In a saturated solution of only ferrous hydroxide it is calculated that $[FeOH^+]$ is 1.76×10^{-5} M and $[Fe^{++}]$ is 0.18×10^{-5} M. The pH of this saturated solution is calculated to be 9.32 in good agreement with the value of 9.4 reported by Shipley and McHaffie.[8]

If the iron in such a solution is present mostly as $FeOH^+$ then the solubility of $Fe(OH)_2$ reported by Lamb[2] from conductivity measurements (1.35×10^{-5} M) would be approximately half as great as the true value, since Lamb assumed completely dissociation into Fe^{++} and OH^- ions. The results of Lamb, therefore, do not disagree with ours.

The data in the present work agree fairly well with the results of Whitman[1] (solubility), Lamb,[2] Bineau,[3] Shipley and McHaffie[8] and Randall.[10] The data of Elder[7] may be in error due to possible coprecipitation and slow precipitation near the end-point in the titration of ferrous chloride with sodium hydroxide. The data of Krassa,[5] Britton[6] and Shrager[9] may be considered not to apply to the present case. An examination of the work of Murata[4] indicates that equilibrium had not been attained in his experiments, consequently the solubility reported by him is low. On the other hand the higher value of the solubility product obtained by Arden[11] in his titration may be due to supersaturation. It was observed in the present work that in the precipitation of ferrous hydroxide the pH had not decreased to a constant value within 24 hours.

Solubility of Ferrous Hydroxide in Ammonia Solutions.—Weitz and Müller[17] report that insoluble hexammine salts precipitate upon the passage of ammonia into solutions of ferrous salts. However, in the present work it was found that there was little tendency for the formation of these salts in solutions which were up to 1 M in ammonia. On the other hand, evidence for the formation of soluble ammino-iron(II) complexes was obtained. In solutions that were 0.1 M in ammonium chloride the solubility of ferrous hydroxide increased with the ammonia concentration. The total iron concentration in an ammoniacal solution that was 0.1 M in ammonium chloride and at a pH of 10.44 was found to be 2×10^{-4} M after 4 days of rotating at 25°. The concentration calculated from our values of $S_{1Fe(OH)_2}$ and $S_{2Fe(OH)_2}$ is about 2×10^{-6} M. If a coördination number of 4 is assumed the "constant" $[Fe^{++}][NH_3]^4/[Fe(NH_3)_4{}^{++}]$ is calculated from the data to be about 2×10^{-4}. This is about the value expected considering the correlation between the second ionization potential and the stability constant as shown by Martell and Calvin.[18]

Acknowledgment.—We wish to thank the U. S. Public Health Service for a grant which enabled the present work to be carried out.

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(17) E. Weitz and H. Müller, *Ber.*, **58**, 363 (1925).

(18) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 189.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF MINERAL INDUSTRIES, THE PENNSYLVANIA STATE COLLEGE]

Fluoride Models for Oxide Systems of Dielectric Interest. The Systems KF–MgF$_2$ and AgF–ZnF$_2$

BY R. C. DEVRIES AND RUSTUM ROY

RECEIVED NOVEMBER 3, 1952

Phase equilibrium relations have been determined in the systems KF–MgF$_2$ and AgF–ZnF$_2$. In the former system, two compounds, KF·MgF$_2$ and 2KF·MgF$_2$, have been found, melting congruently at 1070° and incongruently at 846°, respectively. Only one compound AgF·ZnF$_2$ is found in the second system; this melts congruently and shows a complete series of solid solutions with AgF. Other than the fact that both the 1:1 molar ratio compounds do have the perovskite structure, the "model" relations with the system BaO–TiO$_2$—which has four compounds—are very poor. It has also been found that the difficulties in these fluoride systems are commensurable with the difficulties involved in obtaining the high temperatures required for studying their oxide counterparts.

Introduction

The concept of model structures as introduced by Goldschmidt in 1926,[1] provides a method for the study of higher melting compounds by use of their lower melting models. A common example is that of silicates and their fluoride models. Although structurally the models and their more strongly bonded counterparts are often very similar, their phase relations have not always proved to be exactly the same, though some examples of remarkable similarity exist, *e.g.*, Na_2BeF_4 and Ca_2SiO_4.[2,3] Therefore the concept as applied to phase relations has come to be recognized as a tool but one to be used with some reservations. In earlier investigations in this Laboratory this has been amply demonstrated.[3–5]

With the interest in titanates and particularly the perovskite type structure in relation to dielectrics, fundamental research in TiO$_2$-containing systems or in systems containing similar structures is of increasing importance. However, a system such as BaO–TiO$_2$ presents certain technical difficulties, particularly the high temperatures involved and the ease of formation of barium platinates, that make feasible the consideration of lower melting fluoride model systems as one method of attacking the problems. Therefore as an indirect method of attack on the system BaO–TiO$_2$, two fluoride model systems, KF–MgF$_2$ and AgF–

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(1) V. M. Goldschmidt, *Skrift. Norske. Vid. Akad. Oslo. Mat. Nat. Kl.* No. **8**, 7 (1926).

(2) A recent summary has been given by E. Thilo, *Z. physik. Chem.*, **199**, 125 (1952).

(3) D. M. Roy, Rustum Roy and E. F. Osborn, *J. Am. Ceram. Soc.*, **33**, 85 (1950).

(4) W. E. Counts, Rustum Roy and E. F. Osborn, *J. Am. Ceram. Soc.*, **36**, 12 (1953).

(5) D. M. Roy, Rustum Roy and E. F. Osborn, *ibid.*, in press.

ZnF_2 were studied. These systems might be expected to be models of the system $BaO-TiO_2$ on the basis of the nearly equal radii of K^+, Ag^+ and Ba^{++} and of Mg^{++}, Zn^{++}, Ti^{++++}. However, the results obtained show that in this case neither of the fluoride systems is a reasonably close "model" of the system $BaO-TiO_2$ providing another example of the limited applicability of this principle.

Previous Work.—The system $KF-MgF_2$ has been reported on by Bergman and Pavlenko[6] and also by Remy and Seemann.[7] Although Bergman and Pavlenko published no diagram for the binary system, a diagram can be constructed from their ternary diagram for the system $KF-MgF_2-LiF$. They reported the melting point of the 1:1 molar ratio compound as 1050°.

The general outline of the system as reported by Remy and Seemann is the same as that of Bergman and Pavlenko with the exception of several additional unexplained heat effects in the former; their diagram is, moreover, theoretically incorrect. Their melting temperature for $KF \cdot MgF_2$ is 1080°.

In view of the interest in $BaO-TiO_2$ and the number of compounds reported in it, it seemed advisable to reinvestigate $KF-MgF_2$. Since the "model" relations were found to be very poor, it was thought that more polarizable cations were needed in the fluoride systems to imitate Ba^{2+} and Ti^{4+}. Ag^+ and Zn^{2+} were chosen. Neither NiF_2 nor CoF_2 were available for this study.

Experimental Procedure.—The general procedure was to make mixtures using the purest grade chemicals and to melt these mixtures or otherwise mix them in such a manner as to ensure homogeneity. Since in each of the systems certain unique techniques are involved they are considered in the general discussion of each system.

The data were secured predominantly by means of differential thermal analysis although visual thermal methods and high temperature X-ray methods were also employed. The mixtures were also examined optically and by powder X-ray diffraction methods; a Norelco Geiger-Müller spectrometer was used throughout, with Cu radiation filtered through nickel.

The furnace used is a 1.5″ diameter chromel-wound furnace which slides horizontally to permit centering and arrangement of the sample. It provides an even temperature zone of about 1.5″ in length. Both stainless steel blocks (with either two or three symmetrically arranged holes $^3/_{16}$″ in diameter) and separate platinum crucibles were used to hold the samples. Liners for the blocks were made of gold foil (0.001″ thick) which was rolled and hot worked to fit closely and to be leakproof to water. With the exception of the liners containing alumina (reference material), the liners had to be changed frequently since it was not always possible to clean them thoroughly without distorting them. The block which was used also necessitated the use of cumbersome devices to support it from one end only, and it acted as a heat reservoir causing considerably delay when the heating was stopped and the cooling begun. The use of three 1-cc. platinum crucibles suspended from a four-hole ceramic "spaghetti" rod which also carries the thermocouple wires was found to be more practical. Chromel-alumel couples were used initially, but it was found that the attack by fluoride vapors was so vigorous that one could not rely on the thermocouple for even one run; and in one case after only a few runs a measuring couple (which only dips into the alumina) was found to be reading 80° low at 500°. Pt-Pt·10Rh[8] couples proved to be satisfactory in spite of the smaller e.m.f. The furnace temperature was raised and lowered both by manually turning up a Variac at fixed intervals and by use of a motor drive with a proportional timer. While manual operation is far from desirable, the recorded heating curves of furnace temperature *vs.* time are quite smooth. The motor drive consists of a high torque $^2/_3$ r.p.m. synchronous reversible motor geared down to drive the Variac to 110 v. in about an hour. This rate may be decreased by almost any fraction by a four r.p.m. timer which may be set to break the circuit for any fraction varying between $^1/_3$ and $^1/_1$ of the circle. A heating rate of 10°C./min. proved satisfactory for most runs.

For the recording of the differential and furnace temperatures a six-point "synchrobalance" Brown electronic recorder was used. For added sensitivity for the differential temperature record, the full scale span of the instrument is only 3.8 mv. To record furnace temperatures, variable negative (or positive) signals in series with all points permit setting any point at any part of the scale.

The records for the unknown mixture and the calibrant were recorded on contiguous points, and for all the runs the temperature rise was recorded on the same chart, both by manual recording and also usually as an automatic record.

In determining temperatures of heat effects it was found that the very first change of slope in the curve corresponded very closely to the given fixed points for the calibrants. Hence, in each curve this initial break, and not the position of the maximum deflection or the point of maximum slope, was taken as the temperature of the phase change. All mixtures were heated to above their liquidus temperatures for the heating curve, and the cooling curve was obtained by cooling the furnace at a regular rate. On occasion the heating and cooling curves were repeated after partial cooling, if, for instance, a slower heating rate would separate two closely spaced heat effects. Each point on the system was run at least twice. This is not the normal operating procedure, but it was considered necessary for two reasons. First, it provides a check on the reproducibility to be expected in these fluoride systems; and secondly, it was considered necessary since some of the earlier work was done with chromel-alumel thermocouples.

The apparatus was calibrated at the following points: the melting point of sodium chloride taken as 801°; the melting point of sodium carbonate, 851°; and the inversion in potassium sulfate taken as 584°. The latter was used in the majority of the runs and was by far the most satisfactory (especially at the lower temperatures) since no melting was involved at this point.

Discussion of the System $KF-MgF_2$.—Thirteen compositions were prepared and studied. Considerable difficulty in weighing KF or MgF_2 in humid weather was encountered. These salts of C.P. grade were dried at 400° and stored in desiccators over P_2O_5. The mixtures were mixed only by gentle shaking in the weighing bottle, transferred to platinum crucibles, and melted as rapidly as possible by introducing the crucible into a furnace already at the desired temperature, usually about 1200°. Some matter was lost by volatilization, but weighing showed the amount to be small. It was neglected since the errors involved elsewhere were quite as large. Optical examination by the petrographic microscope of many of the mixtures showed the presence of MgO in traces.

The first few differential thermal analysis runs were performed with the stainless steel block. The fluorides when molten tended to "creep" out around the rim of the hole and into the adjacent chambers containing alumina or the calibrating material. The remainder of the runs were made in platinum crucibles with a calibrant being run with each mixture. In the center was placed the alumina, with the reading couple and one end each of two other differential couples. On either side, were the calibrating substance and the sample being studied.

The data obtained are presented in Table I, and drawn up into the simplest interpretation of the phase diagram for the system $KF-MgF_2$ in Fig. 1. The points have a reproducibility of ±3°, but the over-all accuracy is probably closer to ±5°. It will be seen from the diagram that there are two compounds, corresponding to the compositions $KF \cdot MgF_2$ and $2KF \cdot MgF_2$. The former, a cubic

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[6] A. G. Bergman and S. P. Pavlenko, *Compt. rend. acad. sci., U.R.S.S.*, **30**, 818 (1941).

[7] H. Remy and W. Seemann, *Rec. trav. chim.*, **59**, 516 (1940).

[8] At a later stage some of the runs were repeated with a 40% Au, 60% Pd *vs.* 90% Pt-10% Rh couple which gives 5 times as great an e.m.f. and has since proved eminently suitable for halide systems.

TABLE I

DATA FOR SYSTEM KF–MgF$_2$

Mole % KF	Mole % MgF$_2$	M.p., °C.	KF–K$_2$MgF$_4$ Eutectic	KMgF$_3$–MgF$_2$ Eutectic	Solidus	Liquidus	Remarks
100.0	0.0	850^{1a}					
90.0	10.0		776^{3}			803^{3}	
80.0	20.0	850^{2}	778^{2}				
75.0	25.0	852^{2}	782^{2}			903^{2}	
66.7	33.3	846^{2}	780^{3b}			998^{3}	
60.0	40.0	844^{2}	778^{2b}			1036^{2}	
57.0	43.0				973^{1b}	1043^{1}	807, Xl.^{c} 920, Xl. + L.^{c}
54.0	46.0	842^{4b}	777^{2b}		1000^{7}	1039^{2b}	960, Xl.^{c} 1030, Xl. + L.^{c}; 816,^{2} sub-solidus heat effect
52.0	48.0	843^{6b}	778^{1b}		1008^{4}	1058^{1b}	900, 960, Xl.^{c} 1025, Xl. + L.^{c}
50.0	50.0	1070^{8a}					1095^{6}, unexplained heat effect
48.0	52.0					1072^{3}	997^{5}, sub-solidus heat effect 835^{1}, unexplained heat effect
45.0	55.0			1006^{2}		1068^{6}	
36.5	63.5			1007^{2}		1048^{2}	
25.0	75.0			1012^{2}		1114^{2}	
Average:		846	778	1008			

[a] Congruent melting points not included in average. Superscript, number of runs averaged for temperature of heat effect. [b] Anomalous heat effects—probably explained by fractional crystallization—see text. [c] Visual observation. Xl., crystals; L, liquid.

crystal with the perovskite structure, is congruently melting. Optical and X-ray data are listed in Table II. It was quite difficult to obtain a powder pattern for 2KF·MgF$_2$ due to its extreme deliquescence. The sample had to be mounted in Canada balsam and protected by a covering layer of the same. The values are therefore not very accurate. However, for KMgF$_3$ we obtained a_0 = 3.98 com-

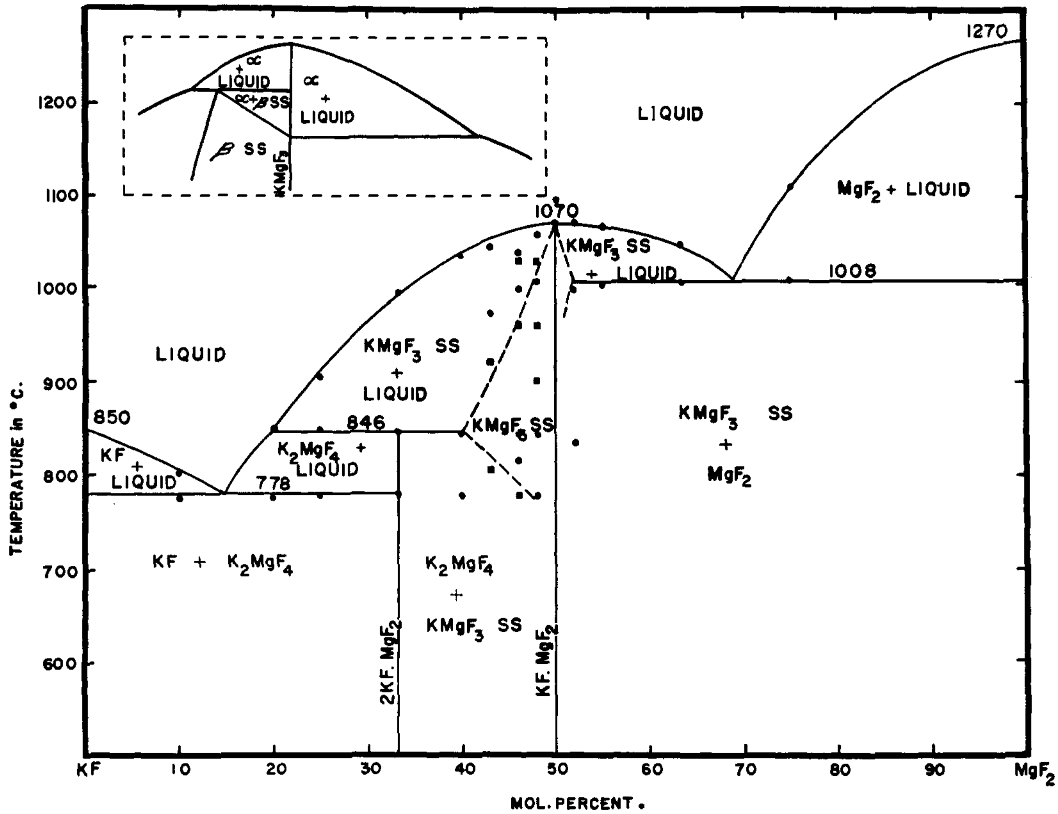

Fig. 1.—The system KF–MgF$_2$. The inset shows a possible alternative for the high temperature region near the KMgF$_3$ composition. Such a possibility could not be eliminated, although the simple construction—shown in the main diagram—is preferred. Square points indicate high temperature visual observations; round points represent data obtained by differential thermal analysis.

TABLE II

DATA FOR COMPOUNDS BETWEEN KF AND MgF_2

$KF \cdot MgF_2$: occurs as rounded anhedral, equant grains; $n = 1.404 \pm 0.002$ (Na light)		$2KF \cdot MgF_2$: occurs as sub-equant, sub-rounded rectangular plates with one pronounced cleavage; $n_g = 1.385 \pm 0.003$, $n_p = 1.382 \pm 0.003$(Na light); parallel extinction; positive elongation: biaxial − ve, large 2V	
"d" values, Å.[a]	I/I_0	"d" values, Å.[a]	I/I_0
2.80	0.4	6.61	0.3
2.29	.45	3.30	.15
1.990	1.0	2.95	.25
1.625	0.45	2.81	.2
1.408	.35	2.59	.15
1.259	.15	2.196	1.0
1.201	.70	2.136	0.25
1.150	10	1.989	.2
		1.730	.1
		1.650	.3
		1.475	.2
		1.373	.05
		1.300	.07
		1.237	.03
		1.195	.07
		1.182	.05
		1.174	.03
		1.145	.03

[a] Values obtained with a 90° Norelco G–M-counter spectrometer; filtered Cu radiation.

pared to that of Roberts,[7] $a_0 = 3.980 \pm 0.002$. Except for the area in the vicinity of $KMgF_3$ the system is quite straightforward. There is a eutectic between MgF_2 and $KMgF_3$ at 69 mole % MgF_2 and 1008°. $KMgF_3$ has been assigned the melting point 1070°. The liquidus drops very slowly to the peritectic, at 20.5 mole % MgF_2 and 846°, which is the incongruent melting point of the compound $2KF \cdot MgF_2$. Lastly, there is the eutectic at 778° between KF and $2KF \cdot MgF_2$ at 15 mole % MgF_2. The melting point of KF was found to be 850°, comparing well with the literature values.[9] The incongruent melting point of $2KF \cdot MgF_2$ was found to be very sharp and quite constant. Moreover, it is not affected by small changes in composition, and we were able to use this melting point as a reference point in differential thermal analysis of this and similar systems. It has the advantage over a pure compound that it does not melt from all solid to all liquid, but rather to liquid + solid. It does not have to be stoichiometrically perfect to give the correct temperature. Two anomalies in the data should be pointed out. Small heat effects have been observed in the mixtures between $KF \cdot MgF_2$ and $2KF \cdot MgF_2$ at 778° and other inconsistent heat effects have been observed between 40 and 50 mole % MgF_2 at or above 846°.

Unless an inversion were to be postulated in $2KF \cdot MgF_2$ at a temperature coinciding with the eutectic, these heat effects are probably best explained as follows: A mixture at, say, 45 mole % MgF_2 would, under equilibrium conditions, crystallize to a single solid solution phase at 950°. On further cooling it would exsolve into $2KF \cdot MgF_2$ and a $KMgF_3$ solid solution beginning at 800°. Under non-equilibrium conditions such as must prevail during the rapid cooling of a melt of crucible size a different sequence of events takes place. The solid solutions which form first would not continuously redissolve and form as required by equilibrium conditions, and hence the mixture would contain solid solutions of compositions ranging from 41 to 49 mole % MgF_2. The liquid composition meanwhile would approach the peritectic point (20.5% MgF_2) and except in the unlikely event of complete resorption, would move on down to the eutectic, crystallizing finally to KF and $2KF \cdot MgF_2$, at 778°. Meanwhile, the exsolution of the mixture of solid solutions would occur, and leave in the final solid mix, KF, $2KF \cdot MgF_2$ and $KF \cdot MgF_2$.

Such an explanation is borne out by the fact that we have been able to detect KF in these mixtures by petrographic microscopic observations, and the observation that the anomalous effects were more pronounced on cooling curves where the rate of cooling is very rapid than on heating curves which are made with materials more closely approaching equilibrium. Furthermore, the same explanation will account for the majority of the unexplained effects in the work of Remy and Seemann.[7]

The data obtained on mixtures near the compound $KMgF_3$ also indicate that some amount of solid solution toward the KF side must exist, and considerably less toward the MgF_2 side. Besides the thermal effects, evidence for solid solution in $KMgF_3$ was obtained by observing visually the first appearance of liquid in several mixtures. Thus the 46 and 48 mole % mixtures show no liquid at 960°.

The extremely flat liquidus on one side of the compound $KMgF_3$ found in all three studies is worthy of note. This together with the presence of a persistent heat effect at 1095°, suggested the possibility that the effect which has been attributed to the liquidus, may in reality be due to an inversion, or an inversion followed closely by the liquidus. Another method for checking the melting point of $KMgF_3$ was tried unsuccessfully. Large single crystals—cubes about 1 mm. on the edge—were held for about five minutes at increasing temperatures between 1050 and 1100 and air-quenched, an attempt to see when the crystal first rounded, or flowed. Due to the high volatility of the fluoride, in most cases, nothing at all was left after the run. To investigate both these points mixtures containing 43, 46, 48, 50 and 52 mole % MgF_2 were prepared, thermally analyzed, and examined Unfortunately the data obtained did not decide the issue, and in the inset in Fig. 1 we show the region near the compound in a not-impossible diagram which could be reconciled with the data. The only difference will be seen to be the existence of an inversion of $KMgF_3$ just below its melting point.

The System AgF–ZnF_2.—AgF and ZnF_2 were both obtained through the courtesy of the Harshaw Chemical Company. No analysis was available and no special purity claimed. The only check made on these materials was on their X-ray diffraction patterns. A small amount of $ZnF_2 \cdot 4H_2O$ was found in the ZnF_2 sample, which could have been picked up during the preparation of the sample for X-ray examination. On attempting to dry the ZnF_2 at 300° it

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(9) "Data on Chemicals for Ceramic Use," (Bull. Natl. Res. Council 118, June, 1949) Natl. Acad. Sci., Washington, D. C., 1949.

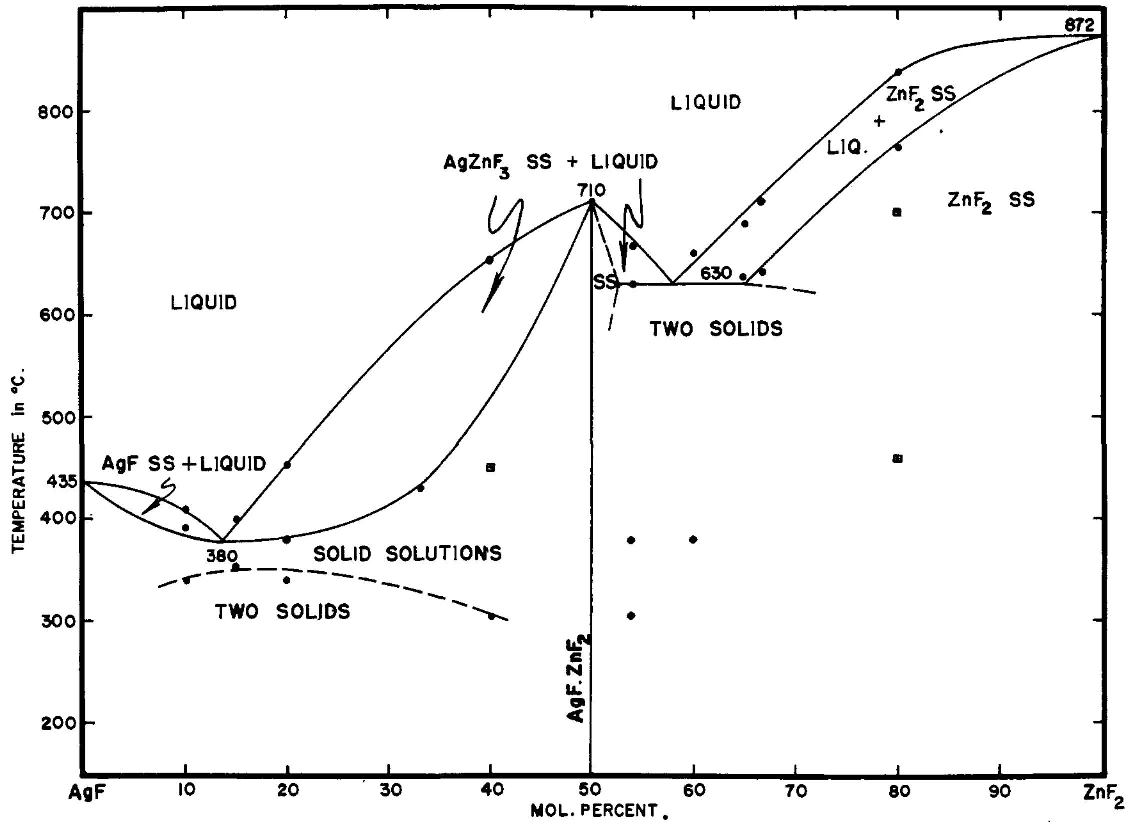

Fig. 2.—The system AgF–ZnF$_2$. Square points are those determined by high-temperature visual or X-ray methods. Dots represent DTA data.

was found to be continuously losing weight. After 21 hours it had lost 9% of its original weight. Ten mixtures were studied in this system. The difficulties encountered in this system are very considerable. In addition to the usual difficulties of working with molten fluorides, both these compounds are particularly volatile and the silver fluoride is unstable toward light. Its purity is also impossible to determine, and, on heating, it tends to deposit metallic silver, which alloys with both the platinum crucibles and the thermocouples. The melts were therefore made in a heavy silver crucible which could be cleaned and machined inside. Liners for the differential thermal analysis apparatus were also made from silver foil, or separate silver crucibles were used.

The data obtained and the equilibrium diagram drawn are shown in Table III and Fig. 2. The melting point of AgF was found to be 435 ± 2° in excellent agreement with literature values.[8] Only one compound exists in the system, AgZnF$_3$, which is an isotropic cubic phase (refractive index 1.620 ± 0.005) with the perovskite structure $a_0 = 3.98 \pm 0.01$ Å. It appears that a complete series of solid solutions with a minimum exists between AgF and AgZnF$_3$, the minimum occurring at 380° and 14% ZnF$_2$. The presence of such extensive solid solution was surprising, especially in view of the fact that at room temperature X-ray patterns showed virtually no solid solution. The exsolution dome is seen to be quite close to the solidus temperatures, a feature noticed in many fluoride and other halide systems. Direct confirmation of the existence of the solid solution was made by visual observation of samples inserted for a few minutes in a furnace at the desired temperature. Thus the 40 mole % ZnF$_2$ mixture being quite unchanged (*i.e.*, no liquid developing) at 450° (70° above the minimum) cannot be accounted for on any other basis. Toward the ZnF$_2$ side there is a eutectic at 630° and 58 mole % ZnF$_2$. There is probably a little solid solution of ZnF$_2$ in AgZnF$_3$, but this is not well established. From the ZnF$_2$-end solid solutions extend in as far as 67 mole % ZnF$_2$. The shape of the solidus is somewhat unusual, but could not be very precisely determined. The exsolution curve in this system must also lie

TABLE III

DTA DATA FOR THE SYSTEM AgF–ZnF$_2$

Composition, mole % AgF	Composition, mole % ZnF$_2$	Exsolution dome	Temperature of heat effects, °C.[a] Solidus	Liquidus	Remarks
90.0	10.0	341^2	395^2	411^3	
85.0	15.0	354^1		400^1	
80.0	20.0	341^1	380^1	452^2	
66.7	33.3		433^2		
60.0	40.0	305^1		655^1	Visual observation shows no liquid at 450°
50.0	50.0			710^2	
46.0	54.0		630^1	667^1	Unexplained effects at 301^1 and 380^1
40.0	60.0		661^1		Unexplained effect at 380^1
35.0	65.0		639^1	687^1	
33.3	66.7		641^1	712^1	
20.0	80.0		766^1	838^3	Visual observation shows no liquid at 700°. High-temp. XRS data show 2 phases at 460°

[a] 1, 2, 3 . . ., indicate number of separate runs.

at high temperatures. The melting point of ZnF_2 is given from the literature as 872°.[8] A check was obtained on a strip furnace run which indicated only that the m.p. was above 860° and below 885°. A high temperature X-ray diffraction study of the 80 mole % ZnF_2 mixture was undertaken in the hope that an accurate and direct estimate of the exsolution temperature might be obtained. The amount of $AgZnF_3$ in the sample as judged by the relative peak heights definitely appeared to decrease from room temperature to 325° and further to 450°. However, above this temperature the ZnF_2 is quite unstable in air and reacts to give ZnO, the pattern for which appears in a fresh sample in 15 minutes at 600°. Visual observation also established the existence of an unreacted solid phase present when this mixture was held at 700° as described above. Accuracy in this second diagram is poor, being about ±10° and ±1.5% on composition.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. Merrill W. Shafer in the preparation of the mixtures, and differential thermal analyses in the system AgF–ZnF_2. This work was supported by the Frequency Control Branch of the Squier Signal Laboratory of the U. S. Army Signal Corps at Fort Monmouth, New Jersey. The project was under the general supervision of Dr. E. F. Osborn, Associate Dean of the School of Mineral Industries, to whom the authors are indebted for guidance throughout this work.

STATE COLLEGE, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

A Millicoulometer Method for the Determination of Polarographic *n*-Values

BY THOMAS DE VRIES AND JAMES L. KROON[1]

RECEIVED JANUARY 2, 1953

It is possible to determine the value of *n*, the number of faradays per mole of electrode reaction, by using two polarographic cells in series and extending the electrolysis until a reasonable decrease in the concentration of the reducible or oxidizable compounds has occurred. The method was shown to give results within 2% for several inorganic and organic compounds.

There is much interest in knowing the number of electrons, *n*, involved per molecule during the reaction at the dropping mercury electrode. The use of the Ilkovic equation, $i_d = 607nD^{1/2}Cm^{2/3}t^{1/6}$, to determine *n* from the average diffusion current, i_d, and other quantities, requires a knowledge of the diffusion coefficient of the substance undergoing electrochemical reaction. This obviously has its limitations. Another method based on a fundamental equation for the polarographic wave, $E_{d.e.} = E_{1/2} - 0.0591/n \log i/(i_d - i)$, is even more restricted because it applies only to electrochemically reversible reactions. Lingane[2] developed a method in which the current used during the reaction at a large stirred mercury cathode was integrated with a hydrogen–oxygen volume coulometer. Bogan[3] and co-workers designed an electronic circuit incorporating a Weston integrating relay to be used in conjunction with a dropping electrode to measure the millicoulombs effecting a measurable change in concentration in a micro H-cell.[4] Because such apparatus is not generally available, a method was devised which requires no elaborate equipment.

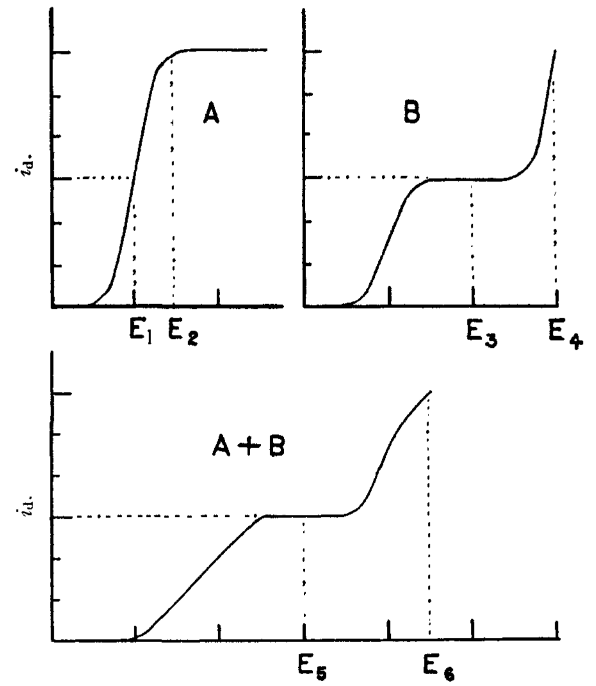

Fig. 1.—Idealized polarographic waves for materials A and B when the same current passes through both cells.

Apparatus.—When current is passed through two polarographic cells in series, an equivalent amount of electrochemical reaction will occur in each cell. The change in concentration in each cell can be determined from the decrease in wave height, and a comparison of these changes leads to a determination of the number of electrons used in a unit of reaction for an unknown substance in terms of a known in one of the cells. The potential across the two cells is held at a constant value but it must be selected with a knowledge of the polarographic behavior of the ions in cell A for which *n* is known and for the compound in cell B for which *n* is to be determined. If products are formed during prolonged electrolysis which give waves at a higher potential than the primary reaction, no difficulty will arise if a careful choice is made of the total voltage across the two cells.

In Fig. 1 are given idealized polarographic waves for compounds A and B, and the composite curve which is obtained when a potential is impressed across both cells in series. When a potential E_5, which is the sum of E_1 and E_3, is im-

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(1) Material abstracted from a thesis to be submitted by J. L. Kroon for the degree of Doctor of Philosophy.

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