

ure of the latter one may consider the quantity  $2b$ , where  $b$  is defined by the expression

$$\pi b^2 L = V_0 \quad (2)$$

*i.e.*, one imagines the polymer chain surrounded by a cylindrical envelope of radius  $b$ , so that this envelope completely fills out the volume  $V_0$  occupied by the polymer coil. The quantities  $b$ ,  $1/\kappa$  (in cm. units) and their ratio,  $b\kappa$ , are given in the last three columns of Tables I and II. It is seen that in all cases,  $b$  is considerably larger than  $1/\kappa$ .<sup>16</sup> This means that in a large portion of the solution inside the polymer sphere the potential is equal to or close to zero, just as it is in the solution outside the polymer sphere. If  $b$  were smaller than  $1/\kappa$ , *i.e.*, if  $b\kappa < 1$ , the potential fluctuations would be smaller and the theoretical treatment involving the smeared out charge would be more appropriate.<sup>17</sup>

(16) It is noteworthy that this is even true in the 0.1966 *M* NaBr solution in which the polymer is very close to the theta point.<sup>16</sup>

(17) It can be shown that  $b\kappa$  is related to  $f$  by the equation  $(b\kappa)^2 = (4e^2/DkT)(P_w/L)(1/f)$  which reduces to  $b\kappa = 3.34 f^{-1/2}$  in our case. Thus,  $b\kappa < 1$  corresponds to  $f > 11.2$ .

However, with the large values of  $b\kappa$  encountered here, the smeared out charge model does not give even an approximately realistic picture of the behavior of the potential inside the polymer coil. In further support of this argument, it is seen in Table II that the discrepancy between  $(e\psi/kT)_m$  and  $e\zeta/kT$  increases rapidly with increasing  $b\kappa$ .

It is therefore concluded that a more appropriate and realistic model of a polyelectrolyte in solutions containing fairly high concentrations of simple electrolyte would be a rather loosely coiled chain, each section of which is enveloped by a double layer of cylindrical symmetry as proposed by Overbeek and Stigter.<sup>11</sup> For many purposes, the curvature of the chain could be neglected and a uniformly charged rod substituted to obtain a first approximation. While the P.B. equation has not yet been solved for this case, a semi-theoretical treatment of Donnan equilibria using this model has produced good results.<sup>18</sup>

(18) U. P. Strauss and P. Ander, *THIS JOURNAL*, **80**, 6494 (1958).  
NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

## Observations on the Differential Thermal Analysis of Copper Sulfate Pentahydrate

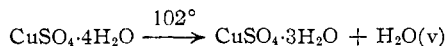
BY ARNOLD REISMAN AND JOAN KARLAK

RECEIVED FEBRUARY 26, 1958

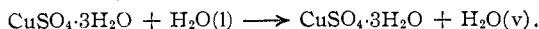
An analysis of the applicability of differential thermal analysis to processes involving the depletion of one component is presented using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as an example. It is demonstrated that the complex nature of the non-equilibrium dehydration process can readily lead to a misinterpretation of the nature of the observed differential peaks. In addition, it is shown that slight variations of experimental conditions affect the results considerably, thereby accounting for the apparent discrepancies between different studies.

### Introduction

The thermal behavior of copper sulfate pentahydrate was described in 1936 by Taylor and Klug.<sup>1</sup> On the basis of DTA and weight loss experiments a new hydrate of  $\text{CuSO}_4$ , coordinating four molecules of water, was postulated. Borchardt and Daniels,<sup>2</sup> in a re-evaluation of the earlier work, showed that the differential peak attributed by Taylor and Klug to the transformation



was in reality due to the process



Several years ago, in conjunction with studies of other hydrates, DTA traces of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were recorded in order to obtain characteristic heating curves of a "known" hydrate. These experiments gave results which were in disagreement with those of the 1936 work and when compared with the later effort, were found to agree insofar as the actual stages of dehydration were concerned, but to disagree markedly with respect to the reported dissociation temperatures.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  frequently has been used as a classic example in describing isovolumic and isobaric dehydration phenomena. In order to account for the

noted discrepancies, and thereby avoid further confusion, it was felt that a critical analysis of the DTA technique, as applied to the isobaric process, was necessary. The experiments to be recounted were not restricted to  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Studies of the hydrates of alkali metal carbonates and alkali niobates gave results which led to the same conclusions, but need not be discussed here.

### Experimental Procedure

**DTA.**—The basic methods and apparatus have been described previously.<sup>3-5</sup> In order to facilitate weighing of the samples after each dehydration step, 1 cc. platinum or gold-20% palladium crucibles were employed which had the thermocouple protective capsules welded centrally in them. A  $1/8$ " platinum spacer was placed at the bottom of each thermocouple protective well so that the junction rested in the center of the sample. Duplicate experiments were performed with the containers normally employed, and the resulting DTA graphs were identical within experimental limits.

Sample size was varied between 0.25 and 0.5 g., and heating rates of  $0.4^\circ/\text{minute}$  or less were used in most "equilibrium" experiments. The data were recorded on a Leeds and Northrop X-Y recorder having a basic X sensitivity of  $2.5 \text{ mv./}10''$  and a Y sensitivity of  $10 \text{ mv./}10''$ . In order to resolve closely occurring heat effects, temperatures were generally measured on the X axis. Differential signals were amplified to provide final sensitivities of 5, 10 or  $15 \mu\text{v./inch}$ . Alundum powder served as ballast in all experiments.

(3) F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *THIS JOURNAL*, **79**, 2039 (1957).

(4) A. Reisman, F. Holtzberg and E. Banks, *ibid.*, **80**, 37 (1958).

(5) A. Reisman, *ibid.*, **80**, 1877 (1958).

(1) T. I. Taylor and H. P. Klug, *J. Chem. Phys.*, **4**, 601 (1936).

(2) H. J. Borchardt and F. Daniels, *J. Phys. Chem.*, **61**, 917 (1957).

**Reagents.**—Four different lots of Mallinckrodt Analytical Reagent  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were examined. They were found to contain approximately 4.9 moles  $\text{H}_2\text{O}$ /mole  $\text{CuSO}_4$ . The materials were sieved to determine the approximate particle size distribution, and the different fractions were examined as described in the Discussion section. All experiments were performed on one batch of the pentahydrate having a particle size distribution,  $>16 - 28.4\%$ ,  $<16>40 - 48.2\%$ ,  $<40>60 - 11.6\%$ ,  $<60>80 - 4.4\%$ ,  $<80>140 - 4.1\%$ ,  $<140 - 3.3\%$ . It is to be emphasized, however, that when the precise experimental conditions were duplicated, the traces obtained using samples from different batches were identical within the limits of experimental error.

### Discussion of Experimental Results

The dissociation of a hydrate system, in a Differential Thermal Analysis, is a complex phenomenon because the dehydration, depending on the experimental conditions, deviates to a lesser or greater extent from an equilibrium process. In order that the discrepancies among the several DTA studies may be explained, it is of value to trace the dissociation path.

The dehydration chamber is assumed to be in perfect contact with the ambient at temperature  $T$  and aqueous partial pressure  $P$ . If, at the start of an experiment, the hydrate system I has an equilibrium aqueous vapor pressure  $P - \Delta P$  and its saturated solution has an equilibrium aqueous vapor pressure  $P + \Delta P'$ , the system I will neither effloresce nor deliquesce; the conditions for stability being satisfied. If the temperature of the chamber is raised continuously to a temperature  $T'$  where the system I aqueous vapor pressure is  $P$ , a further increase of the temperature to  $T' + \Delta T'$  will cause an increase in the system I vapor pressure to  $P + \Delta P''$  and dehydration will commence. It is evident that if the system were permitted to equilibrate at  $T' + \Delta T'$ , dissociation would continue until a stable system was generated. The temperature  $T' + \Delta T'$  can therefore be described as the dissociation temperature of the hydrate and will be variable within the normal limits of ambient aqueous tension variation.

In the dynamic DTA experiment, however, system I is not permitted to equilibrate at  $T' + \Delta T'$ , and as seen in Fig. 1 the beginning of the first dehydration stage is evidenced by a deviation from the base line.<sup>6</sup> As the aqueous vapor pressure-temperature curve of a hydrate ascends steeply, the vapor pressure increase/unit time, at constant heating rate, will increase logarithmically. Consequently the latent heat absorption/unit time will also increase logarithmically, and the observed differential peak may erroneously be attributed to an isothermal process. This point is emphasized with reference to Fig. 2 which is a DTA trace of a sample of 0.375 g. of Alundum powder and 0.175 g. of admixed water heated at  $0.4^\circ/\text{minute}$ . In this experiment the complexities of the hydrate dissociation have been minimized and the trace relates more nearly to the latent heat of transformation of  $\text{H}_2\text{O}$ . The sloping of the base line begins at room temperature since the ambient aqueous tension was only 13 mm. The deviation increases rapidly and before the sample

(6) All experimental dissociation temperatures referred to in the text pertain to the onset of non-isothermal dehydration processes. These temperatures were chosen by extrapolating the maximum peak inflection back to its intersection with the base line.

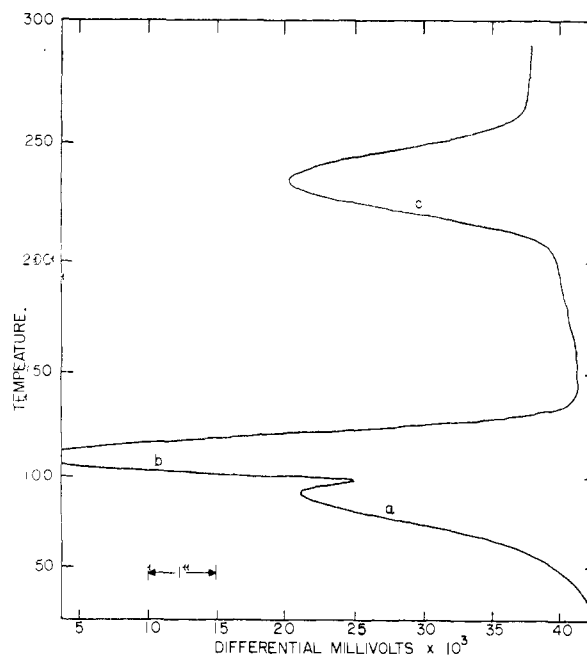


Fig. 1.—DTA trace of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ : particle size,  $<16>40$  mesh; heating rate,  $0.4^\circ/\text{min.}$ ; ambient aqueous tension, 11.5 mm: a,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} - \text{CuSO}_4 \cdot 3\text{H}_2\text{O} - \text{vapor}$ ; b,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} - \text{CuSO}_4 \cdot \text{H}_2\text{O} - \text{vapor}$ ;  $\text{CuSO}_4 \cdot \text{H}_2\text{O} - \text{CuSO}_4 - \text{vapor}$ .

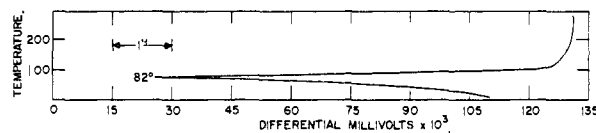


Fig. 2.—DTA trace of Norton Alundum RR 90 mesh + admixed water. Heating rate  $0.4^\circ/\text{min.}$ ; ambient aqueous tension, 13 mm.

vapor pressure has reached approximately 760 mm., all of the water has evaporated, and the rate of sample temperature return to the base line depends on the time constant. If insensitive equipment had been used, the initial sloping would not have been detectable until the water loss per unit time had become appreciable, in which case some meaningless temperature would have been chosen. As seen from Fig. 2 the peak temperature is  $82^\circ$  which merely represents depletion of the water or analogously hydrate system I. Thus it would appear that in a DTA experiment where there is constant depletion of some component and/or insensitive equipment is employed, results are obtained which can be completely misinterpreted.

Experimentally, the more complex hydrate dissociation will be a function of the particle size, the heating rate, the nucleation rate, the ambient aqueous tension, the vapor pressure-temperature curve of the hydrate system, the latent heats of hydration and vaporization, the furnace geometry and sample packing. Each of these factors will in some way affect the attainment of equilibrium during the experiment. For example, even at heating rates of less than  $0.4^\circ/\text{minute}$ , a typical analysis gave values of  $-2.12$ ,  $-1.84$  and  $-1.00$  moles  $\text{H}_2\text{O}$  lost for the three dehydration stages of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

When the vapor pressure-temperature curves of successive hydrate systems are close to one another, further complexities arise as demonstrated with reference to Fig. 3. Curve "a" corresponds to

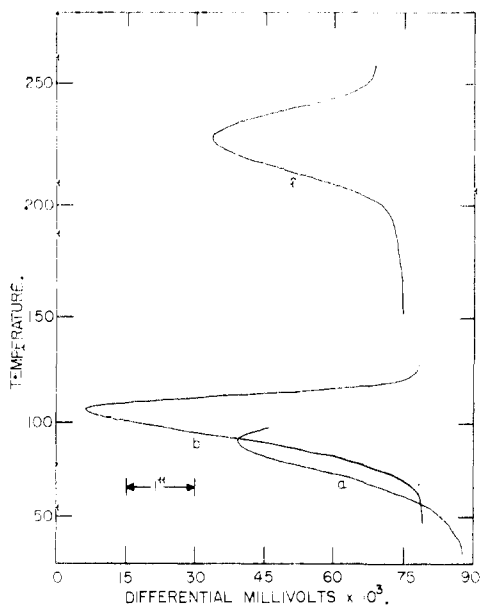


Fig. 3.—DTA traces of systems: a,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ - $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ -vapor; b,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ - $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ -vapor; c,  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ - $\text{CuSO}_4$ -vapor; heating rate,  $0.4^\circ/\text{min.}$ ; ambient aqueous tension, 11 mm.; particle size,  $<16>$  40 mesh.

the dehydration of the system  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ - $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ -vapor. After dehydration was complete the sample assembly was withdrawn and placed in a small vial. The furnace was cooled and a heating curve "b" was then taken of the system  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ - $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ -vapor. The same procedure was followed for the monohydrate obtaining curve "c." As seen, the curves for the systems I and II overlap, which means that depending on the sample size, heating rate, etc., the temperature selected for the second dissociation process can be varied almost at will. This point is reinforced by reference to Fig. 4. In this case the particle size of the pentahydrate was material greater than 325 mesh and less than 200 mesh. The other experimental conditions were held as nearly constant as possible. The "temperature" of the second dissociation was apparently lowered  $20^\circ$  as compared to Fig. 1. Comparison of the third dissociation stage shows a temperature lowering of approximately  $40^\circ$ . In this experiment the greater surface area of the particles enabled more rapid attainment of "equilibrium" with the ambient, and as expected the dehydrations proceeded at lower temperatures. Another factor that affects the so-called dissociation temperatures is the heating rate. Large heating rates prevent equilibrium of the crystallites with the ambient because the dissociation is both nuclei and diffusion dependent. The net effect is to cause an apparent suspension of the dissociation to higher temperatures. Thus an increase in the rate to  $1^\circ/\text{minute}$  resulted in a shift of the "dissociation temperatures" by as much as  $30^\circ$ .

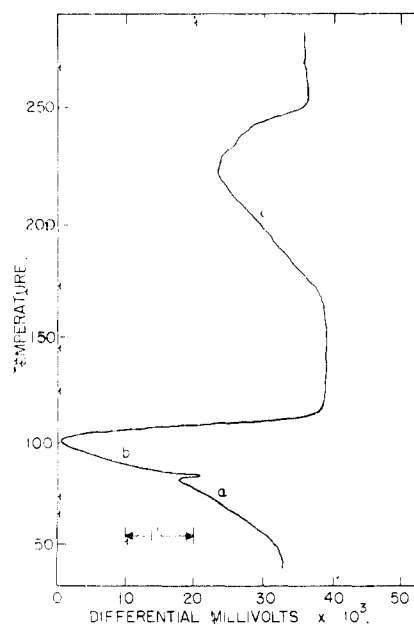


Fig. 4.—DTA trace of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; particle size,  $<200>$  325 mesh; heating rate,  $0.4^\circ/\text{min.}$ ; ambient aqueous tension, 6 mm. a, b, c, see Fig. 1 and 3.

One further extremum is of interest; the furnace chamber is always approximately saturated with water. This situation is demonstrated in Fig. 5 in which a crucible containing 10 g. of water was sus-

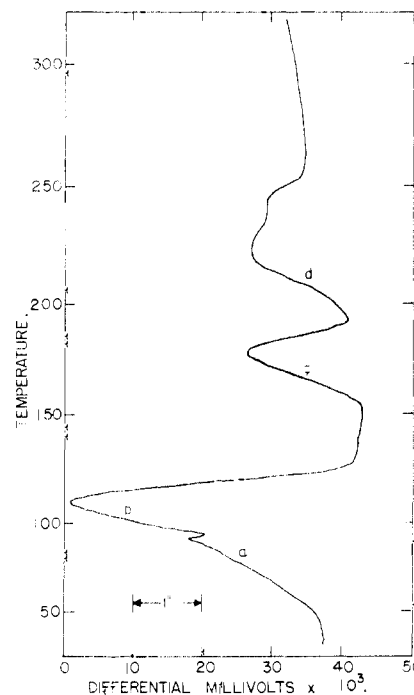


Fig. 5.—DTA trace of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ : furnace atmosphere saturated with water vapor; heating rate  $0.4^\circ/\text{min.}$ ; particle size,  $<16>$  40 mesh; ambient aqueous tension, 8 mm. a,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(s) + 2\text{H}_2\text{O}(l)$ ; b,  $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{O}(g)$  (from satd. soln.); c,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}(s) \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O}(s) + \text{H}_2\text{O}(g)$ ; a, b, c legends after ref. 2, d, presumably  $\text{CuSO}_4 \cdot \text{H}_2\text{O}(s) \rightarrow \text{CuSO}_4(s) + \text{H}_2\text{O}(g)$ .

pended beneath the barrel assembly,<sup>3</sup> so that the furnace, to a first approximation, was saturated with water vapor during the course of the experiment. The first three peaks have been adequately described by Borchardt and Daniels. Peak 3 now overlaps peak 4 as per the previous discussion. However, a new anomaly is introduced in that peak 4 is partially resolved into a doublet, the cause of which has not been ascertained.

In none of the experiments were the molecular rotation heat effects, reported by Taylor and Klug, observed. These authors were aware of the effect of particle size on the shape of a DTA curve but applied a completely different interpretation to its effects which is inconsistent with the preceding discussion. Ignoring for the moment the peaks obtained by them which correspond to the quadruple point and boiling of the saturated solution, the apparent isothermal nature of the peak due to the process system II  $113^\circ$  system III<sup>1</sup> is merely a result

of the experimental conditions. The first two processes are isothermal, but again the combination of experimental circumstances can lead to erroneous interpretation of the results, because of slope deviation prior to the isothermal halts, and difficulty in maintaining equilibrium during the transformations.

Borchardt and Daniels do not discuss the possible effects of particle size, furthermore the heating rates employed by them were extremely high, *ca.* 25 times greater than used in the present study. This primarily, in combination with the fact that their apparatus was less sensitive, by a factor of at least 4, than that used in the present work, explains the much higher apparent dissociation temperatures obtained by them. These differences amount to as much as  $100^\circ$  in a temperature interval of only  $250^\circ$ . It is of interest that examination of the DTA curves presented by Borchardt and Daniels show, in all cases, that the peaks were not at all indicative of isothermal processes.

While only a few of the determining factors have been discussed, these serve to illustrate the difficulties inherent in DTA hydrate studies.

It is contended that aside from the dubious applicability of DTA to the observation of transformation or boiling phenomena which in the absence of other information readily can be misinterpreted, the technique, when employed for hydrate studies, does not result in a definitive experiment.

**Acknowledgment.**—The authors are indebted to Dr. F. Holtzberg for his many stimulating discussions.

NEW YORK, NEW YORK

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

## Heterogeneous Equilibria in the Systems $\text{Li}_2\text{O}$ -, $\text{Ag}_2\text{O}$ - $\text{Nb}_2\text{O}_5$ and Oxide-Models

BY ARNOLD REISMAN AND FREDERIC HOLTZBERG

RECEIVED MAY 15, 1958

On the basis of the relative structural stability of interacting oxide end members, a qualitative model system theory for complex reactions is discussed. The heterogeneous equilibria in the  $\text{Li}_2\text{O}$ -,  $\text{Ag}_2\text{O}$ - $\text{Nb}_2\text{O}_5$  systems have been examined using DTA, X-ray and density techniques and compared with the system  $\text{Na}_2\text{O}$ - $\text{Nb}_2\text{O}_5$ . All three generate compounds having base to acid ratios of (I) 1:14, (II) 1:4, (III) 1:1 and (IV) 3:1. The silver and sodium analogs are believed to be isostructural. In the  $\text{Li}_2\text{O}$ - $\text{Nb}_2\text{O}_5$  system, I and II melt incongruently at  $1268$  and  $1231^\circ$ , respectively; III and IV melt congruently at  $1253$  and  $1408^\circ$ , respectively; III exhibits no first-order heat anomalies in the temperature interval, room temperature to its melting point; IV undergoes a sluggish phase transformation at  $1056^\circ$ .  $\text{AgNbO}_3$  exhibits thermal anomalies at  $292$  and  $578^\circ$  and dielectric anomalies at  $60$  and  $292^\circ$ . Ceramics of the silver salt gave fairly well defined hysteresis loops characteristic of a ferroelectric compound, but X-ray data show the presence of "extra lines" which are indicative of a multiple unit cell and are normally attributed to an antiferroelectric structure.

### Introduction

Several earlier papers have discussed the phase relationships in the anhydrous systems  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  with  $\text{V}_2\text{O}_5$ ,<sup>1</sup>  $\text{Nb}_2\text{O}_5$ ,<sup>2,3</sup> and  $\text{Ta}_2\text{O}_5$ .<sup>4</sup> Whereas the status of each of the above systems was generally confused by the large number of reported compounds, the  $\text{Li}_2\text{O}$ - $\text{Nb}_2\text{O}_5$  interaction presented no such difficulty since only one compound,  $\text{LiNbO}_3$ ,<sup>5</sup> had been identified. Similarly in the system  $\text{Ag}_2\text{O}$ - $\text{Nb}_2\text{O}_5$  only  $\text{AgNbO}_3$ , as the mono or dihydrate had been reported.<sup>6</sup> The choice of the  $\text{Li}_2\text{O}$  and  $\text{Ag}_2\text{O}$  systems as subjects of the present investigation was dictated on several counts; a knowledge of the meta

salt fields was necessary, preparatory to studies of mixed meta salt interaction involving either  $\text{LiNbO}_3$  or  $\text{AgNbO}_3$ ; the fact that the "ionic radius" of  $\text{Ag}^+$  lies between that of  $\text{Na}^+$  and  $\text{K}^+$  presented a distinct possibility that  $\text{AgNbO}_3$  would exhibit dielectric properties not unlike  $\text{NaNbO}_3$  or  $\text{KNbO}_3$ ; the systems represented one further phase of the extensive series of investigations being conducted by the Chemistry and X-Ray groups at this Laboratory.

### Experimental Procedure

**Reagents.**—Mallinckrodt analytical grade  $\text{Li}_2\text{CO}_3$  dried in  $\text{CO}_2$  at  $400^\circ$ , in gold-20% palladium and Fisher certified  $\text{Ag}_2\text{SO}_4$  dried at  $200^\circ$  in silver served as basic components in all reactions. The "High Purity"  $\text{Nb}_2\text{O}_5$  purchased from the Fansteel Co. was dried at  $1100^\circ$  in platinum prior to use.

**Sample Preparation.**—Cooling curve samples were weighed so as to yield 6-8 g. of melt after completion of reaction. The dried components for each composition were rolled in a glass vial and loaded into a 10-cc. platinum crucible. After the crucible was positioned in the DTA furnace, the temperature was raised  $100^\circ/\text{hr.}$  until the sample

(1) F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *THIS JOURNAL*, **78**, 1536 (1956).

(2) A. Reisman and F. Holtzberg, *ibid.*, **77**, 2115 (1955).

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(4) A. Reisman, F. Holtzberg, M. Berkenblit and M. Berry, *ibid.*, **78**, 4511 (1956).

(5) B. T. Matthias and J. P. Remeika, *Phys. Rev.*, **76**, 1886 (1949).

(6) C. W. Balke and E. F. Smith, *THIS JOURNAL*, **30**, 1637 (1908).