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SOLUBILITY RELATIONS AMONG SOME FISSION PRODUCT FLUORIDES IN $NaF-ZrF_4-UF_4$ (50-46-4 mole %)

W. T. Ward, R. A. Strehlow, W. R. Grimes, and G. M. Watson

Among the undesirable effects of fission product accumulation in a circulating-fuel reactor, two are of especially great chemical interest. Precipitation of a fission-product fluoride (in a heat exchanger, for example,) might result in a termination of reactor operation or, conceivably, in a more serious misadventure. In addition, the accumulation of high cross-section materials results in a loss of economic utility of the fuel. In this respect the rare earth elements samarium, europium, and gadolinium, are of prime importance since these three elements are expected to account for significantly more than half of the poisoning by non-gaseous elements. While this accumulation is certainly not unique to circulating-fuel reactors, its consideration is appropriate in this work because of the possibility of carrying out a continuous poison depletion operation.

In an effort to obtain information regarding these effects, a study of the solubility relations among some of the fission products in a fuel mixture has been carried out. Because the fission products formed in greater yields include several of the rare earths, rare gases, alkaline earths and the 4d transition elements (particularly elements Nos. 41-46), the selection of subjects for initial study was made after a consideration of relative importance based

on fission yield and thermal neutron cross sections of the various products. This report presents some of the data which has been obtained in this laboratory on the solubility of BaF_2, LaF_3, CeF_3, SmF_3, and YF_3 in a 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. In addition to delineating the allowable rare earth concentration limits, data based on these experiments 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°C, 730°C, 640°C, 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 obtained in the initial determinations were analyzed by members of the ORNL Analytical Chemistry Division 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 involving the use of radioactive tracers was developed and has proved to be very successful.

Materials and Apparatus

Oxide- and water- free solvent mixture was supplied by members of the ORNL Chemistry Division and was used without further treatment.

The various radioactively-labeled fission-product fluorides were prepared by members of the ORNL Analytical Chemistry Division. A few millicuries of the most suitable radio-isotope* in the form of an aqueous HCl solution of the chloride was mixed with an aqueous solution of the same, but inert, fission product. The resulting solution was treated with an aqueous hydrofluoric acid solution which yielded a precipitate of the fission product fluoride. This precipitate, after centrifuging, washing, and recentrifuging, was dried in a vacuum oven.

The number of millicuries required 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), Y^{91} (58 days), and Ba^{133} (9.5 years).

The reactor vessel, made of 1/4" thick nickel, had an internal diameter of 2" and was 17" long. A section of 1/2" nickel pipe

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* Obtained from ORNL Radioisotopes Sales Division.

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 accomodated a thermocouple well, a connection to a pressure gage, and a dip leg (a piece of 1/4" tubing extending to 1/4" 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 two inches were used. Later, as the precision of the method became known, a charge weighing but 200 grams was contained in a one 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. Due to the fact that a temperature gradient was found to exist in the first experiments of the series, an auxiliary variac-controlled calrod heater was placed under the reactor vessel. The power input was adjusted so as to minimize the temperature inequality.

The filter sticks were constructed from sintered nickel or copper discs with nominal pore size of 0.0004". The discs were welded into sections of 3/8" tubing about 1 1/4" long. The open end of the tubing was reduced in diameter and welded to a 22" length of 1/8" tubing. This was slipped through a Teflon gasket in a threaded cap which fit the 1/2" 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 filter stick connected as described above 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 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 5-8 gram sample so obtained was then analyzed.

A set of standard samples made up for each batch of labeled material consisted of one gram of the solvent ($\pm$ 5%) plus varying amounts of accurately weighed tracer-containing fluoride salt. These standards were placed in cork stoppered glass tubes which fit in a well counter. A blank was prepared which contained only solvent. The four filtrates obtained at the successive temperatures in a run were separately ground up. One gram samples ($\pm$5%) of each filtrate, accurately weighed, were placed in similar tubes and counted with the standards and blank. The reading of the blank was subtracted from the other readings to adjust for both background and the uranium counts. The count obtained 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 percent of fission product to be made.

Three experiments were made in which the solubilities of two separately labeled fluorides were measured. By selection of the pairs in a way such that their half lives were sufficiently different it was possible to simultaneously determine the weights of each of the fission products contained in the filtrates. This technique involves the filtrates being counted several times and requires that the differences in decay rates be utilized in the determination.

Results

The solubility of CeF_3 was determined in several different experiments, either as the prime objective or as the first step in a multi-purpose experiment. The solubilities determined in four of these experiments are shown graphically in Figure 1, where the logarithm of the solubilities in weight percent 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. It can be seen that the precision is approximately $\pm 5\%$.

The solubilities obtained for LaF_3, SmF_3 and YF_3 (single experiments) are shown plotted in the same way along with the Ce curve in Figure 2. The same data converted to mole % are shown in Figure 3. An interesting correlation is that the solubilities of the

fluorides decrease with increase of positive ion size.

BaF_2 was found to be completely soluble in the solvent in amounts up to 1/3 BaF_2 - 2/3 solvent, which was the maximum amount of BaF_2 added.

Several experiments were run to determine what effect the presence of a second fission-product fluoride would have on the above solubilities. The solubility of BaF_2 was not noticeably affected by the addition of 14 wt % CeF_3. However, the solubilities of both CeF_3 and SmF_3 were appreciably lowered by the addition of a second fluoride as shown in Figures 4, 5, 6, and 7.

There is good indication based on petrographic observation that the precipitating phase for the solvent used in this work is the rare-earth fluoride. For those compositions containing less than about 42 mole % ZrF_4 the precipitating phase is $NaCeF_4$. No examinations of the barium or yttrium containing systems have yet been made to determine the nature of the primary phase in these systems.

The Tables I - XV present in detail the experimental results.

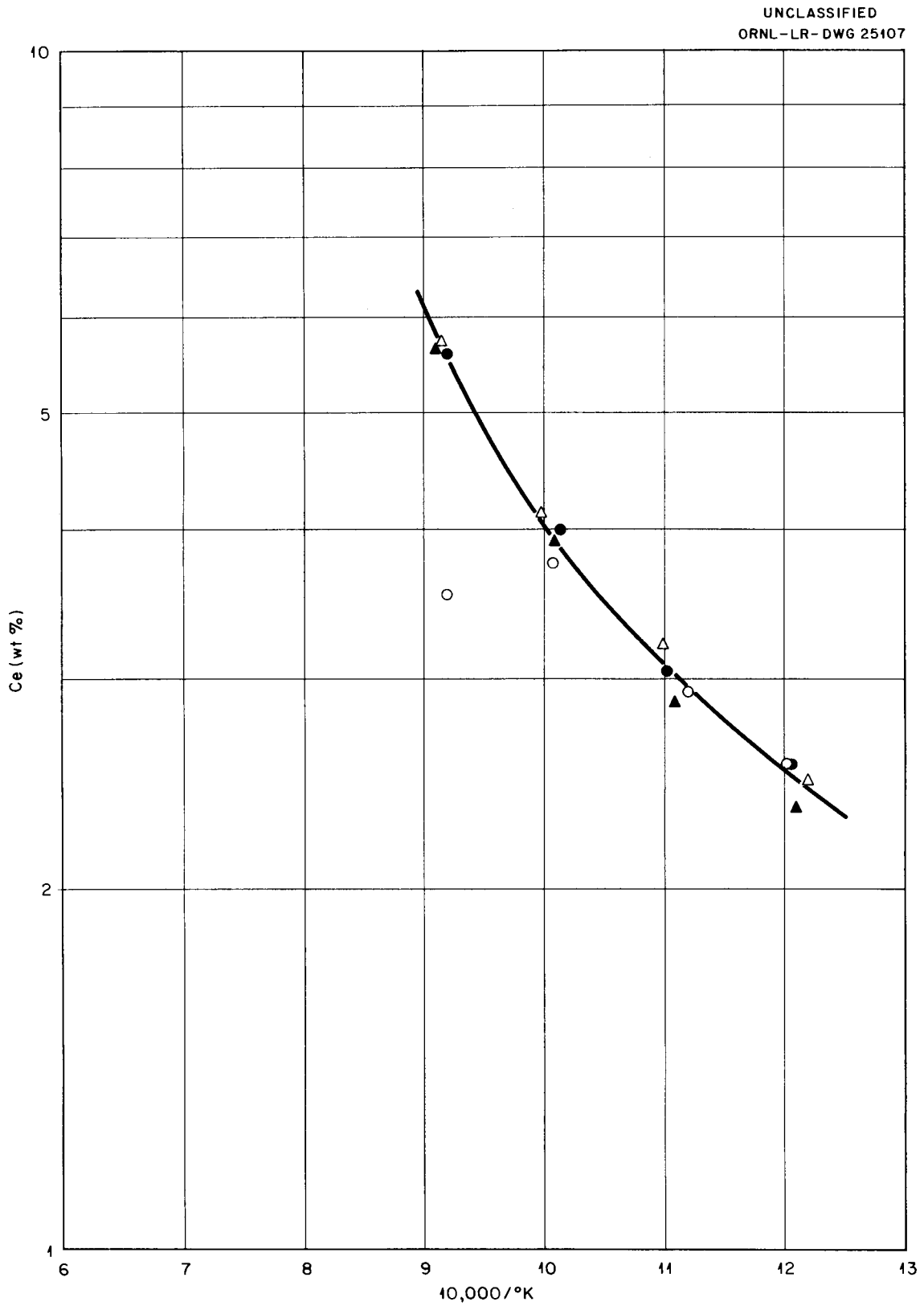

Fig. 1. Solubility of CeF_3 in $NaF-ZrF_4-UF_4$ (50-46-4 mole %) as Determined in Four Separate Experiments.

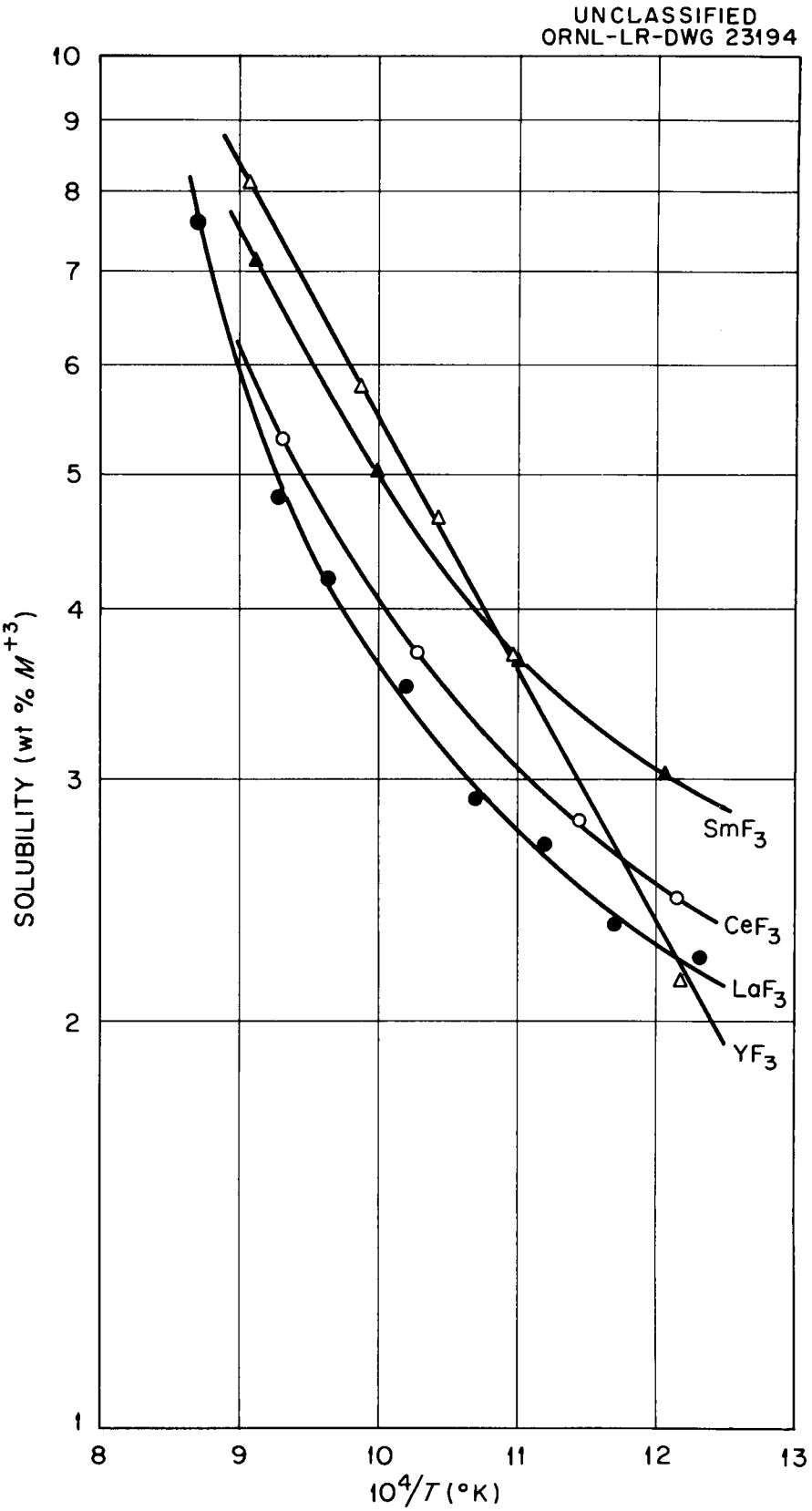

Fig. 2. Solubility of LaF_3, CeF_3, SmF_3, and YF_3 in $NaF-ZrF_4-UF_4$ (50-46-4 mole %).

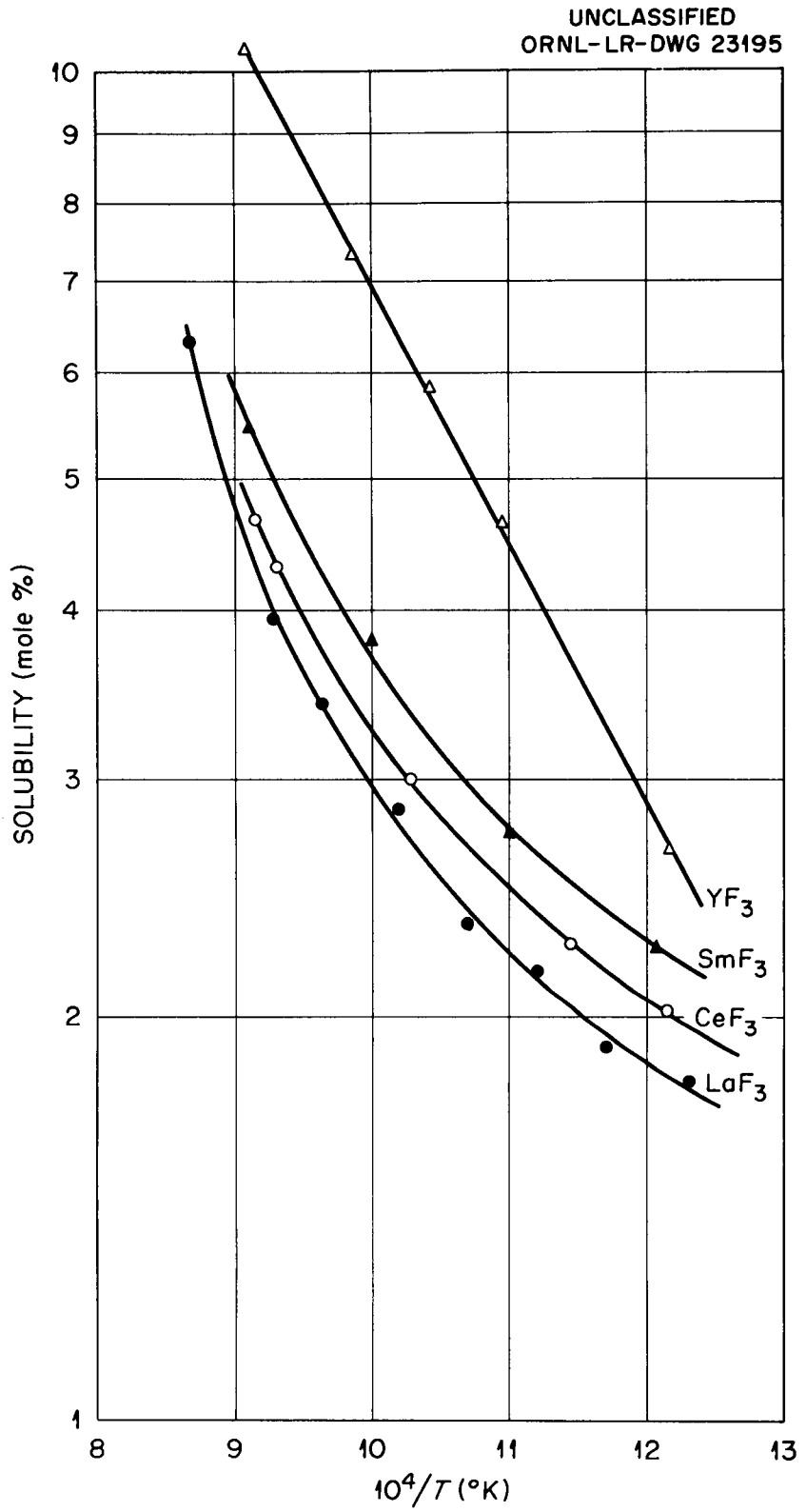

Fig. 3. Solubility of LaF_3, CeF_3, SmF_3, and YF_3 in $NaF-ZrF_4-UF_4$ (50-46-4 mole %).

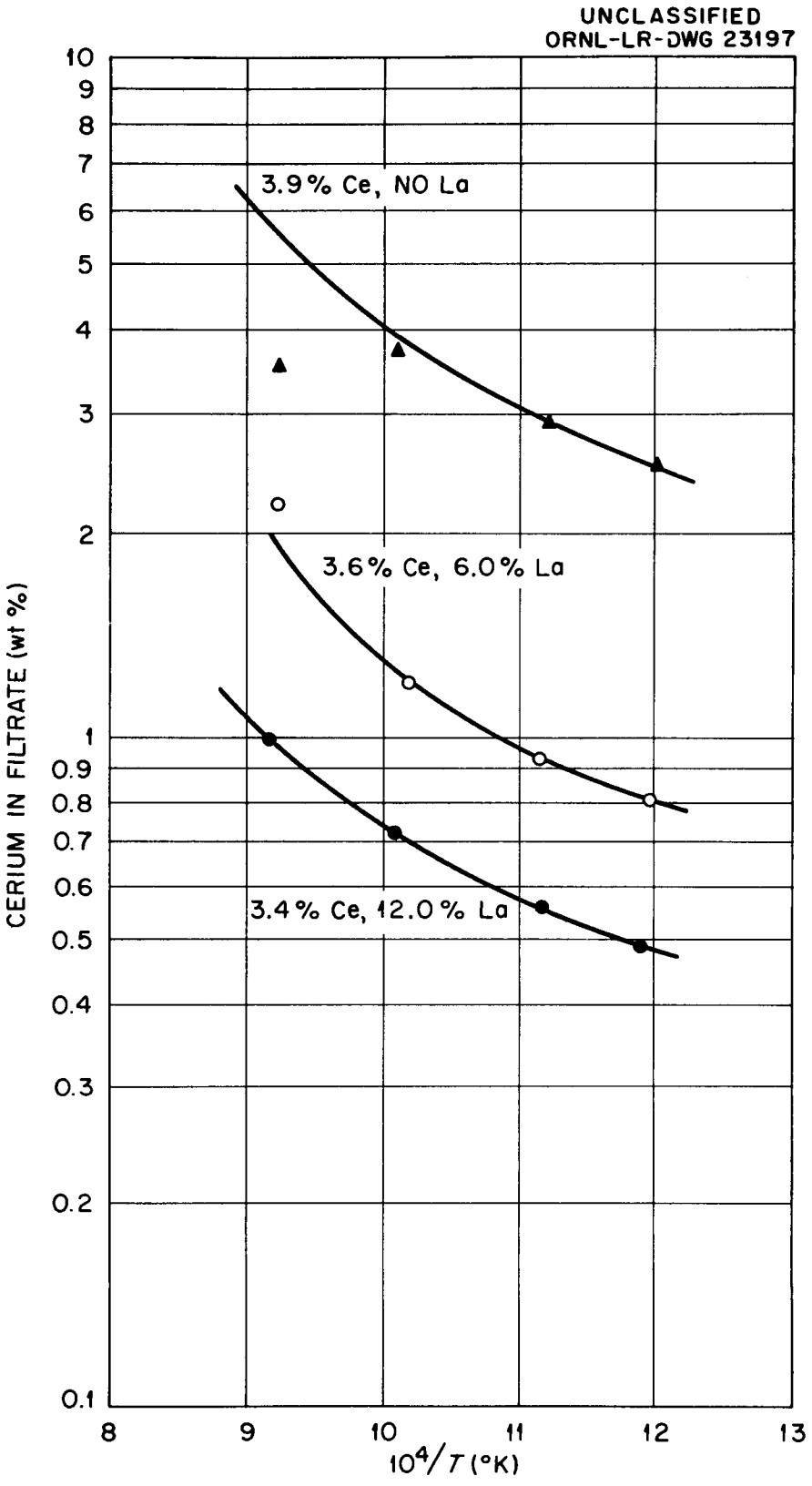

Fig. 4. Effect of LaF_3 on the Solubility of CeF_3.

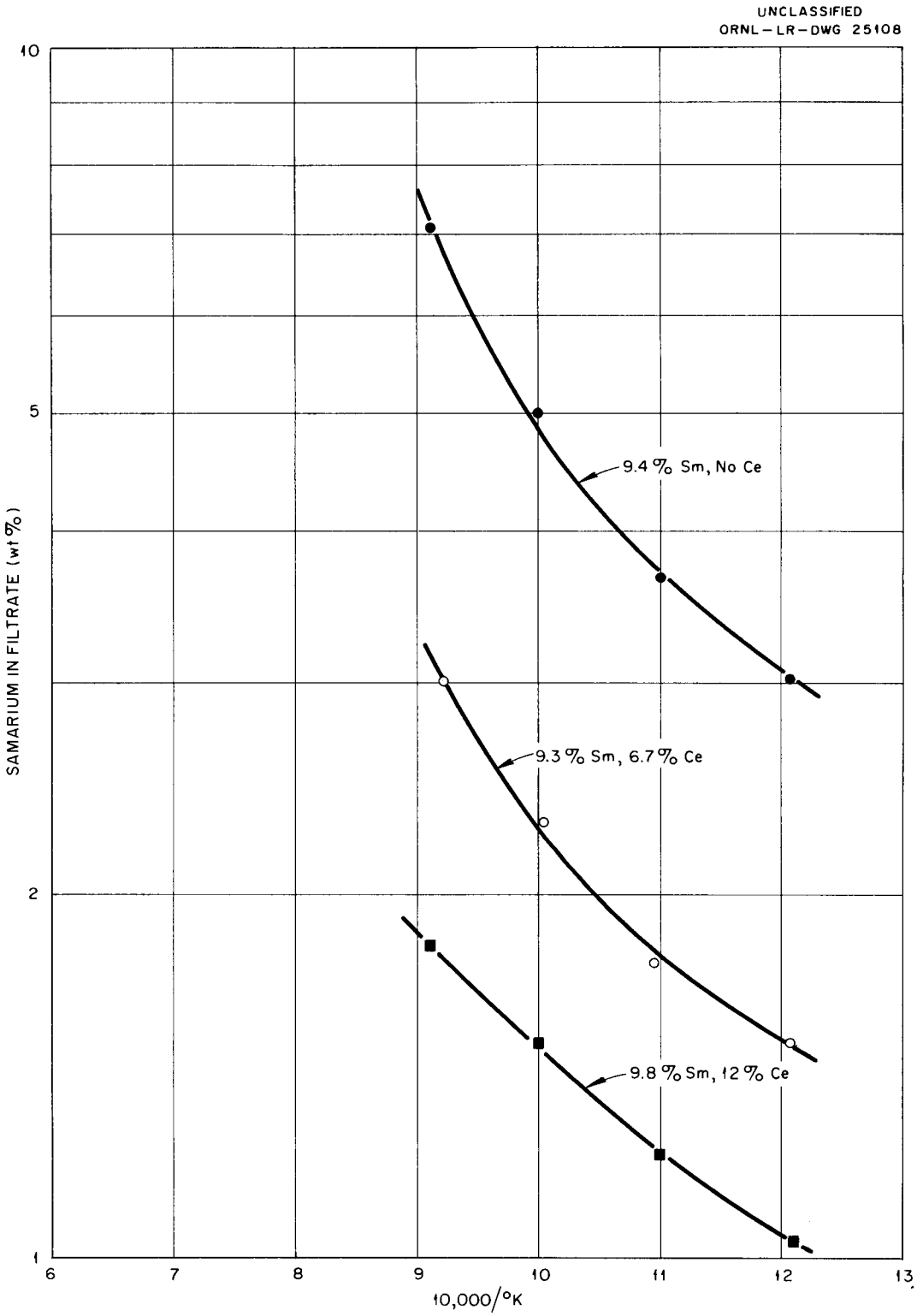

Fig. 5. Effect of CeF_3 on the Solubility of SmF_3.

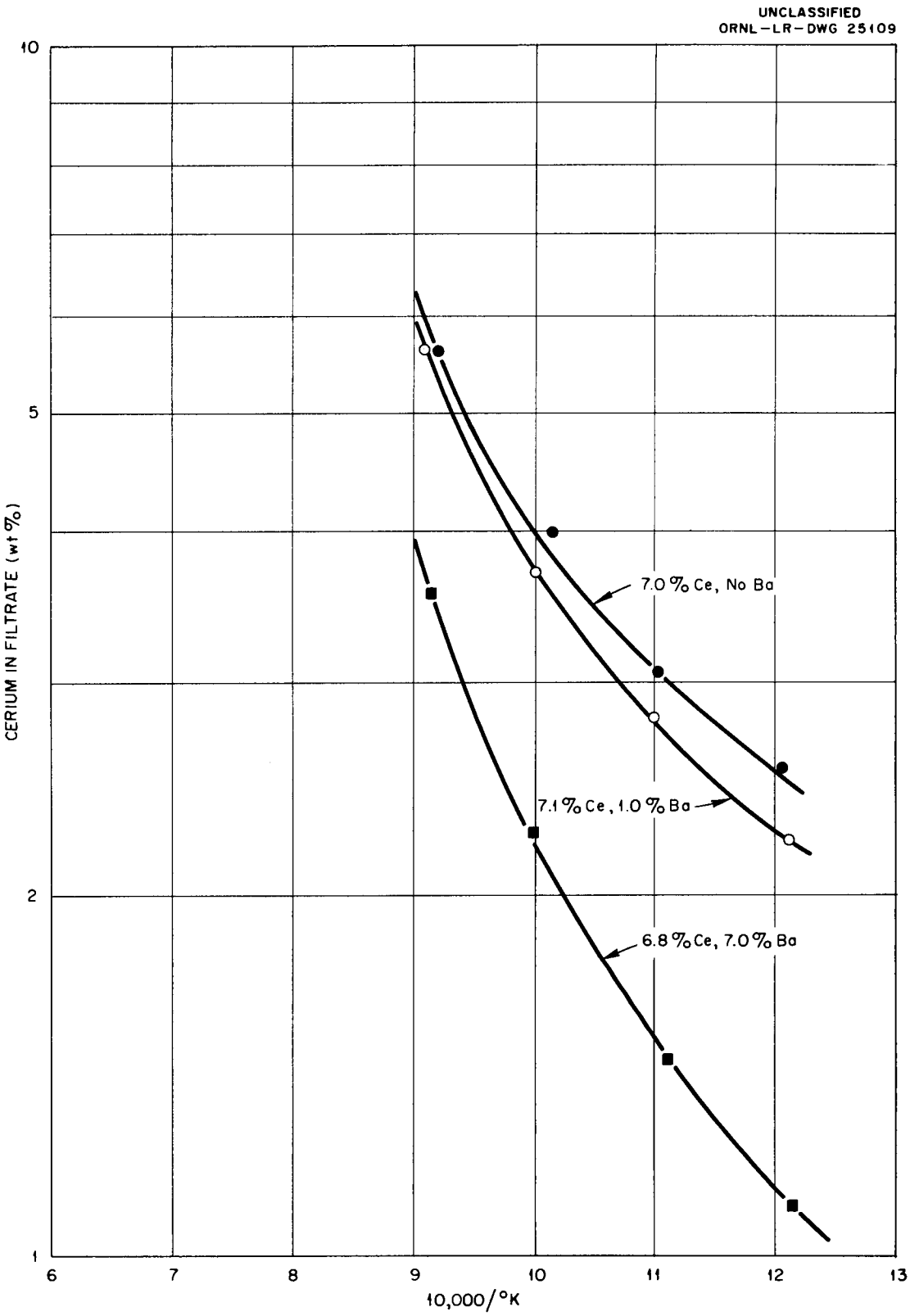

Fig. 6. Effect of BaF_2 on the Solubility of CeF_3.

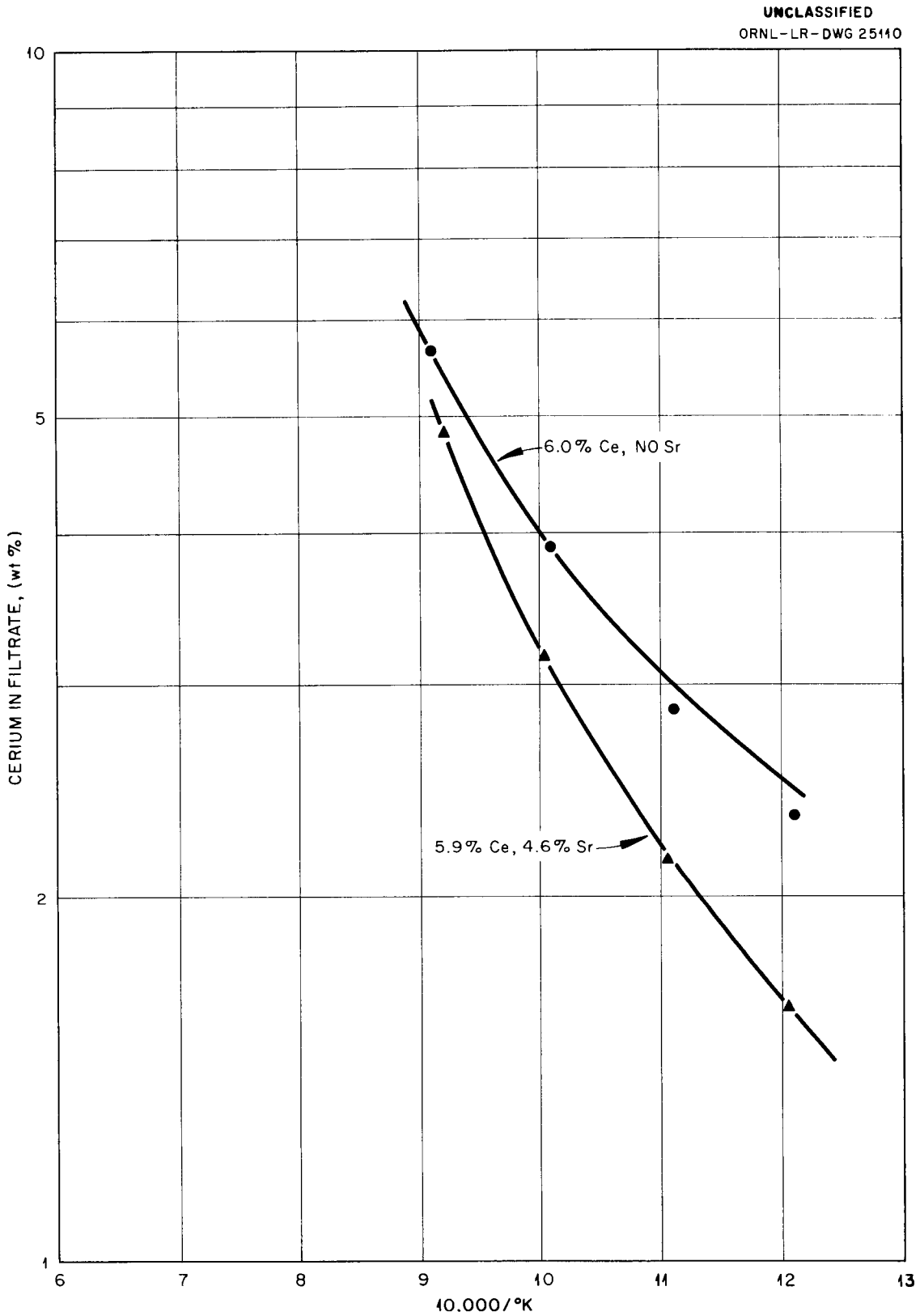

Fig. 7. Effect of SrF_2 on the Solubility of CeF_3.

Table 1

Solubility of CeF_3 over the 550 - 850°C Temperature Range

Cerium content in initial charge - wt % Ce							
3.9		7.0		6.2		6.0	
Filtrate		Filtrate		Filtrate		Filtrate	
Temp. °C	Wt. % Ce	Temp. °C	Wt. % Ce	Temp. °C	Wt. % Ce	Temp. °C	Wt. % Ce
812	3.53	812	5.60	820	5.73	825	5.65
718	3.75	712	3.99	729	4.12	718	3.90
619	2.93	634	3.04	638	3.20	628	2.87
559	2.54	556	2.54	548	2.47	554	2.34

Table II

Solubility of LaF_3

Initial Charge: 9.1 wt % La			Initial Charge: 5.4 wt % La	
Temperature (°C)	La in Filtrate Wt. %	La in Filtrate Mole %	Temperature (°C)	La in Filtrate Wt. %
877	7.59	6.33		
805	4.81	3.95	808	4.67
764	4.19	3.41		
707	3.51	2.86	718	3.23
662	2.90	2.35		
619	2.68	2.17	613	2.40
582	2.35	1.89		
539	2.22	1.78	553	2.16

Table III

Solubility of LaF_3 in Presence of BaF_2 and SrF_2

Initial Charge: 5.4 wt % La, no Ba or Sr (see above Table)		Initial Charge: 5.6 wt % La, 1.0 wt % Ba and 1.0 wt % Sr	
Temperature (°C)	La in Filtrate Wt. %	Temperature (°C)	La in Filtrate Wt. %
808	4.67	808	3.84
613	2.40	608	1.91

Table IV

Solubility of CeF_3 in Presence of LaF_3

Initial Charge Contained 3.6 wt % Ce and 6.0 wt % La		Initial Charge Contained 3.4 wt % Ce and 12 wt % La	
Temperature (°C)	Wt % Ce in Filtrate	Temperature (°C)	Wt % Ce in Filtrate
810	2.22	818	0.99
708	1.21	718	0.72
624	0.93	622	0.56
563	0.81	568	0.49

Table V

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

	Temp. (°C)	Time after Melting, hours	Ce in Filtrate Wt %	Approx. Ce-La Content in Reactor, Wt %
Before LaF_3 addition	559	-	2.54	3.9 Ce, no La
After LaF_3 addition	558	1.33	1.23	3.6 Ce, 6.0 La
"	561	3.25	1.14	" "
"	559	6.0	1.05	" "
"	574	22.5	0.87	" "
"	563	"Infinite"*	0.81	" "

* Time considered "infinite" because temperature had been raised to >800°C for more than an hour and >600°C for several hours before dropping back to the temperature indicated, thus insuring equilibration since the equilibrium distribution is independent of temperature.

Table VI

Solubility of SmF_3

Samarium content of Initial Charge: 9.4 wt % Sm

Temp., °C	Sm in Filtrate Wt %	Mole %
823	7.09	5.46
728	5.01	3.80
636	3.65	2.74
556	3.02	2.26

Table VII

Solubility of SmF_3 in Presence of CeF_3

Initial charge contained 9.3 wt % Sm and 6.7 wt % Ce		Initial charge contained 9.8 wt % Sm and 12 wt % Ce	
Temp., °C	Wt % Sm in Filtrate	Temp., °C	Wt % Sm in Filtrate
812	3.00	823	1.81
723	2.29	728	1.50
640	1.76	636	1.22
556	1.50	553	1.03

Table VIII

Solubility of CeF_3 in Presence of BaF_2

Cerium and Barium Concentrations in Reactor, wt %

7.0 % Ce, no Ba		7.0 % Ce, 1.0 % Ba		6.8 % Ce, 7.0 % Ba	
Temp. (°C)	Ce in Filtrate wt %	Temp. (°C)	Ce in Filtrate wt %	Temp. (°C)	Ce in Filtrate wt %
812	5.60	823	5.63	820	3.54
712	3.99	724	3.68	727	2.26
634	3.04	638	2.79	627	1.45
556	2.54	552	2.22	550	1.10

Table IX

Solubility of CeF_3 in Presence of SrF_2

Cerium and Strontium Concentrations in Reactor, wt %			
6.0 % Ce, no Sr		5.9 % Ce, 4.6 % Sr	
Temperature (°C)	Ce in Filtrate wt %	Temperature (°C)	Ce in Filtrate wt %
825	5.65	813	4.84
718	3.90	724	3.17
628	2.87	633	2.15
554	2.34	557	1.62

Table X

Solubility of YF_3

Y Content in Initial Charge, wt %			
7.58 % Y		10.4 % Y	
Temperature (°C)	Y in Filtrate wt %	Temperature (°C)	Y in Filtrate wt %
828	8.10	839	10.76
740	5.76	686	4.63
639	3.68		
549	2.13		

Table XI

Solubilities of YF_3 and SmF_3 (Double Tracer)

Composition in Reactor: 9.04 wt % Y; (12.51 mole % YF_3); 10.16 wt % Sm (8.30 mole % SmF_3)

Temperature (°C)	Y in Filtrates		Sm in Filtrates	
	Wt % Y	Mole % YF_3	Wt % Sm	Mole % SmF_3
830	5.97	7.88	5.42	4.23
736	3.79	4.88	3.18	2.42
642	2.60	3.30	2.06	1.55
551	1.85	2.34	1.45	1.08

Table XII

Solubilities of CeF_3 and LaF_3 (Double Tracer)

Composition in Reactor									
6.1 wt % Ce, 1.9 wt % La					5.7 wt % Ce, 8.4 wt % La				
	In Filtrate					In Filtrate			
Temp. (°C)	Wt % Ce	Mole % CeF_3	Wt % La	Mole % LaF_3	Temp. (°C)	Wt % Ce	Mole % CeF_3	Wt % La	Mole % LaF_3
814	4.08	3.33	1.25	1.03	816	1.89	1.54	3.11	2.55
726	3.06	2.47	0.96	0.78	723	1.52	1.23	2.19	1.78
636	2.27	1.82	0.71	0.57	632	1.16	0.93	1.62	1.31
553	1.79	1.43	0.51	0.41	553	0.95	0.76	1.36	1.10

Table XIII

Solubilities of CeF_3 and SmF_3 (Double Tracer)

Composition in Reactor									
4.88 wt % Ce, 1.96 wt % Sm					4.8 wt % Ce, 6.5 wt % Sm				
	In Filtrate					In Filtrate			
Temp. (°C)	Wt % Ce	Mole % CeF_3	wt % Sm	mole % SmF_3	Temp. (°C)	wt % Ce	mole % CeF_3	wt % Sm	mole % SmF_3
848	3.45	2.81	1.37	1.04	845	2.52	2.08	4.28	3.29
750	3.07	2.49	1.39	1.05	740	1.67	1.36	3.01	2.28
648	2.22	1.79	1.15	0.87	657	1.21	0.98	2.40	1.81
558	1.70	1.36	0.94	0.70	564	0.90	0.72	1.82	1.36

Table XIV

Solubility of BaF_2

Reactor Content (calculated), wt %					
21.2 % BaF_2 (16.6 % Ba) 78.8 % Solvent		33.1 % BaF_2 (26.0 % Ba) 66.9 % Solvent		28.4 % BaF_2 (22.2% Ba) 14.3 % CeF_3 57.3 % Solvent	
Temp. (°C)	Filtrate Wt % Ba	Temp. (°C)	Filtrate Wt % Ba	Temp. (°C)	Filtrate Wt % Ba*
838	16.8	852	26.2	843	25.0
708	17.0	755	26.0	738	25.7
573	17.0	655	26.3	644	26.2
		561	26.6	571	26.5

* It should be noticed that the apparent generation of Barium is due to a difference between the calculated reactor composition and the actual liquid composition in presence of undissolved material.

TABLE XV

Control Samples, Mixed Tracer Experiments

Control Sample Number	Actual Amount Added (weighed out) milligrams		Calculated from Counting Data milligrams		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 =		1.9%
	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%

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 this respect by more than 20 %. The differences between the solubility of YF_3 and the rare earth fluorides are, of course, much more pronounced but perhaps are related to the different crystal structure of YF_3.

Yttrium fluoride has been reported[1] to be dimorphic and to possess in one of its crystal modifications a fluorite-related structure. This differs from the lanthanum and cerium fluorides which crystallize in the fluocerite structure (hexagonal) occurring naturally as a solid solution of formula (La, Ce, $\cdots$)F_3. The orthorhombic structure shared by most of the rare-earth trifluorides from samarium to elements of higher atomic number is apparently belied by the strikingly analogous solubility behavior of SmF_3. This fact is possibly related to a correlation noticed between the solubilities and the cube of the rare-earth ionic radii.

Graphically interpolated solubilities of the three rare-earth fluorides, LaF_3, CeF_3, and SmF_3, are shown in Table XVI. Of the three tri-positively charged ions, lanthanum has the largest and samarium the smallest radius.

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1. W. Nowacki Z. Krist 101, 273 (1939).

Table XVI

Solubilities of Three Rare-Earth Fluorides in the Solvent ($NaF-ZrF_4-UF_4$, 50-46-4 mole %) Expressed in Mole Percent

Temp., °C	LaF_3	CeF_3	SmF_3	Average
550	1.80	2.02	2.23	2.02 ± 0.23
600	2.04	2.27	2.52	2.27 ± 0.25
700	2.68	3.00	3.38	3.02 ± 0.36
800	4.03	4.30	4.97	4.43 ± 0.54

By multiplication of these percentages by the cube of the ionic radius for each of the three ions, numbers are obtained which are proportional to the volume percentage in the saturated solution. In Table XVII are displayed the results of these multiplications.

Table XVII

The Solubilities of Table XVI Multiplied by r^3

Temp., °C	LaF_3 r = 1.04	CeF_3 r = 1.02	SmF_3 r = 0.97	Average r^3 x mole %
550	2.02	2.14	2.02	2.05 ± 0.08
600	2.26	2.40	2.29	2.31 ± 0.09
700	3.00	3.18	3.07	3.09 ± 0.09
800	4.52	4.56	4.52	4.53 ± 0.03

The deviations from the average appears to have been decreased from ± 12% to ± 4%. While no explanation of this observation is offered it is perhaps significant that neither a factor of the square nor the fourth power of the radius effects as satisfactory a correlation. These results are graphically displayed in Figure 8.

It is seen that solubilities of these fluorides individually are comfortably high for the purposes of 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. As is mentioned above, there exists additionally the 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 9 and 10 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 XII and XIII. It can be readily seen that there is no profound difference between the total rare-earth fluoride solubilities individually and mixed. It should be noticed that the combined solubilities of the two rare-earth fluorides are intermediate between the solubilities of the individual fluorides at the same temperature.

Figure 11 shows the strongly additive nature of the experimental results for 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

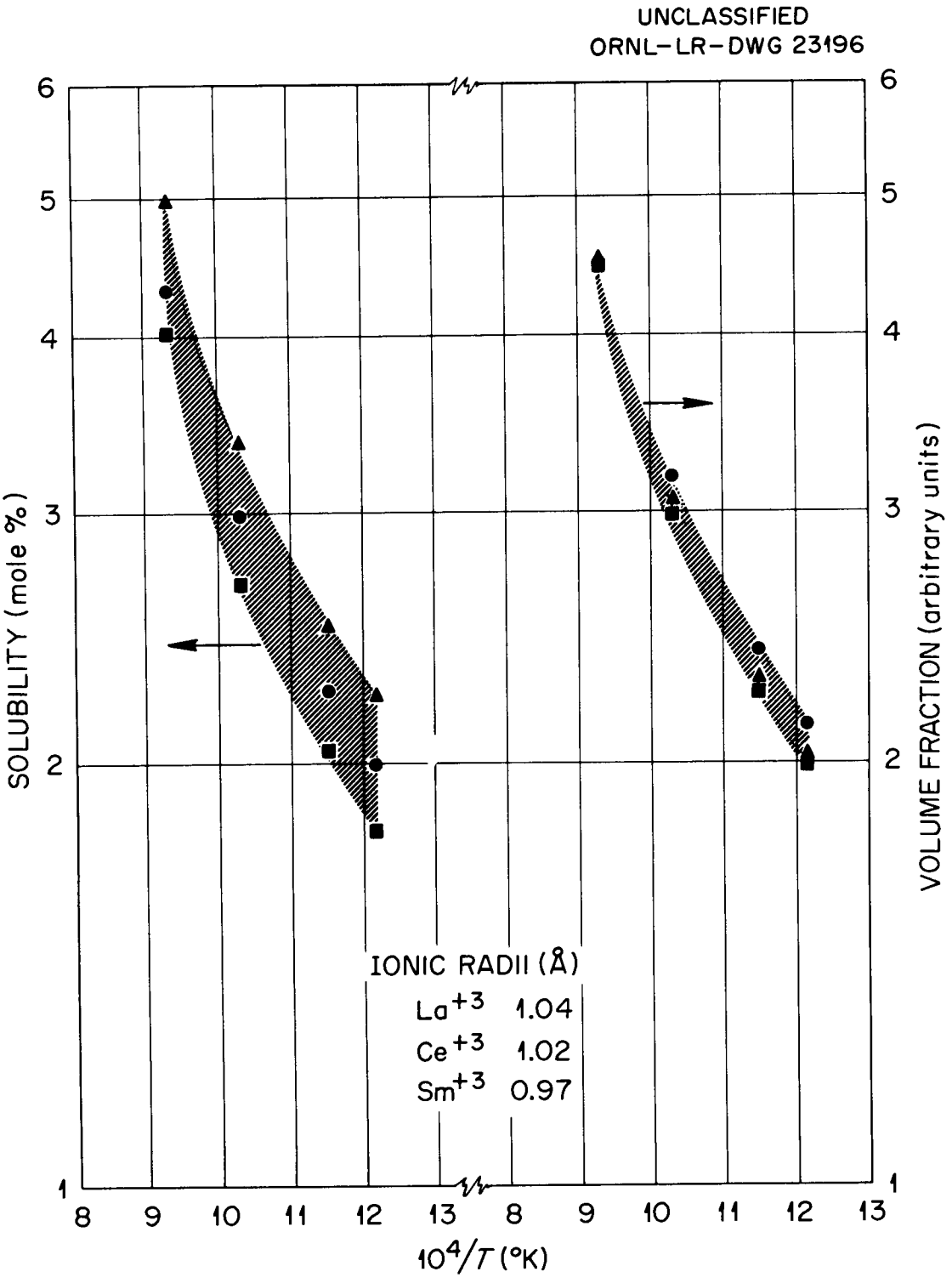

Fig. 8. Solubilities and Volume Fractions of LaF_3, CeF_3, and SmF_3 in $NaF-ZrF_4-UF_4$ (50-46-4 mole %).

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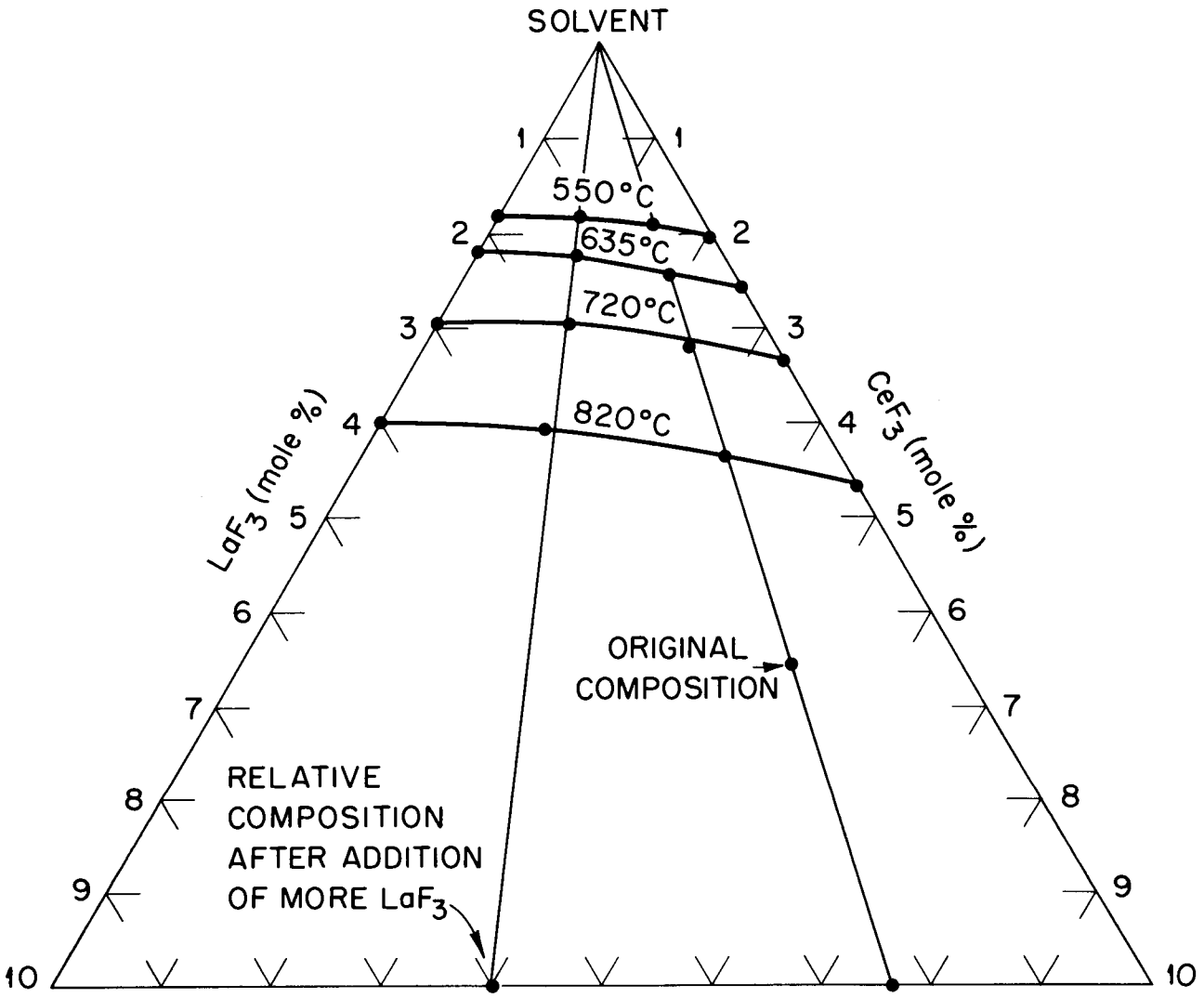

Fig. 9. Portion of Pseudo Ternary System LaF_3-CeF_3-Solvent.

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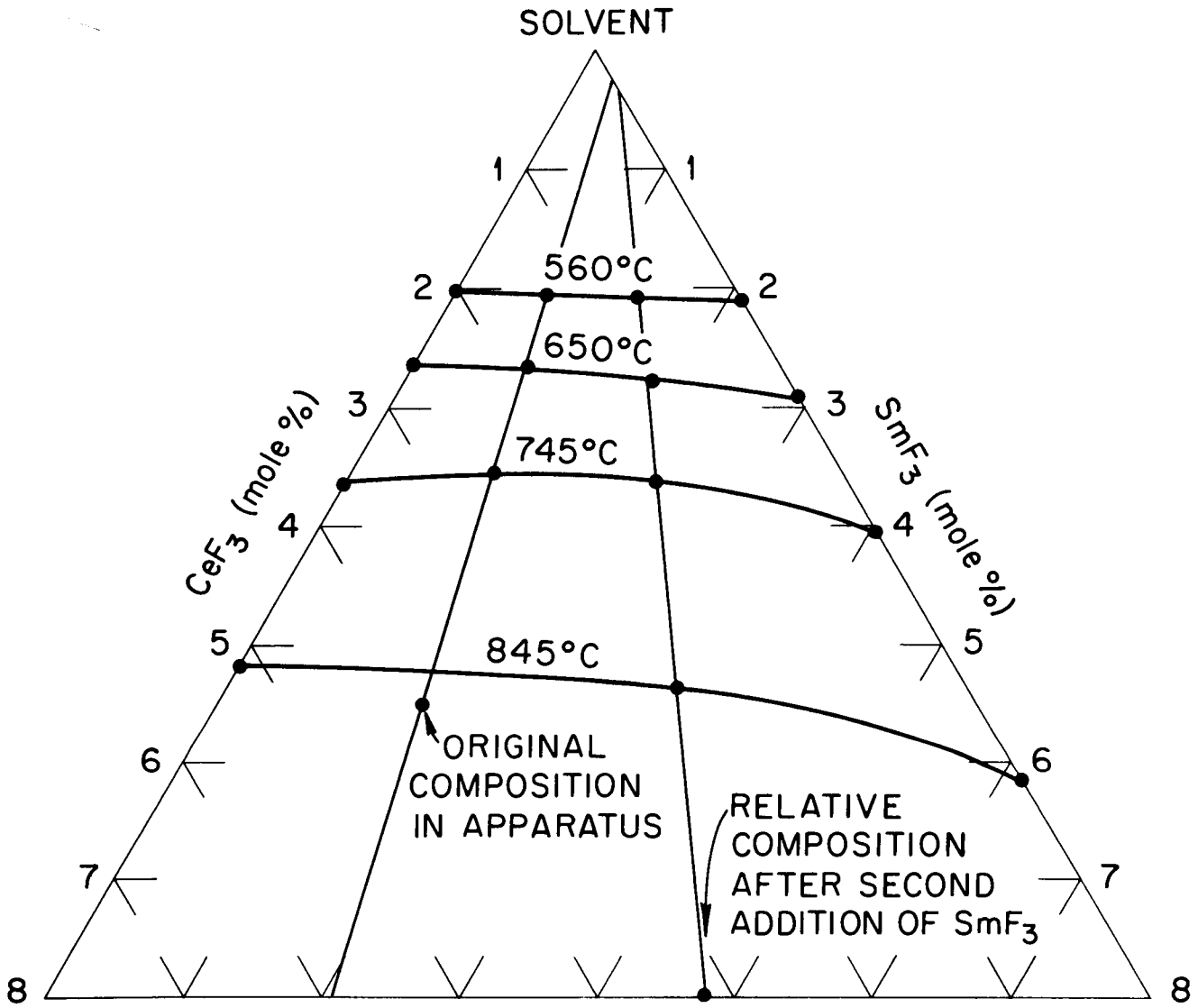

Fig. 10. Portion of Pseudo Ternary System SmF_3-CeF_3-Solvent.

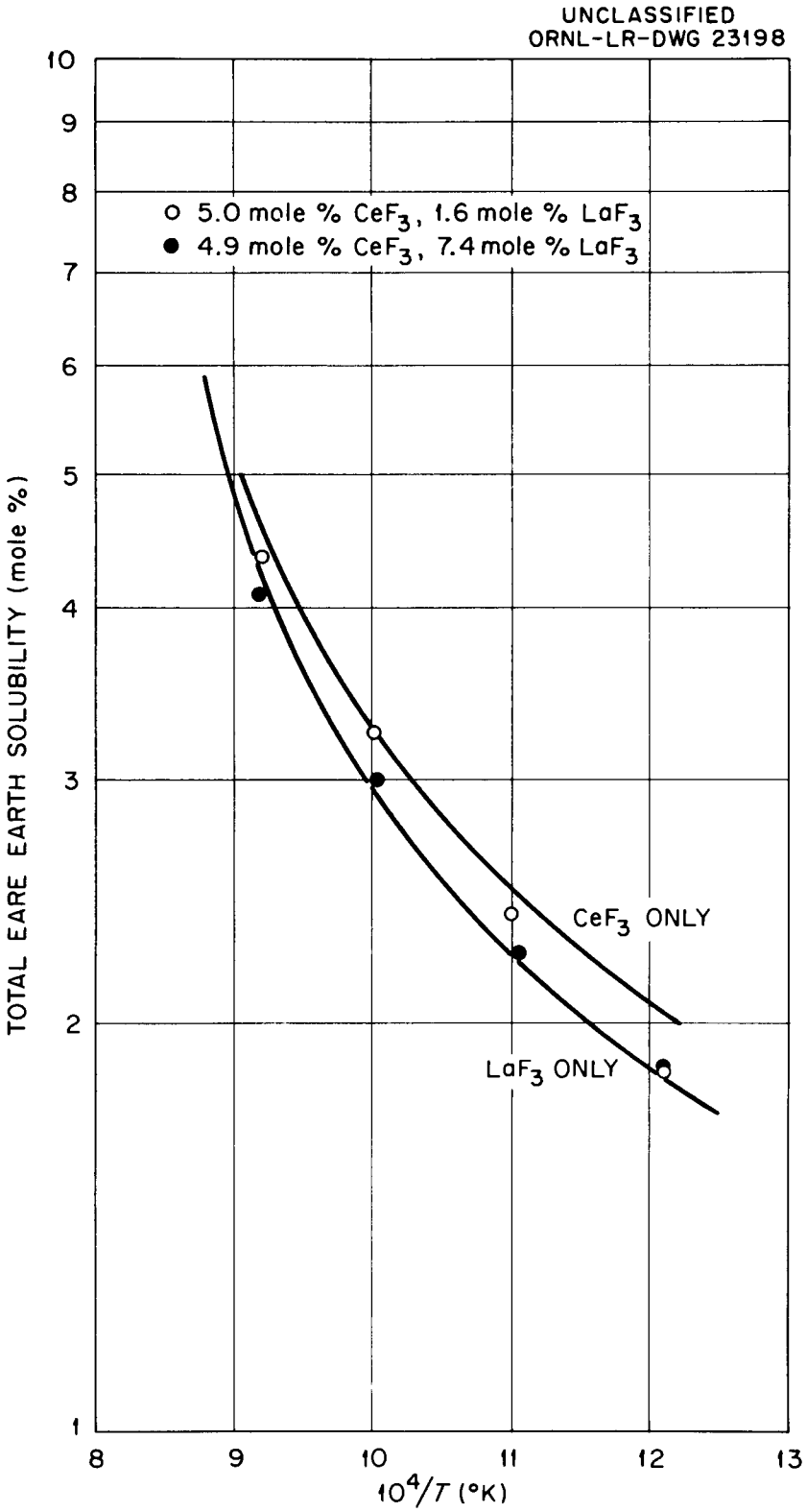

Fig. 11. Additive Solubilities of CeF_3 and LaF_3 in $NaF-ZrF_4-UF_4$ (50-46-4 mole %).

the sums of the LaF_3 and CeF_3 solubilities from Table XII. It will be seen that the combined solubilities as generally intermediate between those for the CeF_3 and LaF_3 and more nearly approximate the value of the predominant solute-constituent.

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

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

(s) = solid

(d) = dissolved

(ss)= solid solution

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

$$(1)\quad K_a = \frac{a_{LaF_3}(ss)\ a_{CeF_3}(d)}{a_{CeF_3}(ss)\ a_{LaF_3}(d)} = K_\gamma \frac{N_{LaF_3}(ss)\ N_{CeF_3}(d)}{N_{CeF_3}(ss)\ N_{LaF_3}(d)} = K_\gamma K_N$$

If K_γ is constant, K_N is constant, since:

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

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

$$(3)\quad N_{LaF_3}(d) = S^o_{LaF_3} N_{LaF_3}(ss) \quad \text{and}$$

$$(4)\quad N_{CeF_3}(d) = S^o_{CeF_3} N_{CeF_3}(ss)$$

where $S^o_{CeF_3}$ 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.

Table XIX

Solubility Relations in the System CeF_3-LaF_3-Solvent

Expressed in Mole Fraction

Temp. (°C)	Solid Composition LaF_3	Solid Composition CeF_3	Exp. Liquid Composition LaF_3	Exp. Liquid Composition CeF_3	Calc. Liquid Composition $S^{o}_{LaF_3} N_{LaF_3}$ (ss)	Calc. Liquid Composition $S^{o}_{CeF_3} N_{CeF_3}$ (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

Substituting (3) and (4) into (1) the following result is obtained:

$$(5) \quad K_N = \frac{S^{o}_{CeF_3}}{S^{o}_{LaF_3}}$$

The experimental values are compared with this result in Table XX. Table XXI 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 from equation (5) considering the fact that the assumption of solid solution for these compounds may be subject to some question in view of their different crystal structures.

Table XX

Solid-Solvent Extraction Coefficients* for LaF_3-CeF_3 in NaF-ZrF_4-UF_4 (50-46-4 mole %)

Temperature (°C)	$(S^o_{CeF_3}/S^o_{LaF_3})$	Experimental K_N^*	
		6.1 % CeF_3 1.9 % LaF_3	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

* $K_N = \frac{N_{LaF_3}(ss)N_{CeF_3}(d)}{N_{CeF_3}(ss)N_{LaF_3}(d)}$

Table XXI

Solid-Solvent Extraction Coefficients* for SmF_3-CeF_3 in NaF-ZrF_4-UF_4 (50-46-4 mole %)

Temperature (°C)	$(S^o_{SmF_3}/S^o_{CeF_3})$	Experimental K_N^*	
		5.3 % SmF_3 4.1 % CeF_3	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

* $K_N = \frac{N_{CeF_3}(ss)N_{SmF_3}(d)}{N_{SmF_3}(ss)N_{CeF_3}(d)}$

Summary

Based upon solubilities of some fission product fluorides in a potential molten salt fuel, it can be seen that insofar as this fuel is concerned, precipitation offers little threat to reactor operation. The solubilities of the three rare earths studied, when considered along with their ionic radii, allow reasonable estimates of the solubility of other rare-earth fluorides to be made. In addition, 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.