

INFRARED OBSERVATION OF THE O-H BAND OF PURE ETHANOL AND ETHANOL SOLUTIONS TO THE CRITICAL TEMPERATURE¹

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The infrared absorption of pure ethanol and dilute solutions of ethanol dissolved in ethyl ether, ethyl vinyl ether, acetone, acetonitrile, pentane, carbon disulfide and carbon tetrachloride has been determined in the $3\ \mu$ region from room temperature to the critical temperatures of the liquids. In the active solvents there is a continuous, linear shift in frequency of the polymer band and no evidence of an equilibrium with free alcohol molecules. The slopes of the frequency *vs.* temperature lines vary from 0.89 for pure alcohol to 0.14 for diethyl ether solution. In the inert solvents, the polymer band behaves as in pure alcohol up to the temperature of its disappearance, but the dimer band seems to depend on the solvent for its frequency and temperature behavior. These observations are discussed in terms of the dimer-polymer models proposed by Pimentel, *et al.*, and the hydrogen bond theory of Finch and Lippincott.

Introduction

The subject of infrared observation of hydrogen bonding has been thoroughly reviewed recently.³ Briefly, the experimental facts which are the background for this study are as follows. In the vapor phase, the O-H vibration yields a sharp peak at about $3750\ \text{cm}^{-1}$; in liquid alcohol only the broad hydrogen bonded band occurs, centered at about $3350\ \text{cm}^{-1}$. The solvents for alcohol can be divided rather sharply into two distinct categories: hydrogen acceptors which form loose complexes and inert solvents. The spectroscopic distinction is that in the complexing solvents alcohols yield only a broad hydrogen bonded O-H absorption, the central frequency depending on the solvent, whereas the inert solvents yield two bands: the sharp unbonded O-H band, distinct and separate, and the broad complexed O-H band. The relative intensities and positions of these bands depend on the solvent, the concentration of alcohol and the temperature.

In this paper some experimental observations of the effect of extremely high temperatures on the O-H bands in both kinds of solvents will be presented. These results will be discussed in terms of the structures and strengths of the complexes between alcohol molecules themselves and alcohol with complexing solvents.

Experimental

The high temperature infrared cell used in this work is illustrated in Fig. 1. The details of its structure will be published elsewhere, but the main features, sapphire windows and Teflon O-ring seals can be seen in the figure. A brass spacer was machined to keep the windows approximately 0.2 mm. apart. The difference in thermal expansion of sapphire and brass operating over the whole length of the windows increases this separation about 15% from room temperature to 250° . The decrease in the density of a liquid under its own vapor pressure over this temperature range is somewhat greater and definitely non-linear. A precise correction of observed optical densities for these two temperature effects would require calibration of the window separation as a function of temperature and pressure, which has not been done. The fact that the two temperature effects are in the opposite direction makes the relative intensities at different temperatures reasonably consistent with each other. However, for experiments done with pure alcohol, with the windows nearly in contact, thermal expansion of a

few microns leads to complete opacity in the spectral region of interest. The results on pure alcohol were obtained in a cell made of "Platinite,"⁴ an iron-nickel alloy with a coefficient of thermal expansion close to that of sapphire. Nevertheless, the recorded infrared absorption is so sensitive to slight variations in light path that no conclusions can be drawn regarding relative intensities at different temperatures. Reliable infrared spectra, where the absorption never exceeds 75 or 80%, are obtained up to the critical point of the alcohol using this cell.

The alcohol and the active solvents were dried over Linde Molecular Sieves. Inert solvents were used as delivered by the manufacturer.⁵ Some separate experiments with added water showed that these results are not altered, hence no special precautions were observed in protecting solutions from the atmosphere or drying inert solvents.

The spectrometer, Perkin-Elmer Model 112 with LiF prism, was modified by the addition of an externally focusing source to reduce the light loss on the walls of the high temperature cell. The entire optical path was enclosed. By sweeping with tank nitrogen, it was possible to reduce the most intense water vapor lines in the $3\ \mu$ region to less than 2% absorption, which was quite essential to some of the results reported.

Background curves were run with the pure solvent in the cell. For the solvents acetonitrile, diethyl ether and acetone, it was necessary to extend the background readings over the entire temperature range, since the overtone and combination bands present in the $3\ \mu$ region are sensitive in frequency and intensity to temperature variation. In all cases, the background was subtracted point by point using a plexiglass triangle of variable height developed by M. Jean-Jacques Martin at the University of Bordeaux for converting per cent. transmission to optical density.

The frequencies reported here are frequencies of the maximum of optical density. Finch and Lippincott⁶ (hereafter referred to as F-L) report frequencies determined by a "center of gravity" method, designed to correct for the dissymmetry of the band. They point out that their method and the method used here give essentially the same results. The prism was calibrated by standard procedures.⁷ Considering the broadness of the bonded O-H band and the personal judgment involved in determining the maxima, these frequencies should be considered significant to $\pm 5\ \text{cm}^{-1}$. These estimates are based on the reproducibility of a frequency reading on several independent determinations.

The concentrations of all solutions were 2% alcohol by volume with the exception of the CS_2 and pentane solutions, which were 4%. This range was chosen for spectroscopic convenience, to yield both free and bound O-H in inert solvents, and, at the same time, to avoid a high percentage of self-associated alcohol in the active solvents. In pentane, concentrations of 1, 2 and 4% yielded the same frequencies; only the relative intensities were affected.

(4) Société Metallurgique d'Imphy, 84 Rue de Lille, Paris (7°).

(5) Grade R. P. chemicals, manufactured by Prolabo, 12 Rue Pelee, Paris XI°.

(6) J. N. Finch and E. R. Lippincott, *J. Phys. Chem.*, **61**, 894 (1957).

(7) A. R. Downie, M. C. Magoon, T. Purcell and B. Crawford, *J. Opt. Soc. Am.*, **43**, 941 (1953).

(1) This research was supported in part by Contract No. AF 49(638)-3 with the Air Force Office of Scientific Research.

(2) This research was carried out while the author was "Professeur Associé" at the University of Bordeaux, France.

(3) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Cal., 1960.

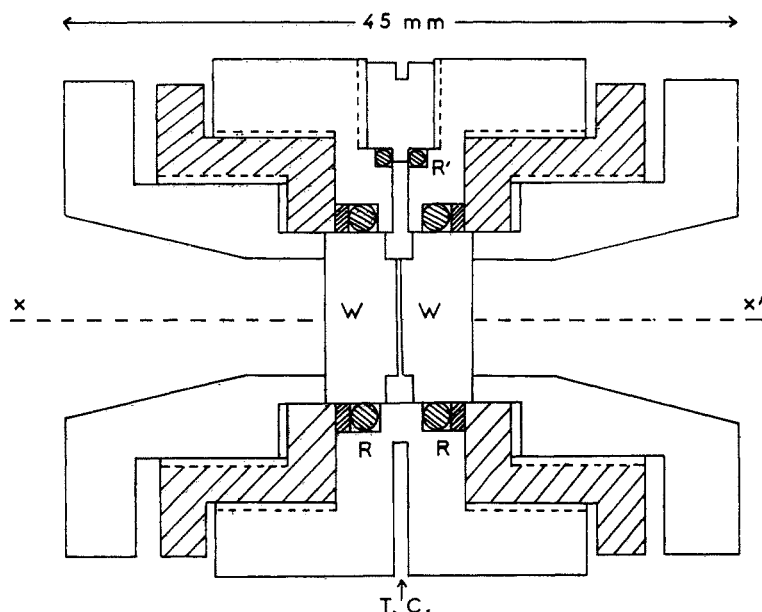


Fig. 1.—High temperature infrared cell: $x-x'$, light path; W, sapphire windows; R, R', Teflon O-rings.

Observations

Figure 2 shows the contours of the infrared absorption of pure liquid ethanol from room temperature to its critical point. Note the drastic change in frequency with little change in shape. There is certainly a considerable diminution of integrated intensity with increasing temperature,⁸ but little change in half width. As already discussed, changes in path length and liquid density make these curves non-comparable as to integrated intensity.

Figure 3 contains an analogous set of curves drawn for 2% ethanol dissolved in acetonitrile, where the relative integrated intensities have some significance. The band widths at half-maximum absorption are nearly equal at all temperatures, a result noted in all the solvents and previously reported by Becker.⁸

The experimental curves are quite identical in acetone, diethyl ether and ethyl vinyl ether; only the frequencies differ.

Significantly, in the active solvents, at no temperature is there an appearance of an unbonded O-H band indicating an equilibrium between different types of alcohol molecules as is observed in inert solvents. The free O-H band could not have been obscured by atmospheric water vapor which was nearly completely eliminated. Liddel and Becker,⁹ in careful measurements of the peak height of the unbonded O-H of methanol in CCl_4 as a function of temperature, report a 50% decrease in peak intensity in going from -10 to 50° . Thus it is possible that we fail to see the free O-H band, not because there is no free O-H present, but due to a decrease in its intensity resulting from some other mechanism.

Ethyl vinyl ether, the weakest hydrogen acceptor solvent used, is an interesting bridging case between the active and inactive solvents. At 150° the frequency of the O-H vibration has

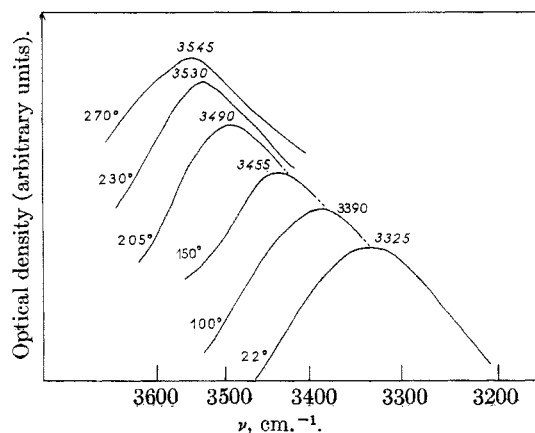


Fig. 2.—Infrared absorption contours of pure ethanol from room temperature to the critical temperature.

reached a value as high as the frequency of the free O-H in some inert solvents. In a sense we have continuously gone over from bound to free O-H.

The experiments in the inert solvents first were run in order to see if the infrared absorption due to the free O-H vibration simply disappeared at a high enough temperature. Figure 4 shows the result for 2% ethanol in pentane. This result is not in contradiction with Liddel and Becker. The apparent growth of intensity of the free O-H with increasing temperature is related to a displacement of the association equilibrium toward free molecules, but at least it shows that 2% free alcohol at 250° in our cell yields a distinct free O-H band. Thus the absence of this band in active solvents proves that a large fraction of the alcohol molecules remain associated with the solvent, even at the highest temperatures here employed.

Figure 5 shows the peak frequencies of the associated O-H bands as a function of temperature for the various solvents used. All the points are fit very well by straight lines. The slope of the individual lines does not seem to be related to

(8) E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1960).

(9) U. Liddel and E. D. Becker, *ibid.*, **10**, 70 (1957).

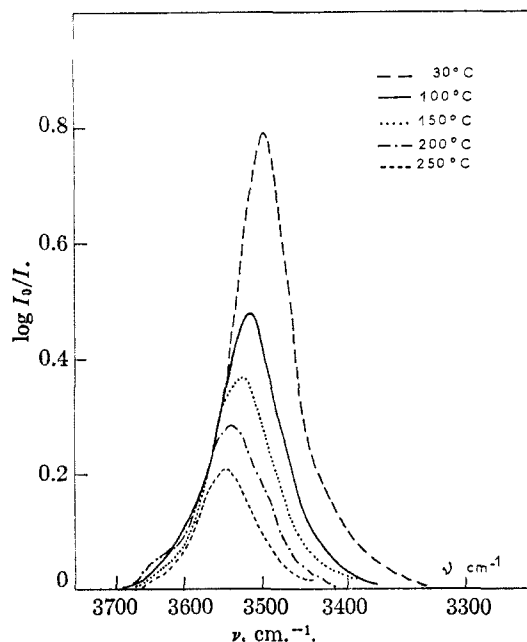


Fig. 3.—Infrared absorption bands of 2% ethanol in acetonitrile.

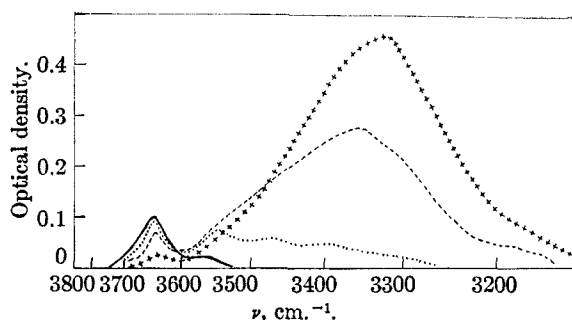


Fig. 4.—Infrared absorption bands of 2% ethanol in pentane: ++++, 25°; ----, 55°;, 100°; —, 250°.

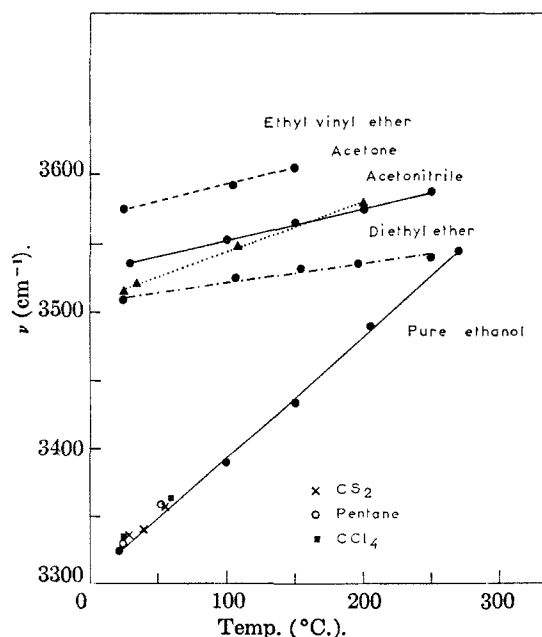


Fig. 5.—Frequencies of the polymer band of ethanol in various solvents as a function of temperature.

$\Delta\nu$, the shift in frequency from its gas phase value, nor does it depend on the thermal expansion coefficient of the solvent. The line representing pure alcohol is characterized both by its large slope and large $\Delta\nu$ at room temperature.

At the lower end of the pure alcohol line are plotted some points representing the frequency of the associated O-H band observed in inert solvents up to the temperature where the displacement of the equilibrium toward free alcohol resulted in the disappearance of this band. These points, representing alcohol in inert solvents associated with itself, fall on the pure alcohol line. They are independent of the particular inert solvent, both in frequency and in slope. This type of hydrogen bonded O-H does not "see" the solvent around it and behaves precisely as it would in pure alcohol to the extent of being independent of the refractive index of the medium. The free O-H band, whose frequency shift with temperature is very small ($d\nu/dt$ is approximately $0.06 \text{ cm.}^{-1}/\text{deg.}$) exhibits a considerable change in frequency with solvent.

There is a third O-H band which appears clearly at slightly elevated temperatures near 3500 cm.^{-1} . It shifts toward high frequency with increasing temperature and then disappears as the temperature continues to rise. There has been much discussion as to the reason for this band, often attributed to alcohol dimers, and the form of the hydrogen bond giving rise to it. We present the frequencies of the dimer and free O-H bands, where they have been observed, in tabular form (Table I).

TABLE I

VIBRATIONAL FREQUENCIES OF THE FREE O-H BAND AND DIMER BAND OF DILUTE ETHANOL SOLUTIONS AT VARIOUS TEMPERATURES

	Temp., °C.	Free O-H frequency, cm.^{-1}	Dimer frequency, cm.^{-1}	Slope of dimer vs. T line, $\text{cm.}^{-1}/\text{deg.}^a$
Solvent pentane	25	3640	..	0.2
	81	3645	3542	
	100	3647	3545	
	150	3650	3555	
	200	3657	..	
Solvent CCl_4	25	3632	..	0.6
	59	3633	3500	
	85	3633	3510	
	105	3635	3520	
	145	3638	3543	
Solvent CS_2	28	3615	..	0.9
	85	3618	3500	
	110	3615	3522	

^a These slopes, determined graphically with few experimental points, are very rough estimates.

We note that the 3500 cm.^{-1} band, whose precise frequency is difficult to determine, does depend on the solvent and follows a temperature behavior analogous with the association bands in active solvents. The conclusion that this band represents an association of the alcohol with the inert solvents is unacceptable for chemical reasons; however, this could be a hydrogen bound O-H of a different type, say the cyclic dimer postulated

from observations of the alcohol spectrum in inert matrices.¹⁰ The sketch in Fig. 6 shows a version of the cyclic dimer and the linear polymer, the latter a less realistic version of Fig. 2-2, ref. 1. Note that the solvent could approach the H-bond in the linear polymer only from above or below the plane of the paper, but the H-bond in the cyclic dimer is fully exposed to solvent influence.

It is true that at first the frequency displacement of the dimer band may be only apparent, since the neighboring polymer band changes so drastically with temperature; however, after about 75° the polymer band has all but disappeared and the subsequent displacement must be attributed solely to the dimer band.

The slopes of the frequency of the polymer band *vs.* temperature for the various solvents are presented in Table II. Our value of 0.89 cm.⁻¹/deg. is in good agreement with the slope of 0.8 found for the polymer band of ethanol in CCl₄ observed by Liddel and Becker⁹ over the temperature range -10 to 50°, but it is in serious disagreement with F-L's value of 0.35, although we observe the same frequencies at room temperature. We have no explanation for this discrepancy. Becker's⁸ value of 0.60 cm.⁻¹/deg. for ethanol in acetone is also in disagreement with our 0.36 for this same quantity. In Fig. 5 note that the first two points near room temperature for acetone present a quite different slope. A complicating feature in studying the O-H band in acetone is the large absorption at about 3400 cm.⁻¹ for acetone itself, a highly temperature dependent band. It now seems desirable in determining the exact shapes of the ν *vs.* *T* graphs for the same observer to cover the entire temperature range from the freezing point to the critical temperature.

TABLE II

SLOPES OF THE FREQUENCY *vs.* TEMPERATURE LINES FOR THE POLYMER O-H BAND OF ETHANOL IN VARIOUS SOLVENTS. (SEE FIG. 5)

Solvent	$d\nu/dT$, cm. ⁻¹ /deg.
Pure ethanol	0.89
Acetone	.36
Ethyl vinyl ether	.24
Acetonitrile	.24
Diethyl ether	.14

F-L present two arguments for believing that the change in frequency is due to the elongation of the O—O distance rather than various polymer equilibria. One is the independence of the polymer frequency of alcohol to concentration in CCl₄ over a ten-fold range of concentrations. The other is that they can account for their observed range of $d\nu/dT$ values with their theory of hydrogen bonding¹¹ by allowing the O—H—O unit to absorb energy as a semi-classical harmonic oscillator as the temperature is raised and then calculating the O—H frequency as a function of the increasing O—H—O distance. Their calculated range of slopes, depending on the number of degrees of freedom permitted classical excitation, is 0.20

(10) M. van Thiel, E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, **27**, 95 (1957).

(11) E. R. Lippincott and R. Schroeder, *ibid.*, **23**, 1099 (1955).

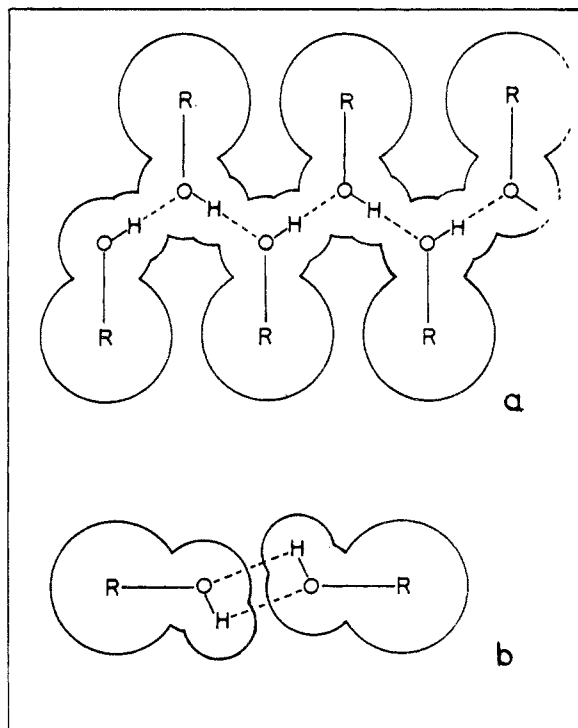


Fig. 6.—Sketch of associated alcohol molecules according to Pimentel, *et al.*: (a) linear polymer; (b) cyclic dimer.

to 0.64. The fact that their theoretical range nearly brackets our observations with such elevated temperatures tends to confirm their model. However, the variation in slopes reported here are most probably related to differences in acceptor properties rather than to differences in degree of vibrational excitation. Our range of solvents is limited by the fact that many of the strong acceptors polymerize at high temperature.

Conclusions

In this paper, the range of state variables over which hydrogen bonding is studied spectroscopically has been enlarged and the new observations have been interpreted by means of models recently proposed. There is still no quantitative theory that ties these models to spectroscopic observations unambiguously; it is hoped that their plausibility has been significantly enhanced by their consistency with these new observations. A major area for contention still remains in the interpretation of the over-all breadth of the bound O—H band. Is its breadth due to a series of *n*-mers or to a single polymeric species with a vibration band broadened by some mechanical or electronic interaction? The papers of Frisch and Vidale¹² and Reid¹³ in addition to F-L show that the broadening can be explained without recourse to *n*-mer equilibria. The author believes that if the equilibrium model were correct, then one would observe a series of stepwise changes in frequency over a large temperature increment, as in the case of the dimer-polymer equilibrium in inert solvents, instead of the continuous linear change observed. Finally, it may

(12) H. L. Frisch and G. L. Vidale, *ibid.*, **25**, 982 (1956).

(13) C. Reid, *ibid.*, **30**, 182 (1959).

be hoped that in the future measurements of integrated intensities may be made up to very high temperatures.

Acknowledgments.—The author is deeply indebted to Prof. M. L. Josien for her hospitality

and her contagious enthusiasm. He also would like to thank Pierre Saumagne and Jean Lascombe for the interest they have taken in this work. The French Atomic Energy Commission very kindly provided support for the cell construction.

FREEZING POINT DEPRESSIONS IN SODIUM FLUORIDE. EFFECT OF ALKALINE EARTH FLUORIDES¹

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Measurements were made of the freezing point depressions of NaF caused by the addition of up to 0.25 mole fraction alkaline earth fluorides. At a fixed concentration the smaller the alkaline earth cation radius, the greater were the deviations from ideal solution behavior. The excess partial molal free energies of solution of NaF, $(\bar{F} - F^0)_{\text{NaF}}$ evaluated from the measurements were all negative and approached zero asymptotically as the mole fraction of NaF approached unity. $(\bar{F} - F^0)_{\text{NaF}}$ at fixed concentration was empirically related to $U + nI_2$ where U is the alkaline earth fluoride lattice energy, n is an arbitrary constant, and I_2 is the second ionization potential of the alkaline earth.

Introduction

Understanding the effects of structural parameters, such as radius, charge and polarizability, on thermodynamic properties in fused salt solutions is a large general problem. One approach to solving this problem is to investigate a thermodynamic property of a solvent in which the type and concentration of solutes can be systematically altered, and then relate variations in this property to structural parameters of the pure solutes. The object of this particular investigation was to measure the depressions of freezing point of the solvent, NaF, and correlate the derived thermodynamic information with the structure of the solutes, the alkaline earth fluorides.

The choices of freezing point depression as the measurement and NaF as the solvent were made after reviewing collections^{3,4} of solid-liquid phase diagrams of fluorides. Where NaF was a component, the high NaF end of the diagram indicated the absence of solid solutions. In other words, pure crystalline NaF was the primary phase on cooling from the liquid state. Furthermore, the activity of NaF could be accurately evaluated from freezing point data because the heat of fusion and heat capacities of NaF are known.⁵

Some information on the desired freezing points is available from the NaF-BeF₂,⁶ -MgF₂,^{7,9} -CaF₂,⁸

-BaF₂⁹ phase diagrams. But these data are not sufficiently precise and consistent to show the relationship between solute structural parameters and the freezing point depression of NaF.

Experimental

Chemicals.—NaF (Mallinckrodt A. R.) was purified by recrystallizing from slowly cooled melts and selecting only clear crystal fragments from the cooled ingot. These melts were contained in graphite or nickel crucibles and were protected by a helium atmosphere. Analyses showed the only impurities exceeding 100 parts per million were Ca, 400 p.p.m.; Al, 300 p.p.m.; O, 300 p.p.m. Commercial CaF₂ (Mallinckrodt A. R.) and BaF₂ (Fisher "Certified") were oven dried at 150° to constant weight before use. Commercial MgF₂ (Baker and Adamson "Purified") and SrF₂ (Baker and Adamson Reagent Grade) were purified in graphite crucibles by first treating with NH₃HF₂ at 250° and then heating to 600° while flushing with a helium stream. Analyses for impurities in MgF₂ in weight per cent. were: Ca, 0.1; Fe, 0.2; Si 0.05; O, 0.11; for SrF₂; Ba, 1.0; Ca, 0.2; K, 0.01; Li, 0.005; Na, 0.02; O, 0.28. BeF₂ (Brush Beryllium) was purified by hydrofluorination at 500°. Impurities in weight per cent. were: O, 0.38; Mg, 0.01; Fe, 0.005; S, 0.058.

Apparatus and Procedures.—The cryoscopic vessel, welded from nickel, provided a cylindrical melt reservoir 6.35 cm. high and 4.8 cm. in diameter, and contained a thermocouple well of 0.64 cm. diameter tubing extending to within 0.64 cm. of the bottom. A vertical tube, 1.3 cm. in diameter and 20.3 cm. high, welded to the top plate of the reservoir, had a side arm through which the vessel could be evacuated. Stirring was accomplished by bubbling argon gas through the melt via a long 0.65 cm. diameter tube which passed through the 1.3-cm. vertical tube and was sealed to it by a gas tight Swagelok fitting. The bubbling rate was measured by merely observing the number of bounces per unit time made by the ball float of a sensitive flow meter (Fischer & Porter Flowrator Model 10A1735). The sample sizes (approximately 1.5 moles of NaF) and low vapor pressure ensured that changes in melt composition due to transpiration were negligible.

The vessel was immersed in a Hevi-Duty 5-cm. tube furnace to a depth of 20.3 cm., to prevent appreciable heat loss from the melt reservoir and thermocouple wires. Vessels, after being charged within a dry box, were evacuated for approximately one hr. while the temperature was raised to 700°. Argon then was passed through at the desired rate.

(1) Presented, in part, before the Division of Physical Chemistry, American Chemical Society, 138th National Meeting, New York, N. Y., Sept., 1960.

(2) Operated for the United States Atomic Energy Commission by the Union Carbide Corporation.

(3) E. M. Levin, H. F. McCurdie and F. P. Hall, *Phase Diagrams for Ceramists*, Part I (1956), Part II (1959), American Ceramic Society, Columbus, Ohio.

(4) R. E. Thoma (ed.), "Phase Diagrams of Nuclear Reactor Materials," ORNL-2548, Nov. 6, 1959.

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(8) P. P. Fedotieff and W. P. Iljinskii, *Z. anorg. u. allgem. Chem.*, **129**, 101 (1923).

(9) G. Grube, *Z. Elektrochem.*, **33**, 481 (1927).