−9.7
		Average error,			1.9%	8.4%
	YF_3	SmF_3	YF_3	SmF_3	YF_3	SmF_3
1	42.3	15.6	41.4	16.3	−2.1	+ 4.5
2	21.6	8.2	20.1	8.6	−6.9	+ 4.9
3	10.3	21.8	8.5	23.6	−17.5	+ 8.3
		Average error,			8.8%	5.9%

Table XIII. Solubilities of Three Rare-Earth Fluorides

(Mole % dissolved in NaF-ZrF_4-UF_4, 50–46–4 mole %)

Temp., ° C.	LaF_3	CeF_3	SmF_3
550	1.80	2.02	2.23
600	2.04	2.27	2.52
700	2.68	3.00	3.38
800	4.03	4.30	4.97

Table XIV. Solubility Relations in the System CeF_3-LaF_3-Solvent

(Mole fraction)

Temp., ° C.	Solid Compn. LaF_3	Solid Compn. CeF_3	Exptl. Liquid Compn. LaF_3	Exptl. Liquid Compn. CeF_3	Calcd. Liquid Compn. $S^0_{LaF_3} N_{LaF_3(ss)}$	Calcd. Liquid Compn. $S^0_{CeF_3} N_{CeF_3(ss)}$
814	0.24	0.76	0.0103	0.033	0.0102	0.035
726	0.24	0.76	0.0078	0.025	0.0071	0.025
636	0.24	0.76	0.0057	0.018	0.0056	0.019
553	0.24	0.76	0.0041	0.014	0.0044	0.016
816	0.60	0.40	0.026	0.015	0.028	0.018
723	0.60	0.40	0.018	0.012	0.018	0.013
632	0.60	0.40	0.013	0.0093	0.013	0.0099
553	0.60	0.40	0.011	0.0076	0.011	0.0082

$$N_{CeF_3(d)} = S^0_{CeF_3} N_{CeF_3(ss)} \qquad (3)$$

and

$$N_{LaF_3(d)} = S^0_{LaF_3} N_{LaF_3(ss)} \qquad (4)$$

where $S^0_{CeF_3}$ is the mole fraction (solubility) of CeF_3 in a solvent at a specified temperature. This is equivalent to saying that isotherms in the pseudo-ternary system CeF_3-LaF_3-Solvent are linear, and that a CeF_3-LaF_3 solid solution is the saturating phase.

Substituting Equations 3 and 4 into 1, the following result is obtained:

$$K_N = \frac{S^0_{CeF_3}}{S^0_{LaF_3}} \qquad (5)$$

The experimental values are compared with this result in Table XV. Table XVI shows the corresponding results for the CeF_3-SmF_3 solid solvent extraction. These results for the SmF_3-CeF_3 determinations are in reasonable accord with those predicted by Equation 5. This work on mixed rare earth fluoride solubilities shows that a rare-earth poison depletion process from a molten fluoride fuel by solid-solvent extraction is chemically feasible.

ACKNOWLEDGMENT

Many interesting and valuable discussions with F. F. Blankenship, M. Blander, R. F. Newton, J. E. Ricci, R. E. Thoma, and H. Insley are gratefully acknowledged. The chemical analyses were performed by members of the Oak Ridge National Laboratory Analytical Chemistry Division. The oxide- and water-free solvent mixtures were supplied by members of the Oak Ridge National Laboratory Chemistry Division and were used without further treatment. The Radioisotope Sales Division of Oak Ridge National Laboratory was the source for the radioisotopes used in this work.

Table XV. Solid-Solvent Extraction Coefficients[a]

(LaF_3-CeF_3 in NaF-ZrF_4-UF_4, 50-46-4 mole %)

Temp., ° C.	$(S^0_{CeF_3} / S^0_{LaF_3})$	Experimental K_N[a] 6.1% CeF_3 1.9% LaF_3	Experimental K_N[a] 5.7% CeF_3 8.4% LaF_3
815	1.09	1.0	1.2
724	1.10	1.0	1.0
634	1.13	1.0	1.0
553	1.12	0.9	1.0

[a] $K_N = \dfrac{N_{LaF_3(ss)} N_{CeF_3(d)}}{N_{CeF_3(ss)} N_{LaF_3(d)}}$

Table XVI. Solid-Solvent Extraction Coefficients[a]

(SmF_3-CeF_3 in NaF-ZrF_4UF_4, 50-46-4 mole %)

Temp., ° C.	$(S^0_{SmF_3} / S^0_{CeF_3})$	Experimental K_N[a] 5.3% SmF_3 4.1% CeF_3	Experimental K_N[a] 1.5% SmF_3 4.0% CeF_3
846	1.18	1.2	
745	1.12	1.4	1.2
652	1.10	1.4	1.3
561	1.08	1.5	1.4

[a] $K_N = \dfrac{N_{CeF_3(ss)} N_{SmF_3(d)}}{N_{SmF_3(ss)} N_{CeF_3(d)}}$

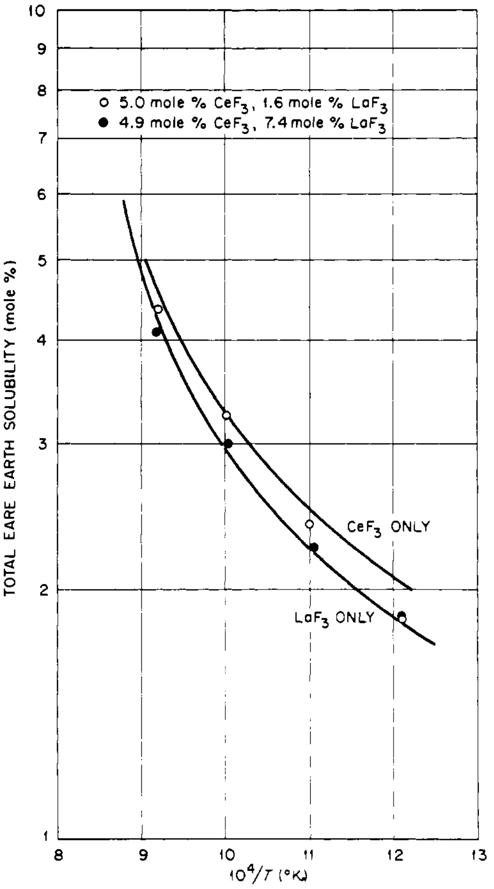

Figure 8. Additive solubilities of CeF_3 and LaF_3 in NaF-ZrF_4-UF_4 (50–46–4 mole %)

LITERATURE CITED

(1) Barton, C. J., Grimes, W. R., Insley, H., Moore, R. E., Thoma, R. E., *J. Phys. Chem.* **62**, 665-76 (1958).

(2) Brewer, L., "Chemistry and Metallurgy of Miscellaneous Materials; Thermodynamics," L. L. Quill, ed., McGraw-Hill, New York, 1950.

(3) Dergunov, E. P., *Doklady Akad. Nauk S. S. S. R.* **60**, 1185-8 (1948).

(4) Goldschmidt, V. M., "Geochemistry," pp. 88-9, Oxford Univ. Press, New York, 1954.

(5) Nowacki, W., *Z. Krist.* **101**, 273 (1939).

RECEIVED for review January 19, 1959. Accepted May 27, 1959.