

$$\begin{aligned} \sin \epsilon_1 \cos \gamma &= -0.4508; \sin \epsilon_1 \sin \gamma = 0.8165 \\ \sin \epsilon_1 &= 0.93268; \sin \gamma = 0.87544; \cos \gamma = -0.48334. \end{aligned}$$

If β is the angle between lone pairs, since

$$\sin(\beta/2) = (\sqrt{3}/2) \sin \gamma$$

then $\beta = 98^\circ 36'$.

In an equivalent orbital representation, there is a single bonding function for HF, which is just ϕ'_1 (or ϕ_1^a). The approximate function may be written in the form

$$\phi_1^a = \chi_B^a = \mu h + \lambda (\cos \epsilon_b s + \sin \epsilon_b z) \quad (13)$$

and from (10) it is found that $\lambda = 0.68469$, $(\lambda/\mu) = 1.55$, $\cos \epsilon_b = 0.75523$ and $\sin \epsilon_b = 0.65547$. The polarity (H^+F^-) is much higher, as measured by (λ/μ) , than the polarity of a function made to give the correct dipole moment. For example, from the previous work,² such a function with $\beta = 98.5^\circ$, will have (λ/μ) about equal to 1.09.

If the angle β between lone pairs is accepted as about 98.5° , it is of interest to compute the position of the ring of maximum electron density in the lone pair region of the molecule. This calculation is interesting in connection with association of HF to form polymers. Electron diffraction experiments¹⁴ indicate that the principal associated form has a zig-zag structure in which the average F-F-F angle is $140 \pm 5^\circ$, and the H atoms are on line with the F atoms to about $\pm 15^\circ$. It might be expected that the H atom of one molecule would attach itself at the position of maximum electron density in the lone pair region of another molecule, and that the polymer is formed by repetition of this process. The calculation of the angle ϕ_{\max} , which the ring of maximum density makes with the bond axis was made in the former paper² for several values of the angle β . The requisite formulas are given in that paper and will not be repeated here. For $\beta = 98.5^\circ$, with the values of the parameters given here from (12) and (13), it is found that θ_{\max} is about 141° .

(14) S. H. Bauer, J. Y. Beach and J. H. Simons, *THIS JOURNAL*, **61**, 19 (1939).

Sources of Integrals.—All integrals over atomic orbitals may be evaluated exactly except two-center exchange integrals, and even for these, five or six terms of the infinite series are sufficient. Formulas suitable for direct numerical evaluation are available for most integrals. A large number of integrals have been evaluated and tabulated by Kotani, *et al.*,¹⁵ but uncertainties in interpolation made recalculation preferable in the present work. These tables, however, served as a valuable check. After most of the required integrals had been calculated, the results and tables of integrals for HF of Kastler¹⁶ became available, and provided additional checks on the integrals.

The one-centered integrals were evaluated from the formulas of Coulson,¹⁷ Barnett and Coulson¹⁸ and Roothaan¹⁹; some integrals were computed by several methods. Two-centered integrals were computed at the normal H-F distance, $1.7328a_0$.¹¹ Two-centered Coulomb integrals were obtained from the formulas of Roothaan.¹⁹ All hybrid integrals were evaluated by the analytical methods of Barnett and Coulson. Two-centered exchange integrals were computed by the methods of Ruedenberg²⁰; numerical integrations were used for his ϕ_{nn} -functions, while his B_j functions were interpolated from the tables of Kotani.¹⁵ Tables of all integrals used in these calculations are available.²¹

(15) M. Kotani, A. Amemiya and T. Simose, *Proc. Phys.-Math. Soc. Japan*, **20**, Extra No. 1 (1938); **22**, Extra No. 1 (1940).

(16) The integrals are tabulated in ref. 5. The author is very grateful to Dr. Kastler for furnishing him a copy of reference 5 before its publication.

(17) C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **38**, 210 (1941).

(18) M. P. Barnett and C. A. Coulson, *Phil. Trans. Roy. Soc. (London)*, **A243**, 221 (1951).

(19) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

(20) K. Ruedenberg, *ibid.*, **19**, 1459 (1951).

(21) Tables of integrals have been deposited as Document 4451 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints or \$1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

The Compound Na_5Pb_4

BY IVAR T. KROHN,^{1a} R. C. WERNER^{1b} AND HYMIN SHAPIRO

RECEIVED SEPTEMBER 22, 1954

A little-known region of the Na-Pb equilibrium diagram, in the vicinity of the composition Na_5Pb_4 , was reinvestigated by means of thermal and microscopic analysis. The work demonstrated the existence of a hitherto unrecognized open-maximum compound at the Na_5Pb_4 composition. The neighboring compound Na_5Pb_2 was shown to be a peritectic rather than an open-maximum compound.

Previous investigations² of the complicated Na-Pb equilibrium system have indicated the existence of five compounds: Na_2Pb_5 , $NaPb$, Na_2Pb , Na_5Pb_2 and Na_4Pb . In addition, although neither compound is formed from melts, Na_4Pb_7 and Na_4Pb_9

(1) (a) The Haloid Corporation, Rochester, N. Y. (b) Mine Safety Appliances Co., Pittsburgh 8, Pa.

(2) M. Hansen, "Der Aufbau Zweistofflegierungen," Julius Springer, Berlin, 1936.

have been reported in liquid ammonia solution.³ The compound Na_2Pb_4 was considered to be formed at 182° by the solid-solid reaction $Na_5Pb_2(s) + NaPb(s) = 3Na_2Pb(s)$. The other compounds in the phase diagram were reported to be of the open-maximum type, with Na_5Pb_2 giving the highest

(3) E. Zintl, J. Goubeau and W. Dullenkopf, *Z. physik. Chem.*, **A164**, 37 (1931).

(4) G. Calingaert and W. J. Boesch, *THIS JOURNAL*, **45**, 1901 (1923)

maximum, as shown by Calingaert and Boesch,⁴ and by Kurnakow and Kusnetzow.⁵

There is a fair degree of agreement on the extent of the α -phase in lead. The solubility of sodium in lead at 20° has been quoted at 3.5 to 5 at. % and at 300° at 8.3 to 18%.⁶⁻⁸

There is considerable doubt about the β -phase compound, Na₂Pb₅, which was suggested by the thermal studies of Mathewson.⁹ The potential measurements of Haber and Sack¹⁰ indicate that the compound is NaPb₂, which cannot be reconciled with more recent measurements. According to other thermal data,⁶ hardness and electrical resistance data,⁷ and X-ray evidence,^{11A and B} this is a phase of variable composition extending from 26.5 to 35.1 at. % Na, which is a solid solution of NaPb₃ in NaPb, corresponding to the AuCu₃ cubic structure.

Marsh and Shoemaker¹² have completely elucidated the structure of the compound NaPb, which gives a well-defined thermal maximum. Stillwell and Robinson¹³ suggested from X-ray measurements that the formula of the compound in the region of 80 at. % Na, which Mathewson⁹ regarded as Na₄Pb, is instead Na₃₁Pb₃. On the other hand, Zintl and Harder¹⁴ have indicated that the compound is Na₁₅Pb₄. Dr. Shoemaker¹⁵ is presently investigating this area of the Na-Pb diagram further.

In the region of the reported compounds Na₅Pb₂ and Na₂Pb, the described maximum was very broad, the thermal data were few, and there were no X-ray measurements. The present investigation is an exploration of this area around Na₉Pb₄ by both thermal and microscopic analysis.

Experimental

Thermal Investigation.—The alloys were prepared in approximately 65-ml. melts either from lead and sodium or from lead and Na₄Pb alloy of known composition under an atmosphere of purified nitrogen or argon. The lead, of purity 99.98%, was obtained from the National Lead Co. The sodium was of over 99.7% purity.

The thermal data presented below were obtained by means of cooling curves on the melts in an iron crucible. Cooling rates were established by the furnace with zero input wattage and were approximately 2.1° per min. at 400° and 0.9° per min. at 190°. Temperatures were determined down to approximately 150° by iron-constantan thermocouples and were recorded by a Leeds and Northrup Speedomax. Agitation of the melts down through the eutectic temperatures was provided by an iron ring immersed in the melt and connected to a Vibratool.

Following completion of the thermal cooling curves, the alloys were broken up at room temperature under nitrogen and chemically analyzed for sodium. The resulting analy-

ses were used to establish the composition of the alloys. The estimated accuracy in analysis was 0.12 at. % Na for an alloy of composition NaPb and 0.31 at. % Na for Na₄Pb.

Microscopic Analysis.—A microscopic examination of the sodium-lead alloys was carried out independently of the thermal analysis and was limited to the region from NaPb to approximately 70 at. % Na. No satisfactory method was developed for alloys containing more sodium. The alloys were freshly prepared from 99.99% Asarco lead and Ethyl Corporation sodium in 1.0-kg. batches in a closed bomb under nitrogen. Chemical analysis was made for both sodium and lead.

Alloy specimens were mounted in either Bakelite or Lucite at temperatures below 120°. Polishing was done under white mineral oil (thinned slightly with No. 9 oil, or refined kerosene) to minimize corrosion of the polished surfaces. Extremely fine polishing of the Na-Pb alloys was impossible because of slow corrosion by dissolved water.

The initial polishing was done on No. 1 emery paper to remove corroded alloy. This was followed by emery papers No. 0, 2/0 or 3/0, and 4/0 used in succession. Final polishing was accomplished by using No. 1000 Aloxite powder on Vel-Chamee cloth. The specimens were rinsed in No. 9 oil between the polishing stages.

The general procedure for etching was as follows. The polished specimen was rinsed quickly in No. 9 oil, after which it was swirled in the etching solution for a definite time. The etched alloy was again rinsed in No. 9 oil and then in heavy white mineral oil for protection during the microscopic examination.

Simple etching of the Na-Pb alloy surfaces during or after the polishing operations by means of the natural action of the atmosphere was unsatisfactory. The etching, which was quite uneven, imparted a gray color to the entire surface.

TABLE I
THERMAL ANALYSIS OF Na-Pb ALLOYS

At. % Na ^a	T, °C. I ^b	Temperature breaks					
		T, °C. II	Min.	T, °C. III	Min.	T, °C. IV	Min.
80.19	386.2						
78.75	386.0			369.5	^c		
76.84	377.4			374.9	21.0		
75.50	382.0			375.3	17.5		
74.00	394.5			373.0	11.0		
73.56	393.2	390.7	^b	377.6	11.0		
72.58	399.8	391.2	6.0	376.3	8.5		
72.43	397.5	390.5	6.0	373.0	4.0		
71.49	399.5	390.5	7.5	372.0	3.0		
71.35	402.5	393.0	5.5	374.0	3.5		
71.12	402.1	391.3	10.0				
70.76	402.0	391.0	2.0	371.0	^{c,d}		
70.51	402.8	387.1	6.0				
70.00	402.6	385.7	3.0				
69.92	402.0	389.0	1.5				
69.41	403.6	391.2	^c				
69.39	403.5					190.5	8.5
68.90	403.4			323.3	0.5	189.2	17.0
68.67	402.0			326.0	2.0	189.5	9.5
67.89	402			332	8.0	190	17.0
66.77	400.0			332.5	15.0	191.0	9.5
66.11	400.0			331.5	14.5	191.5	9.0
59.39	361.0			335.0	21.0	190.0	6.5
58.19	336.0			^c	^c	189.5	4.0
55.42	357.0			333.0	5.5	187.0	1.5
52.34	367.5			332.5	5.0	188.5	2.0
51.01	371.0			333.5	1.5		
50.36	371.5			332.5	1.5	301.0	^{c,d}
48.91	370.0					301.5	4.0

^a Calculated from chemical analysis. ^b Simply a break in curve. ^c Very short halt times. ^d These breaks do not belong in the respective alloy regions and are not shown in Fig. 1. Probably inhomogeneity of alloy. ^e Thermocouple trouble prevented establishing temperature and length of eutectic break.

(5) N. S. Kurnakow and A. N. Kusnetzow, *Z. anorg. allgem. Chem.*, **23**, 455 (1900).

(6) H. Kläiber, *Z. Elektrochem.*, **42**, 258 (1936).

(7) N. S. Kurnakow, S. A. Pogodin, E. S. Shpichinetskii and V. S. Zorin, *Ann. secteur anal., phys.-chim., Inst. chim. gen. (U.S.S.R.)*, **13**, 233 (1940).

(8) N. V. Ageev and N. Ya. Talyzin, *ibid.*, **13**, 251 (1940).

(9) C. H. Mathewson, *Z. anorg. allgem. Chem.*, **50**, 172 (1906).

(10) F. Haber and M. Sack, *Z. Elektrochem.*, **8**, 246 (1902).

(11A) E. S. Makarov and Z. V. Popova, *Izvestiia Akademii Nauk S.S.S.R.*, 377 (1951)

(11B) E. Zintl and A. Harder, *Z. physik. Chem.*, **A154**, 58 (1931).

(12) R. E. Marsh and D. P. Shoemaker, *Acta Cryst.*, **6**, 197 (1953).

(13) C. W. Stillwell and W. K. Robinson, *THIS JOURNAL*, **55**, 127 (1933).

(14) E. Zintl and A. Harder, *Z. physik. Chem.*, **B34**, 238 (1936).

(15) Private communication.

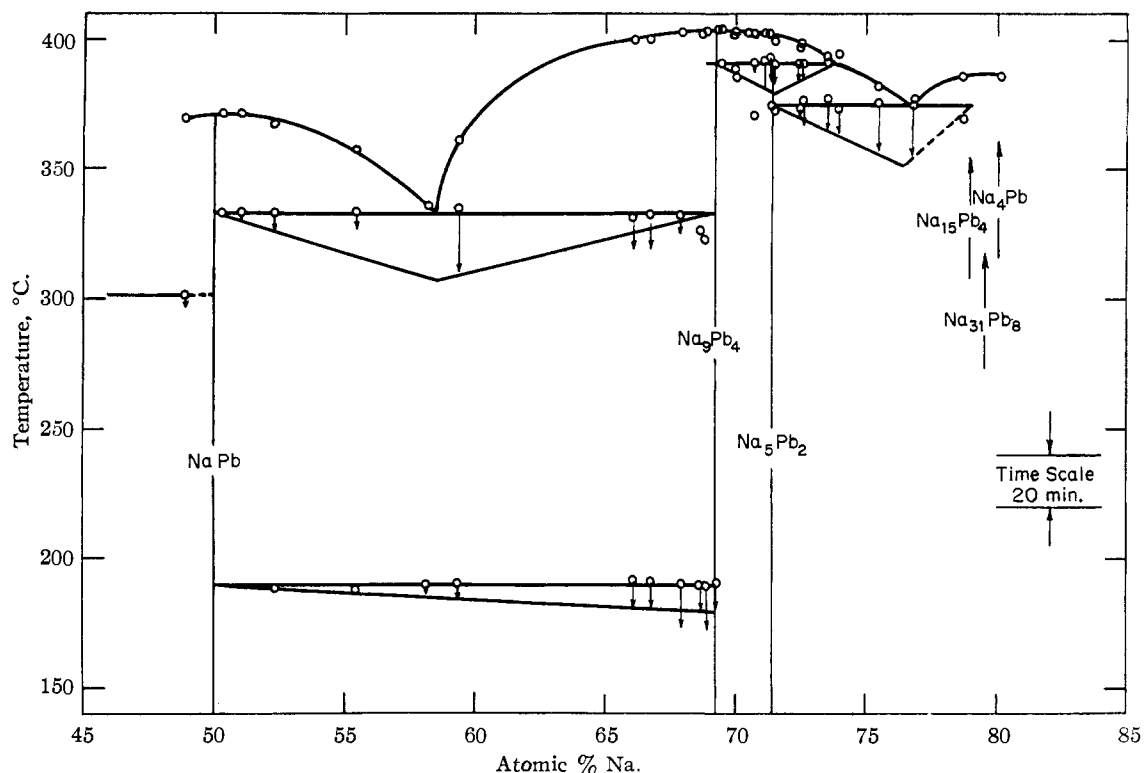


Fig. 1.—Sodium-lead equilibrium diagram.

The solvent used as a base for the etchants was undried benzene. Of numerous etchants tested, 0.5% picric acid, the water dissolved in the benzene, and 0.25% phenol are recommended in the order named. The 0.25% phenol solution etched the 70 at. % Na alloy in satisfactory fashion while the first two etchants did not. Hydrogen sulfide solution was fairly satisfactory, giving colors similar to wet benzene.

Results and Discussion

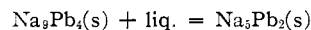
The results of thermal analysis are given in Table I and shown in Fig. 1. Photomicrographs were made of a series of etched alloys ranging in composition from 53.9 to 69.0 at. % Na, but are not reproduced in this paper.

Compound Formation.—In the alloy composition range near 70 at. % Na, previous investigations had indicated the existence of Na_5Pb_2 as an open-maximum compound. As may be seen from Fig. 1, the present work confirms this composition as a compound, but shows that the compound is of the peritectic type. In addition, it is shown that a new open-maximum compound exists at the composition Na_9Pb_4 .

The existence of the compound Na_9Pb_4 , m.p. 403° , was established by the facts that the 333° eutectic isothermal curve and the Na_5Pb_2 peritectic isothermal curve terminated at this composition. Also, microscopic examination confirmed the existence of a single phase in this region. The 69.0 at. % Na alloy, containing slightly less sodium than the theoretical Na_9Pb_4 alloy, consisted mainly of one phase (estimated at 99%).

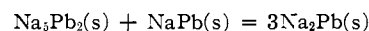
The existence of Na_5Pb_2 as a compound was established by the observations that the 391° halt time was greatest and the 375° eutectic halt (Na_4Pb - Na_5Pb_2) terminated at this composition. For

alloys between the composition Na_9Pb_4 and 75 at. % Na the formation of Na_5Pb_2 may be represented by



at 391° . Above this temperature the compound is unstable.

The 190° Transformation.—In previous investigations the 190° (or 182°) isothermal halt was interpreted as representing the solid-solid reaction



This interpretation was based on the fact that the time of the halt was greatest at this composition, decreasing to zero at the composition corresponding to Na_5Pb_2 and to Na_5Pb_2 - NaPb eutectic. It was not clear, however, why the halt should terminate at the eutectic composition. The present thermal data show that the 190° halt terminates instead at the compositions Na_9Pb_4 and NaPb . No abrupt change in halt time was found at the composition Na_2Pb . Rather, as expected, the halt time increased continuously from zero at NaPb to a maximum at Na_9Pb_4 . Also, microscopic examination of alloys from the Na_9Pb_4 - NaPb eutectic to the Na_9Pb_4 composition showed a continuous increase in the amount of Na_9Pb_4 phase. In particular, separate alloy specimens corresponding to the composition $2\text{Na} + 1\text{Pb}$, quenched, and annealed at 180° for 24 hr., contained clearly visible eutectic in amounts of 40-60%.

This evidence indicates that the 190° isothermal curve does not represent the formation of Na_2Pb but rather a lattice transformation or an order-disorder change involving Na_9Pb_4 . This transformation would be expected to appear also in the alloys

from Na_3Pb_4 to Na_5Pb_2 . However, there were no temperature halts corresponding to the 190° halt in this region during cooling or heating.

Solid Solubility.—According to previous knowledge, Na_5Pb_2 dissolves both sodium and lead, and

NaPb dissolves sodium. The present thermal data show no appreciable solid solubility for either compound. Also, little solid solubility is indicated for the Na_3Pb_4 region.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

The Partial Phase Diagram of the System $\text{CaI}_2\text{-CaF}_2$ ¹

BY WILLIAM J. MCCREARY

RECEIVED NOVEMBER 15, 1954

The phase diagram of the system $\text{CaI}_2\text{-CaF}_2$ is a simple binary eutectic up to 53 mole % CaF_2 . CaI_2 was purified by vacuum distillation. The f.p. of CaI_2 is $783.7 \pm 1.0^\circ$, CaF_2 freezes at $1414 \pm 5^\circ$, and the eutectic composition of 17.5 mole % CaF_2 freezes at $667.9 \pm 2^\circ$.

Introduction

In 1903 Ruff and Plato² published a paper which contained a partial phase diagram for the system $\text{CaI}_2\text{-CaF}_2$. This diagram agrees with the present work only in the composition of the eutectic mixture. The difficulty in obtaining accurate data on this system is due primarily to the nature of the CaI_2 . This salt is very hygroscopic and decomposes readily when heated in air or when heated in any atmosphere when the salt contains moisture. Complete dehydration can be effected by fusing in an inert atmosphere, but the resulting salt is contaminated with CaO .

Furthermore, at the relatively high temperatures required to melt mixtures rich in CaF_2 , the vapor pressure of CaI_2 is sufficiently high to appreciably change the composition of the mixture. This is especially serious when using very small samples necessary for microscopic observation, one of the techniques in the present work.

Ceramic crucibles, such as MgO and CaO , were readily dissolved by the melt at high temperatures, and platinum crucibles deteriorated rapidly. Bare platinum-platinum 10% rhodium thermocouples also dissolved in the melt at high temperatures. Tantalum and graphite appeared to be the least affected of any of the materials used.

Experimental

Preparation of Materials.—Reagent grade CaF_2 (J. T. Baker) was considered to be of sufficient purity for this study and was used as received. Spectrochemical analysis indicated the salt was better than 99.1% pure and an X-ray pattern showed no impurities.

Calcium iodide is a deliquescent salt which is unstable except in a dry, inert atmosphere. The hydrated salt can be prepared, in pure form, by treating CaCO_3 with HI .³ However, attempts to remove H_2O by heating *in vacuo* followed by fusion, or fusing the salt mixed with NH_4I or in an atmosphere of HI ^{3,4} resulted in partial decomposition of the salt.

Wolsky, *et al.*,⁵ prepared CaI_2 of $99.5 \pm 0.5\%$ purity by adding $\text{Ca}(\text{NO}_3)_2$ and NH_4I to liquid NH_3 . The precipitate

of $\text{CaI}_2 \cdot 8\text{NH}_3$ was recrystallized and the NH_3 removed by heating slowly to 190° *in vacuo*.

For this work, CaI_2 was prepared by vacuum distillation. Finely ground reagent grade $\text{CaI}_2 \cdot x\text{H}_2\text{O}$ was partially dehydrated by slowly heating the salt to 120° *in vacuo*. The H_2O was trapped with either P_2O_5 or $\text{Mg}(\text{ClO}_4)_2$. The dried salt was then distilled from a platinum crucible in a quartz tube at approximately 820° , the cooler upper walls of tube serving as the condenser. Pressure of the system during distillation was approximately 0.02μ . The CaI_2 was always handled in an atmosphere of dry helium or argon.

Spectrochemical analysis of the distilled salt indicated less than 166 p.p.m. total cation impurities. Calcium was determined by precipitation of the oxalate from acid solution. The precipitate was ignited at 500° and weighed as CaCO_3 . Iodine was precipitated and weighed as AgI . Results are: theoretical: Ca, 13.64; I, 86.36. Found: Ca, 13.70 ± 0.06 (all deviations are standard = $\sqrt{\Sigma d/n - 1}$); I, 86.11 ± 0.43 .

Experimental Techniques.—Three methods were employed to detect temperatures at which phase changes occurred. The f.p. of pure CaI_2 , pure CaF_2 and the eutectic mixture were determined by conventional cooling curves, wherein a plateau on a time-temperature plot indicated a phase change. This method was not sufficiently sensitive to detect formation of pure crystals in a molten mixture.

Saturation temperatures on mixtures containing not more than 20 mole % CaF_2 were obtained from an inverse-rate plot. In this method the time required for the sample to cool a fixed amount is plotted *versus* temperature, the phase change being indicated by a sudden increase in time.

The salts were contained in either platinum or tantalum crucibles, except that a graphite crucible was used for pure CaF_2 . The average sample weight was about 5 g. The crucible was placed in a quartz tube which was closed with a ground-jointed cap through which a platinum- or tantalum-tipped stainless steel tube was passed. This tube served as a thermocouple well and could be moved vertically for stirring the sample. The gland through which the tube passed consisted of a Pyrex tube which was sealed to the cap and was fitted with surgical rubber tubing whose normal inside diameter was less than the diameter of the steel tube. When the rubber was lubricated with vacuum grease, the steel tube could be moved without changing the pressure in the system.

The furnace was essentially as described by Kracek.⁶ The temperature was controlled by a Wheelco Potentiotorol and the heating or cooling rate could be adjusted to about 2° per minute. All runs were made in an atmosphere of dry argon after outgassing the system by slow heating to 200° *in vacuo*.

It was not possible to obtain saturation temperatures on mixtures containing more than 20 mole % CaF_2 by either of the foregoing methods. On cooling, the melts appeared not to undergo a phase change until the eutectic was reached. The reason for this is not known, unless the heat effect accompanying the formation of pure solid was too small to register.

(1) Work done under the auspices of the Atomic Energy Commission.

(2) W. Plato and O. Ruff, *Ber.*, **36**, 2357 (1903).

(3) G. P. Baxter and F. N. Brink, *THIS JOURNAL*, **30**, 46 (1908).

(4) J. W. Mellor, "A Comprehensive Treatise on Inorganic Chemistry," Vol. III, Longmans, Green and Co., New York, N. Y., 1952, p. 734.

(5) S. P. Wolsky, E. J. Zdanuk and L. V. Coulter, *THIS JOURNAL*, **74**, 6196 (1952).

(6) F. C. Kracek, *J. Phys. Chem.*, **33**, 1287 (1929).