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OCT 5 1964

Oral Presentation - 15th CITCE Meeting, London, England
September 21, 1964

DIRECT SPECTROPHOTOMETRIC STUDIES OF REDOX REACTIONS IN
MOLTEN FLUORIDE SALTS: ELECTROCHEMICAL IMPLICATIONS*

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MASTER

I will first show a few slides to introduce you to the experimental techniques developed for handling corrosive molten fluoride salts for spectrophotometric study.

FIRST SLIDE

This is a cut-away drawing of the original high-temperature cell assembly. Of importance is simply to note that the sample, confined in a windowless container, is placed in the center of the heated portion of the furnace and light from a Cary recording spectrophotometer, model 14, passes through the furnace by means of the light beam ports.

NEXT SLIDE

This is a photograph of the presently used furnace. It is an all nickel apparatus, so that the sample containing compartment is relatively free from possible hydrolytic contaminants. A sample is placed in the compartmented lid in a dry box and then can be transferred to the cell assembly for subsequent melting without exposure to the atmosphere. By means of vacuum and helium gas the atmosphere inside the cell assembly is exchanged with helium and the sample lowered into the heater portion of the assembly, prior to melting, by means of the quartz rod shown.

* Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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NEXT SLIDE

We have developed several types of windowless sample holders, this is one of them (called a captive liquid cell). Liquid is maintained in the plane of the smaller holes in the cell and light passes through the lower, larger, holes for spectral study. The cell is attached to a holder which is cemented to a quartz rod. As explained in the last slide, the sample holder then can be manipulated from outside the cell assembly. In all experiments reported today the sample container was made from Cu except where noted.

If anyone desires more information as to the apparatus and techniques, please contact me after the meeting and I will be glad to discuss the various aspects with you. Since the data acquired from these techniques will be of interest to more people, however, I will proceed to a discussion of results.

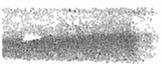
NEXT SLIDE

Shown here are the solvents which we have used in our various spectrophotometric studies along with the composition of the mixtures where applicable and also the melting points. Although not listed on the slide, we have performed some studies in other solvents such as Li-KCl, pure LiCl and other materials which are liquid at temperatures above 100°C. My remarks today will be limited essentially to a discussion of results which were obtained by the use of the first three solvents. The alkali fluoride eutectic is a useful solvent for fundamental research. The next solvent listed will be the coolant salt for the soon to be completed Molten Salt Reactor Experiment which will be operated at Oak Ridge National Laboratory. The third salt listed is the fuel solvent for the same reactor. In the reactor this solvent will

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present or future



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identified as the result of the reaction of Zr metal, the melt remained colorless. From this, it is inferred that Zr is oxidized directly to Zr(IV). This conclusion is in line with the electrochemical findings of D. L. Manning for the polarographic study of Zr in fluoride melts.

NEXT SLIDE

Considering the spectrophotometric observation of the reaction of U and UF_3 with LiF-NaF-KF these reactions can be written. It has not been possible to determine, spectrophotometrically, which of the reactions IIA or IIB occur; possibly both occur. The overall effect of these reactions, however, is that lower valent uranium will be oxidized to U(IV) in this solvent under the experimental conditions of this study. A reaction of small amounts of HF in the sample with U^0 should also have been shown.

NEXT SLIDE

Since it is known that alkali metals are generated by the reaction of active metals with LiF-NaF-KF and since alkali metals are believed to form colored solutions with their respective molten halides, it was of interest to prepare these solutions and obtain their spectra. Since spectrophotometric studies of molten fluoride salts are done in windowless containers, Na or K cannot be added directly to the solution as they would immediately distill out of the melt. It was found that a solution believed to be K and/or Na in LiF-NaF-KF could be prepared, however, by the reaction of an excess amount of Mg or Y with the eutectic. The resultant blue solution exhibits one broad absorption peak as shown here, with a maximum at 615 m μ . The resonance absorption spectra of the alkali metals are seen in the gas phase surrounding the solution. Since Li is not as volatile as the other alkali metals, solutions of Li in the eutectic could be made by direct additions of this metal to the melt. However, as indicated by free energy considerations, Li is



progressing, but this will give you an idea of the reactions that can occur. Uranium has been observed to reduce U(IV) to U(III); beryllium metal has been observed to reduce U(IV) to U(III) and in other experiments in which the surface of a piece of beryllium metal, in contact with melts which contain U and Zr, has been analyzed by x-ray diffraction zirconium metal and uranium metal (as an alloy with Zr) has been found. In experiments designed to produce Zr(III) in such melts by the reaction Zr^0 with Zr(IV), no colored dissolved species has been observed. From this evidence it is concluded that Zr^0 will not react with the solvent and also that a rather obvious way to prepare solutions of Zr(III) is of no value.

The blotted out portion of this slide purported to show that U^0 does not react with solvent. This has not been verified in practice. Since the thermodynamic values for the various products and reactants involved are still open to question, a case could be made for the reaction of uranium with either Zr or Be ions to form U(III). It is also quite possible that U^0 is simply reacting with impurity metal ions in solution, Fe, Ni, Cr, to form U(III). Experimentally it has been shown that U(III) grows into such melts slowly. Work is presently under way to determine the reaction mechanism. I have talked for some time without mentioning the normal spectrophotometric terms such as wavelength, molar absorptivity, etc. I assume that the audience is not here to hear about spectra per se. In this case I should mention, tho, that the U(III) spectrum in the near UV portion is extremely sensitive because of a high molar absorptivity (ca. 500). Putting it another way, one could easily see U(III) concentrations down to some 200 ppm and less. Thus on a molar basis or mole fraction basis in these melts a small amount of U(III) can be readily seen.

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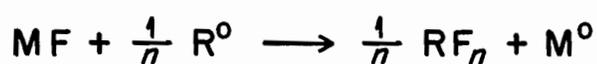
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was carried out with considerable cooperation of G. P. Smith of the Metals and Ceramics Division of Oak Ridge National Laboratory. The spectrum has been interpreted to have probable octahedral symmetry in the alkali fluoride melt. Ni(II) has been studied in many melts, but I believe this is the first case observed for this ion to have peaks of proper position and intensity for simple octahedral symmetry.

LAST SLIDE

The interpretation of this spectrum of FeF_2 in the same alkali fluoride melt is much less precise. The most logical case to be made for this spectrum is that Fe(II) exists mainly in O_h symmetry (causing large peak at 10,000 wave numbers) with a small fraction of the ions in T_d symmetry (causing peak at Ca. 5400 wave numbers). More work of this kind will be carried out as time permits.

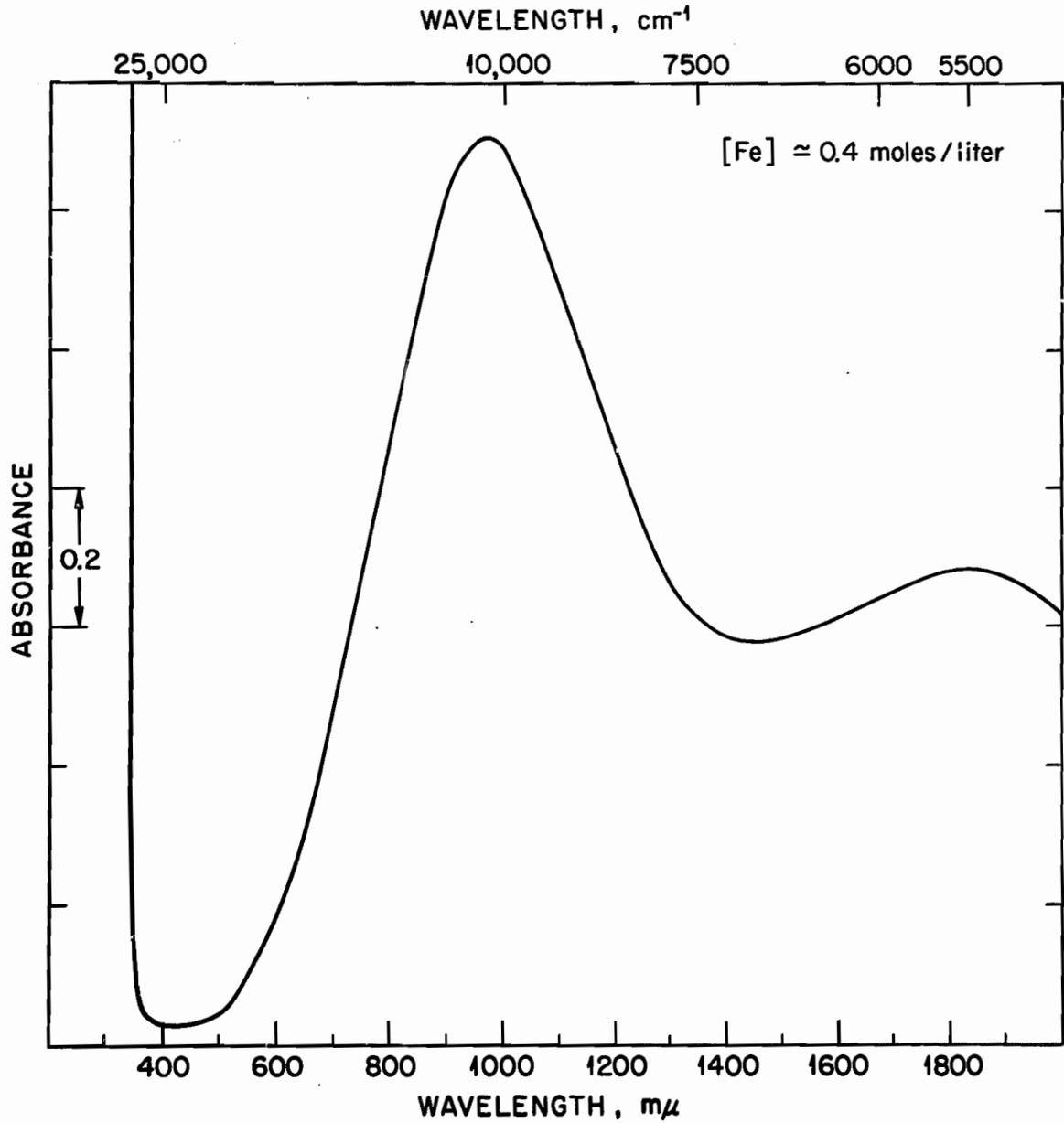
FORMATION OF ALKALI METALS BY REDUCTION OF
ALKALI HALIDES



Temperature 1000°K

| Solvent | R ⁰ | Resonance Absorption Lines Observed | ΔF Reaction/Equivalent Reduced | | |
|------------|--------------------|--|--------------------------------|----|----|
| | | | K | Na | Li |
| LiF-NaF-KF | Fe | None | 44 | 47 | 56 |
| | Cr | None | 38 | 41 | 50 |
| | U | K, Na | 16 | 19 | 28 |
| | (UF ₃) | K, Na | 20 | 23 | 32 |
| | Zr | K, Na | 17 | 20 | 29 |
| | Mg | K, Na | -3 | 0 | 9 |
| | Y | K, Na | -2 | 1 | 10 |
| | Li | K, Na | -12 | -9 | — |
| LiCl-KCl | U | None | 30 | 25 | 26 |
| | Mg | None | 25 | 20 | 21 |
| | Ca | K (Na impurity) | 5 | 0 | 1 |

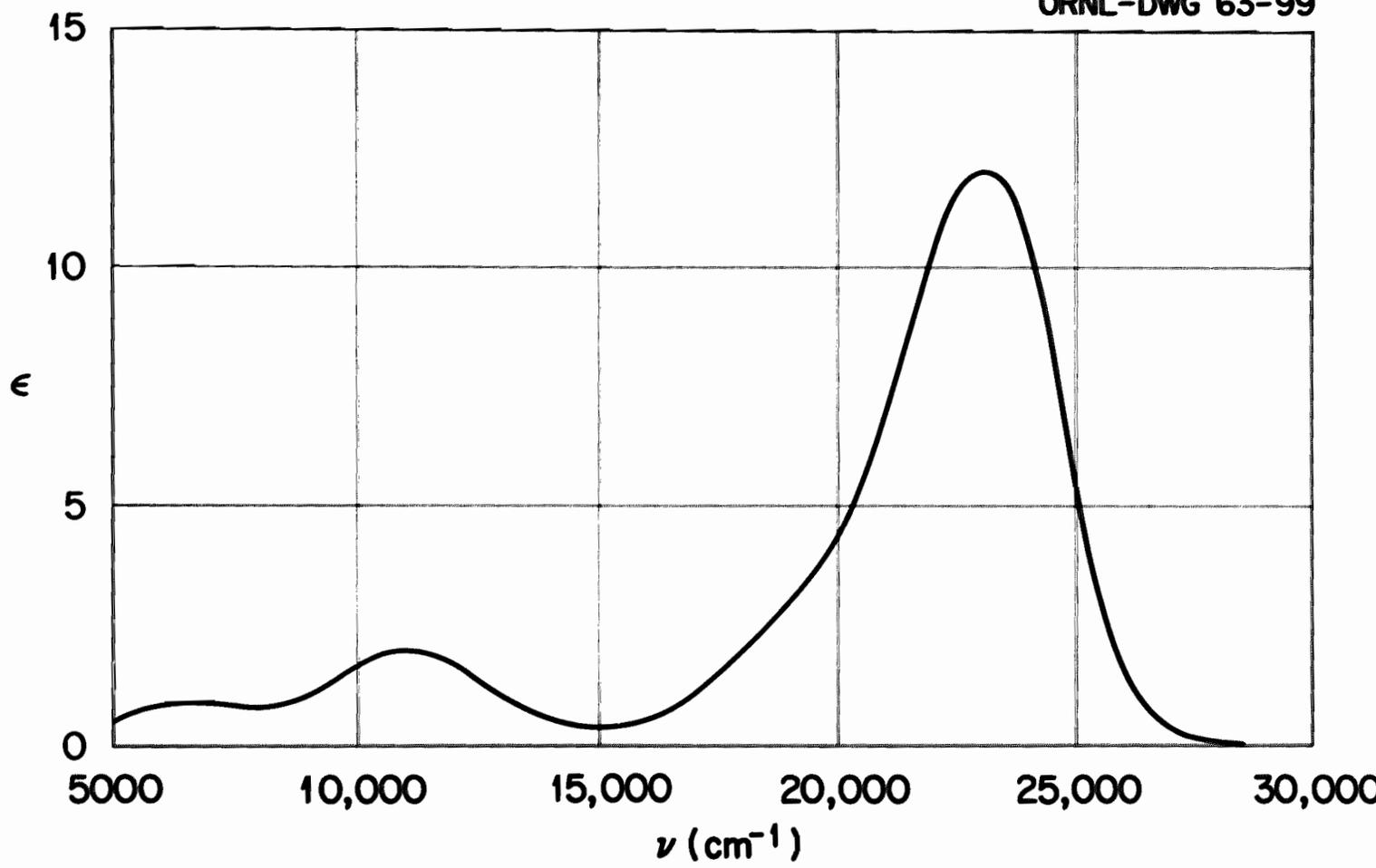
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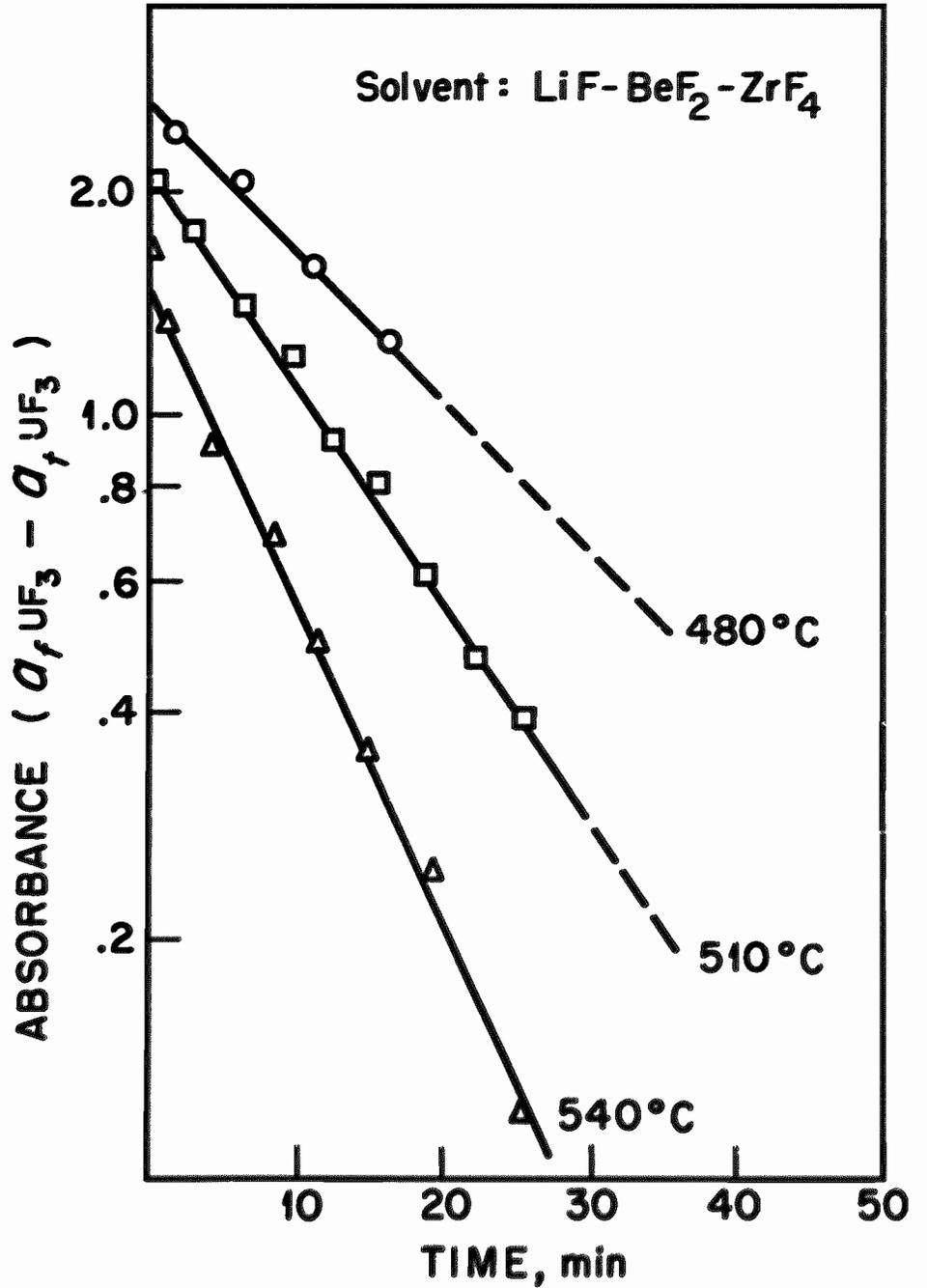
Spectrum of FeF₂ in Molten LiF-NaF-KF at 525°C.

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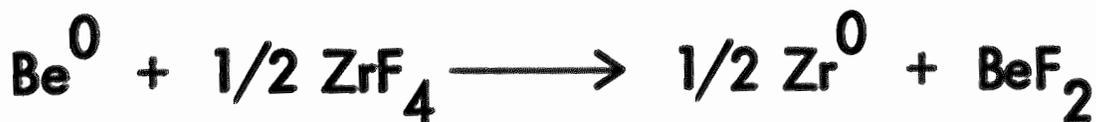
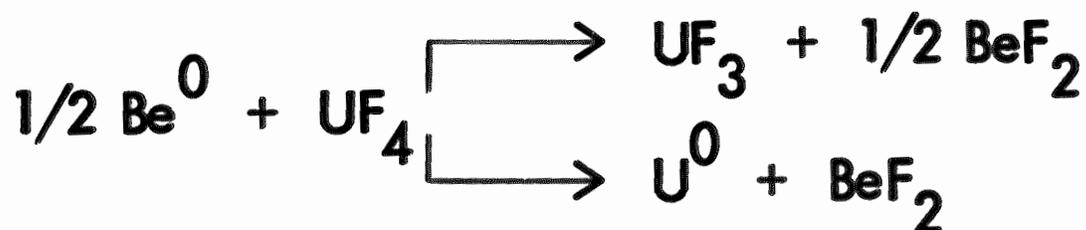
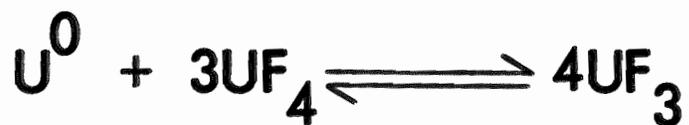


Spectrum of NiF_2 in LiF-NaF-KF at 500°C .

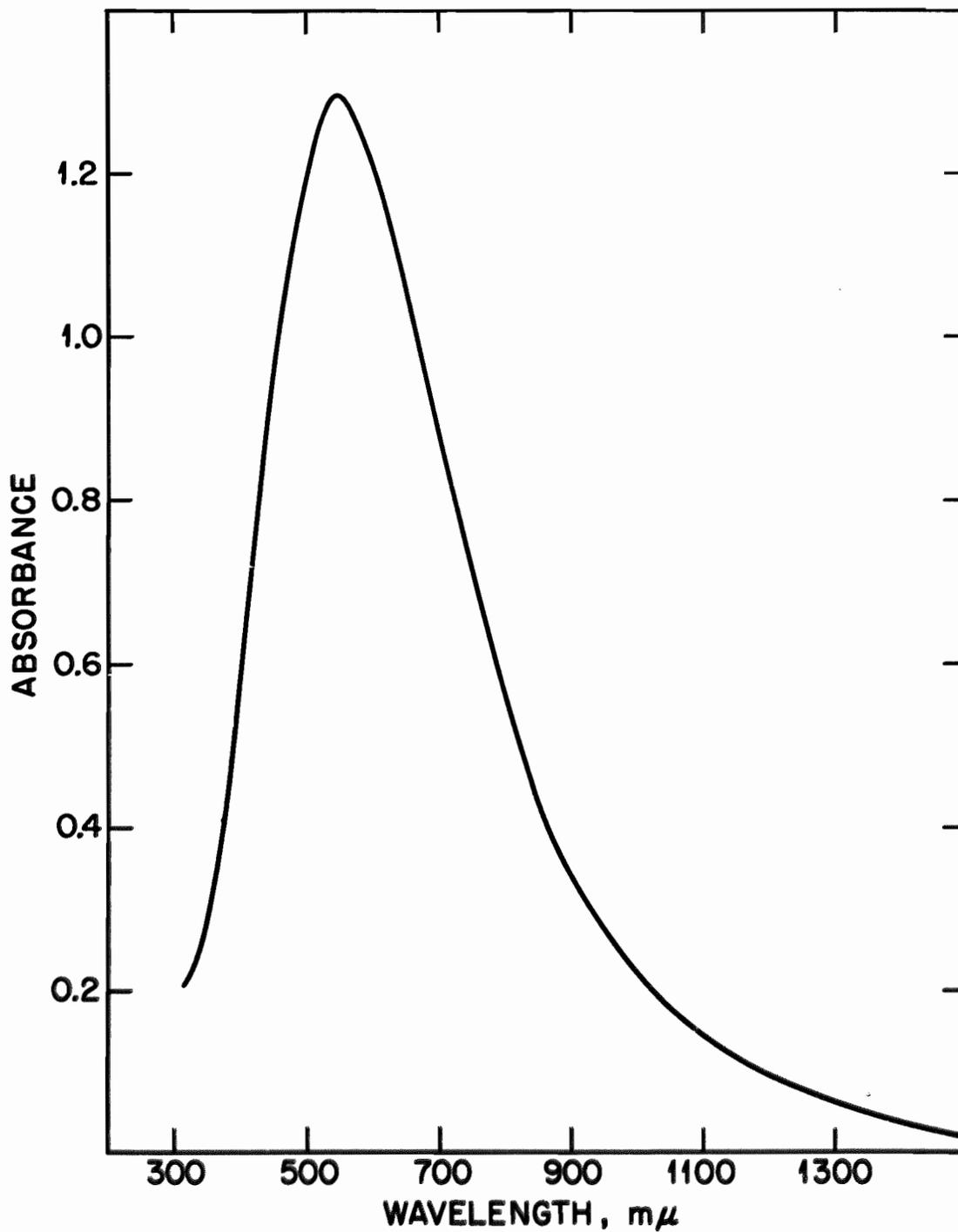


Loss of UF_4 by the Reaction
 $\text{UF}_4 + 1/4 \text{Zr}^0 \longrightarrow \text{UF}_3 + 1/4 \text{ZrF}_4.$

REACTIONS

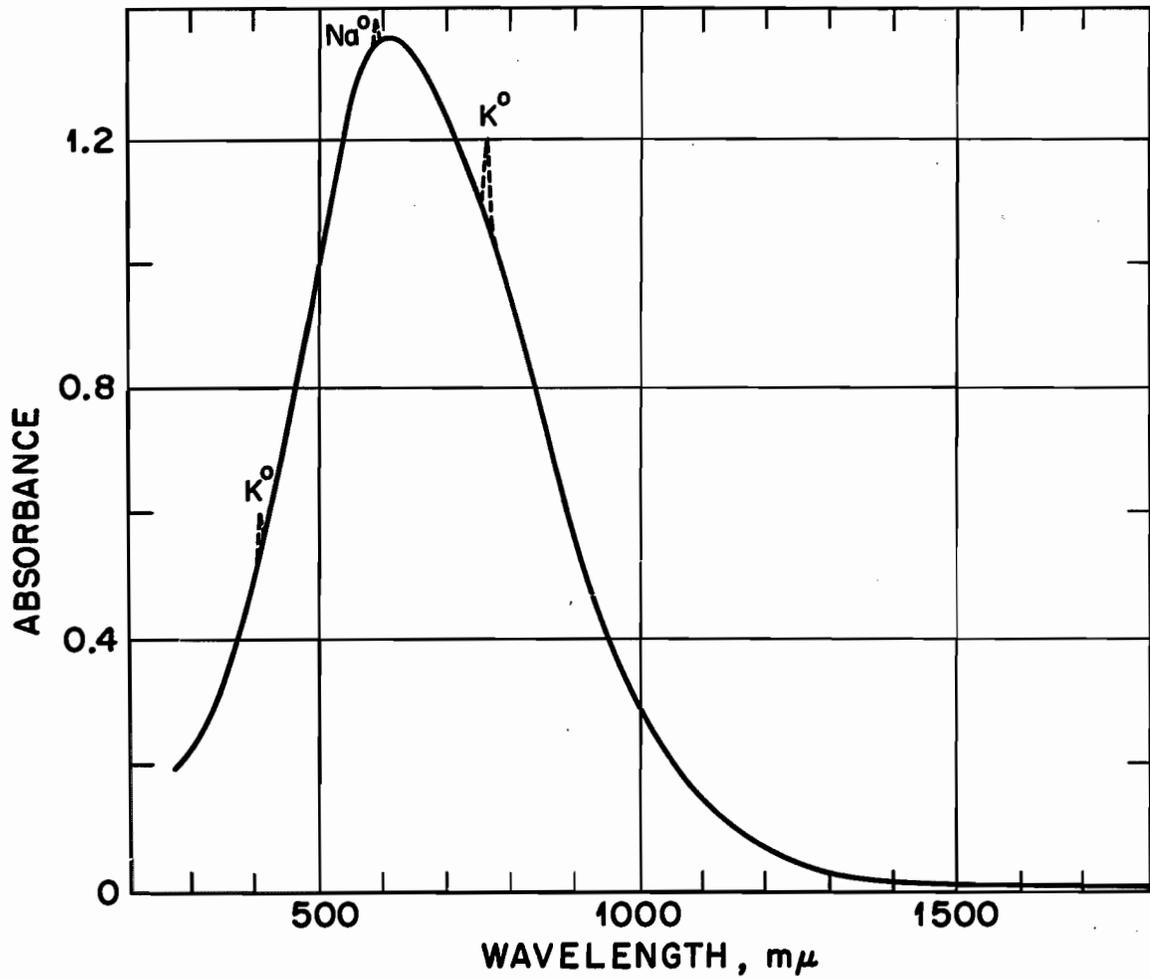


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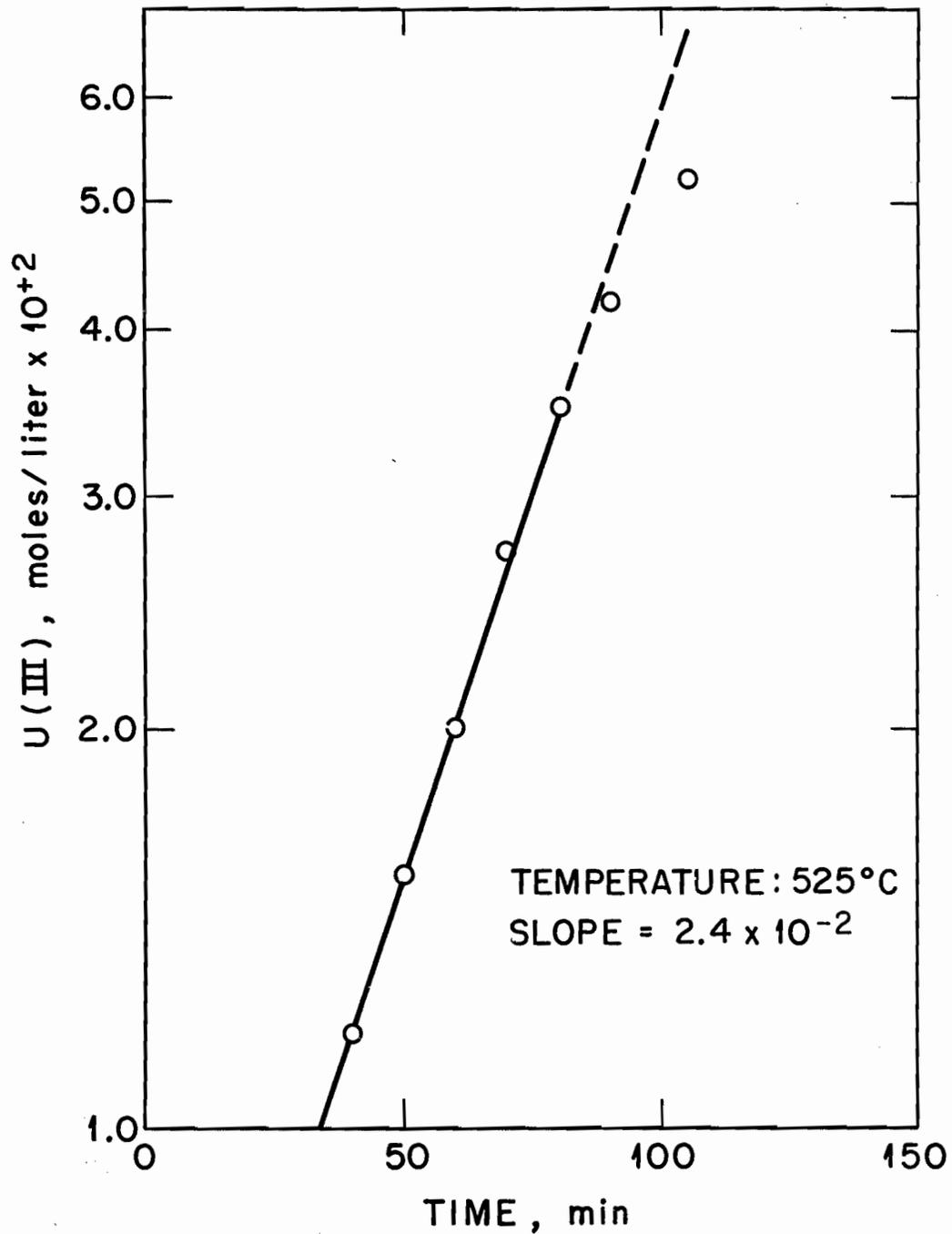
Spectrum of Li^0 in Molten LiCl at 650°C .

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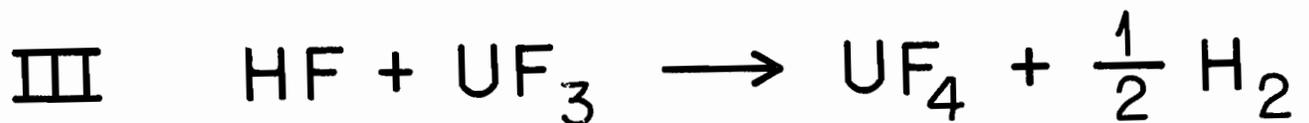
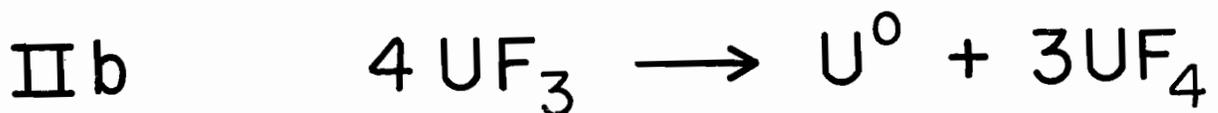
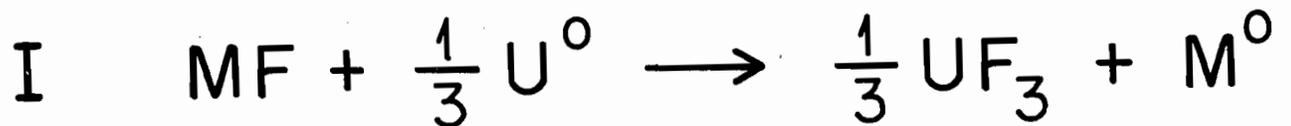
Tentative Spectrum of (Na, K?) in LiF-NaF-KF;
Mg + LiF-NaF-KF at 525°C.

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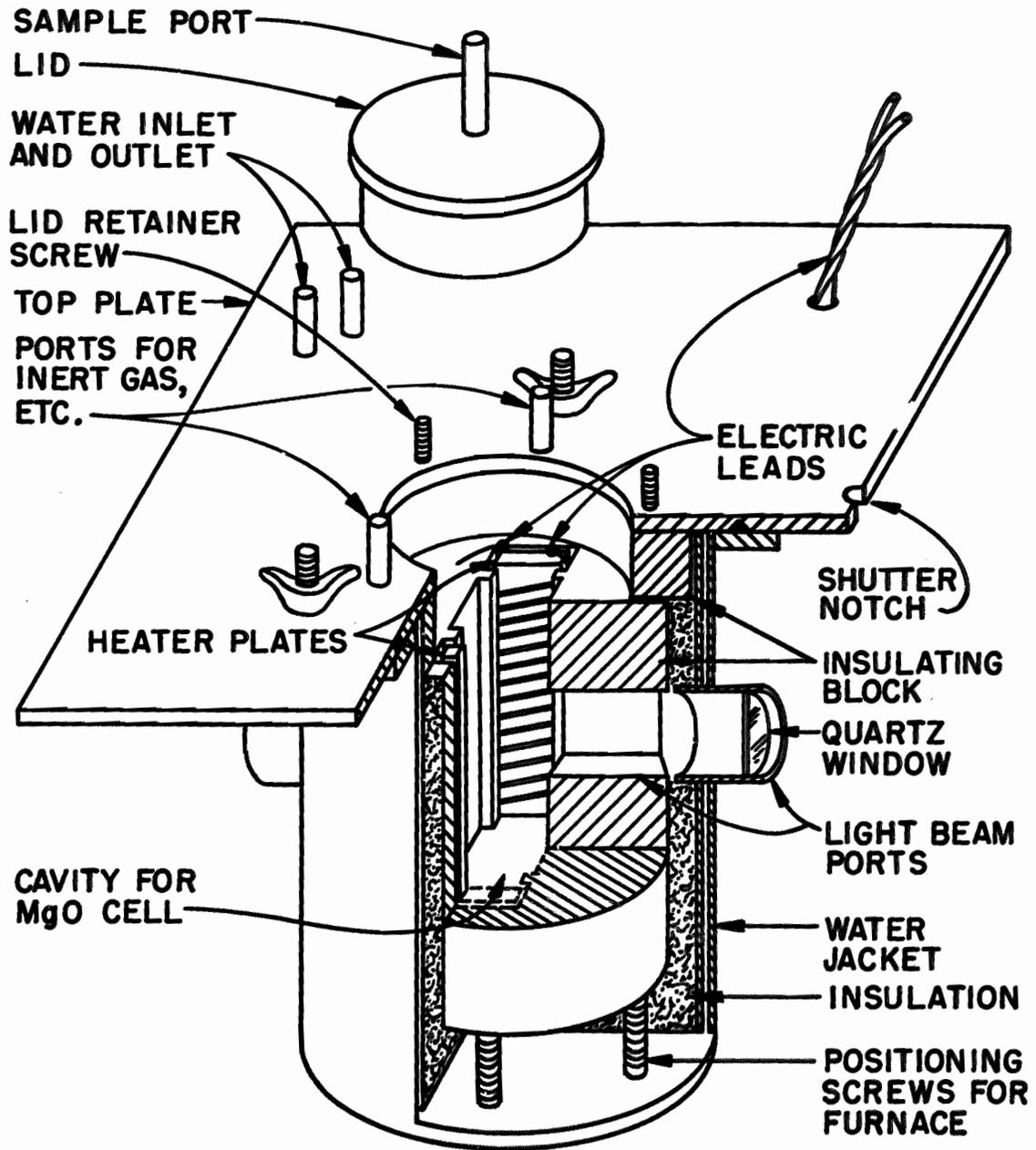


Growth of U(III) in LiF - NaF - KF by
the Reaction $\frac{1}{3} \text{U}^0 + \text{MF} \rightarrow \frac{1}{3} \text{UF}_3 + \text{M}^0$.

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High Temperature Cell Assembly.

MOLTEN FLUORIDE SOLVENTS

| | mole % | m.p. °C |
|--|---------------------------|------------|
| LiF – NaF – KF | 46.5 – 11.5 – 42.0 | 454 |
| LiF – BeF₂ | 67 – 33 | 454 |
| LiF – BeF₂ – ZrF₂ | 65 – 31 – 4 | 450 |
| NaF – ZrF₄ | 50 – 50 | 512 |
| LiF | | 844 |
| NaF | | 985 |
| KF | | 856 |
| RbF | | 760 |
| CsF | | 683 |



LID RETAINING CLAMPS

SHUTTER NOTCH

RETAINING RING

WINDOW

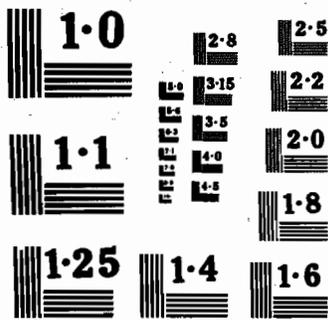
BOTTOM PLATE

COOLING WATER

INSULATING CHAMBER VACUUM



INCH



NATIONAL BUREAU OF STANDARDS
MICROCOPY RESOLUTION TEST CHART

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