ing relationships are apparent upon inspection of the table.

Vapor pressures of *m*-tolyl derivatives are higher than those of *p*-tolyl derivatives for all compounds examined here. This is also true for the *m*-cresol-*p*-cresol parent compounds, where the vapor pressure ratio is 1.025 at 100° C. However, this behavior continues to the boiling point for the derivatives, whereas with the cresols the meta-isomer has the higher boiling point at atmospheric pressure. The greatest vapor pressure difference occurs with the trifluoroacetates where a ratio of 1.080, *m-/p-*, exists at 100° C. The ratio at 100° C. for the pentafluoropropionates is 1.028, indicating that any isomeric effect diminishes when the presence of a larger ester group makes the aromatic portion a smaller fraction of the total molecule. Fluorination of the acetate causes both a marked increase in vapor pressure and an increase in the *m-/p-* ratio, the acetate ratio being 1.021.

The butyl esters show a similar vapor pressure increase upon fluorination. The vapor pressure of the *n*-butyl *tert*-butyl ether is slightly higher than that of the trimethylsilyl analog, which might be expected in view of the higher atomic weight of silicon.

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$CaCl_2$-Rich Region of the $CaCl_2$-CaF_2-CaO System

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Thermal analysis studies of the $CaCl_2$-CaF_2-CaO system show that it contains a ternary eutectic at 625° C. at the composition $CaCl_2$–17 mole % CaF_2–4 mole % CaO, plus ternary peritectics at $CaCl_2$–23 mole % CaF_2–10 mole % CaO and $CaCl_2$–23 mole % CaF_2–13 mole % CaO at 660° and 670° C., respectively. The $CaCl_2$-CaF_2 binary phase diagram determined in this work differs only slightly from those in the literature. However, the $CaCl_2$-CaO diagram was found to have a peritectic point at 18.5 mole % CaO and 835° C. which has not previously been reported. The corresponding incongruently melting compound is $CaO \cdot 2CaCl_2$.

DURING the development, in this laboratory, of nuclear reactor fuel reprocessing methods utilizing molten salts and metals as reaction media, it became necessary to know the liquidus surface of the $CaCl_2$ corner of the $CaCl_2$-CaF_2-CaO phase diagram. Information is available in the literature for each of the three binary systems (*1-5*), but none for the ternary system. Therefore, the portion of the $CaCl_2$-CaF_2-CaO phase diagram of interest was determined by thermal analysis techniques.

EXPERIMENTAL

Procedure. The salt mixture to be investigated was placed in a 1.5-inch diameter Type 304 stainless steel crucible, which was then put into a 2.5-inch tantalum crucible. The space between the two crucibles was filled with powdered zirconia for thermal insulation. These two crucibles were then lowered into a furnace well attached to the bottom of an inert atmosphere (He) glovebox. The salt mixture was heated 50° to 100° C. above the melting point and stirred with a tantalum agitator for at least 1 hour to ensure solution of all components. The salts did not noticeably attack the stainless steel crucible.

A Type 304 stainless steel–sheathed Chromel-Alumel thermocouple was placed in the salt and another was located outside the crucible containing the salt, and insulated from it. The temperatures of the two thermocouples were measured using a two-pen Bristol recorder when heating and cooling curves (both at a rate of about 4° to 5° C. per minute) were run. The heating rate was determined by the voltage applied to the furnace, and the cooling rate was the inherent cooling rate of the furnace after the power was turned off. The temperatures of thermal halts corresponding to the liquidus, eutectic, and other points were determined by comparing the heating and cooling curves of the thermocouple in the salt with that outside the crucible. The thermocouple and recorder used were calibrated as a system at the melting points of aluminum (660° C.) and NaCl (801° C.). The temperature correction (+5° C.) found for these two temperatures was assumed to apply over the whole range of temperature covered in this investigation.

Studies of the ternary system were always begun with a $CaCl_2$-CaF_2 mixture of the desired composition, then incremental additions of CaO were made. At or near the end of a series of CaO additions, samples of the molten salt were taken at a temperature above the liquidus using tantalum tubes with sintered tantalum filters. These were analyzed to determine whether the CaO concentration was in agreement with that calculated on the basis of the amount of CaO added to the original halide mixture.

Chemicals. Reagent grade anhydrous $CaCl_2$ was further dried by passing HCl gas through the solid and molten material for several hours, removing the HCl from the molten salt under vacuum, and filtering the salt into a fused silica ampoule which was later sealed. Calcium oxide was heated at 900° C. under a dry nitrogen stream, and then under vacuum to remove H_2O and CO_2. Calcium fluoride was dried at 800° C. under vacuum. All materials were transferred to and handled in the helium-filled glovebox where the thermal analysis experiments were performed.

Analytical. The CaO in the salt samples was determined by titrating its hydrolysis product, $Ca(OH)_2$, as a strong base. The powdered samples were placed in a known amount of dilute hydrochloric acid to neutralize the $Ca(OH)_2$, then the excess acid was back-titrated with NaOH using a phenolphthalein indicator.

RESULTS AND DISCUSSION

The compositions of the salt mixtures investigated and the thermal halts observed for each are given in Table I. Supercooling occurred in a large number of the cooling curves; therefore, it was necessary to rely on data from the heating curves in these cases. Where the heating and cooling curves were in agreement, the temperatures of the cooling curve arrests are reported. The temperatures in Table I are estimated to have an error of about ±5° C. and the accuracy of the salt compositions is approximately ±3% (relative).

Table I. Halts Observed in Thermal Analysis of the $CaCl_2$-CaF_2-CaO System

$CaCl_2$:CaF_2 Ratio	CaO Concn., Mole %	Temp. of Thermal Halts, ° C.[a] Liquids	2nd	3rd	4th
100:0	0	775			
	2	767	747		
	4	758	749		
	8	754	750		
	11.5	785	750		
	15	813	750		
	28	. . .	835	750	
	35	. . .	835		
95:5	0	745	645		
	2	735	650	625	
	5	725	712	625h	
	8	740h	719	625h	
	12	770	715	625h	
	16	794	699	625h	
	18.5	805	675	625h	
	22	. . .	810	660	625h
90:10	0	708	646		
	3	693	625h		
	6	680	625h		
	9	715	673	625h	
	12	747			
	15	760	660h	625h	
	16	764	630h	625h	
	18	950	774	660h	625h
	22	. . .	772	660h	625h
85:15	0	670	645		
	3	657	625		
	6	680h	645	625	
	9	710h	635h	625h	
	12	724	625h		
	14.5	742	660h	625h	
	15.7	900	746	670h	625h
	20	. . .	746	670h	625h
81:19	0	649	645		
	3	633			
	6	655h	640h	625h	
	9	695h	650h	625h	
	12	710h	655h	625h	
	14.5	720	660	625	
	17	. . .	725	665	625h
78:22	0	670h	647		
	3	665h	635h	625h	
	6	655h	635h	625h	
	9	665	638	625h	
	12	695h	650	625h	
	14	715h	670h	625h	
	18	. . .	715h	670h	625h
75:25	0	685h	647		
	3	680h	635h	625h	
	6	670h	640h	625h	
	9	665h	625h		
	12	675	665	625	
	14	840	685	670	
	18	. . .	685	665	625h
70:30	0	700	645		
	3	685h	640h	625h	
	6	680h	645h	625h	
	9	670h	625h		
	11	700h	670h	625h	
	15	. . .	700h	670h	
65:35	0	715	645		
	2	705	640h	625h	
	4	700	655h	625h	
	6	695	655	625	
	8	690	670	625h	
	10	690h	660h	625h	
	12	700h	655h	625h	
62.5:37.5	2	710h	635h	625h	
	4	705h	650h	625h	
	6	700h	660h	625h	
	8	710h	670h		
	10	715h	665h		
	12	720h	660h		
	12.5	850h	720h	660h	
60:40	0	730	645		
	2	715h	640h	625h	
	4	705	655h	625h	
	6	710	670h	625h	
	8	715h	670h	660h	
	10	725h	690h	670h	660h
52:48	0	780	735	645	
45:55	0	870	735		

[a] Temperatures obtained from heating curves only are indicated by letter h.

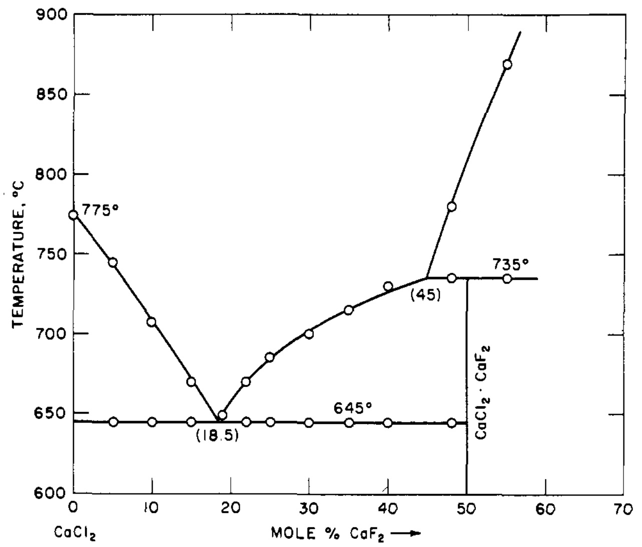

Figure 1. $CaCl_2$-CaF_2 phase diagram

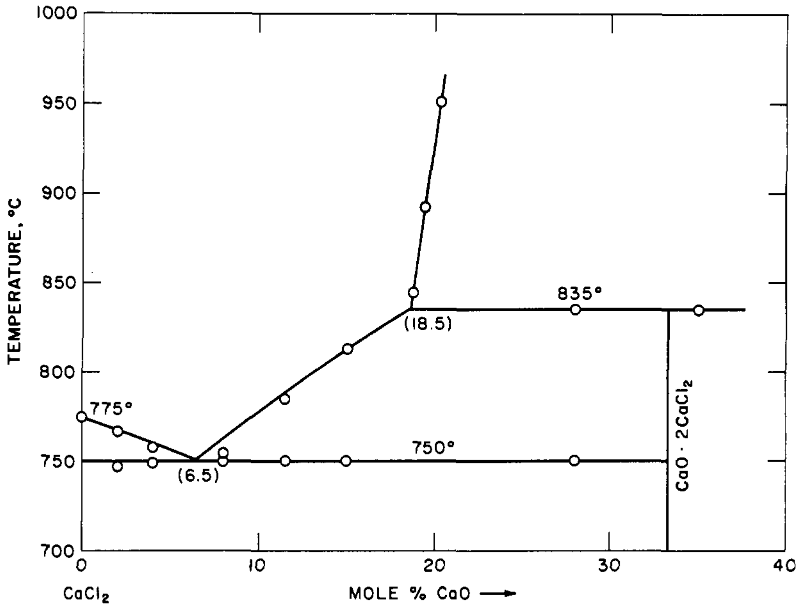

Figure 2. $CaCl_2$-CaO phase diagram

The $CaCl_2$-rich portions of the $CaCl_2$-CaF_2 and $CaCl_2$-CaO binary phase diagrams were obtained during the course of this investigation. The $CaCl_2$-CaF_2 phase diagram in Figure 1 is almost in exact agreement with diagrams given in the literature (*1, 4*). Previous work indicated a peritectic at about 42 mole % CaF_2, whereas the present work suggests that it is at 45 mole % CaF_2. The observed peritectic temperatures are the same. To substantiate the composition of the incongruently melting compound, a 55 mole % CaF_2–45 mole % $CaCl_2$ mixture was held for 16 hours at 820° C., and then cooled to room temperature. X-ray diffraction examination of this salt showed it to be primarily the compound $CaCl_2 \cdot CaF_2$ plus a small amount of CaF_2, which is in agreement with the phase diagram.

The $CaCl_2$-CaO phase diagram is shown in Figure 2. The liquidus points above the peritectic temperature were obtained from analyses of samples of the liquid phase of the $CaCl_2$–28 mole % CaO salt taken at the indicated temperatures. The present work agrees with the older literature data of Neumann *et al.* (*3*), up to about 15 mole % CaO, but not at all with those of Threadgill (*5*). At higher concentrations of CaO, this research indicated a peritectic at 18.5 mole % CaO and 835° C., with the corresponding incongruently melting compound having the composition $CaO \cdot 2CaCl_2$. However, Neumann *et al.* show the formation of the compound $CaO \cdot 4CaCl_2$ and a eutectic at about 800° C. and 22 mole % CaO. Their observation of a thermal halt at 800° C., rather than at 835° C. as in the present work, may be due to supercooling in their system.

The $CaCl_2$-corner of the $CaCl_2CaF_2$-CaO ternary diagram is presented in Figure 3. The system contains a ternary eutectic involving the compounds $CaCl_2$, $CaCl_2 \cdot CaF_2$, and $CaO \cdot 2CaCl_2$ in equilibrium at 625° C. with liquid of the composition $CaCl_2$–17 mole % CaF_2–4 mole % CaO. There are ternary peritectics at $CaCl_2$–23 mole % CaF_2–10 mole % CaO and $CaCl_2$–23 mole % CaO at the temperatures 660° and 670° C., respectively. At the former point $CaCl_2 \cdot CaF_2$, $CaO \cdot 2CaCl_2$, and CaF_2 are in equilibrium with the liquid, while the solids CaF_2, CaO, and $CaO \cdot 2CaCl_2$ are in equilibrium with liquid of the latter composition.

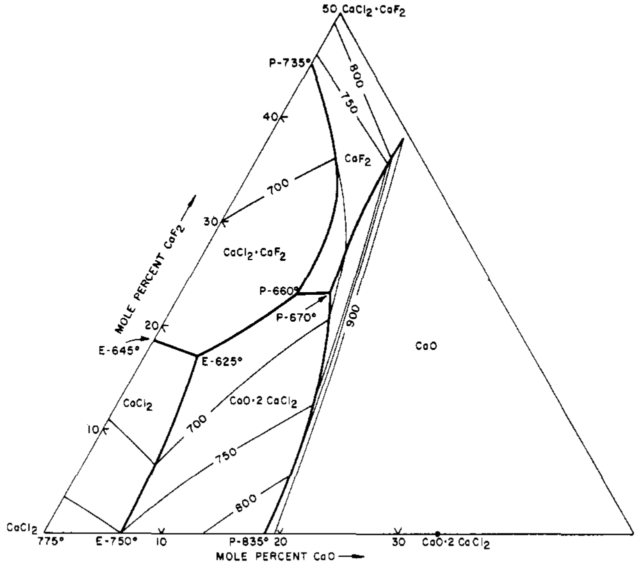

Figure 3. $CaCl_2$ corner of $CaCl_2$-CaF_2-CaO phase diagram

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