pended beneath the barrel assembly,[3] 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 $\xrightarrow{113°}$ system III[1] 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 devation 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° in a temperature interval of only 250°. 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 Li_2O–, Ag_2O–Nb_2O_5 and Oxide–Models

BY ARNOLD REISMAN AND FREDERIC HOLTZBERG

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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 Li_2O–, Ag_2O–Nb_2O_5 systems have been examined using DTA, X-ray and density techniques and compared with the system Na_2O–Nb_2O_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 Li_2O–Nb_2O_5 system, I and II melt incongruently at 1268 and 1231°, respectively; III and IV melt congruently at 1253 and 1408°, 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°. $AgNbO_3$ exhibits thermal anomalies at 292 and 578° and dielectric anomalies at 60 and 292°. 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 Na_2O or K_2O with V_2O_5,[1] Nb_2O_5[2,3] and Ta_2O_5.[4] Whereas the status of each of the above systems was generally confused by the large number of reported compounds, the Li_2O–Nb_2O_5 interaction presented no such difficulty since only one compound, $LiNbO_3$,[5] had been identified. Similarly in the system Ag_2O–Nb_2O_5 only $AgNbO_3$, as the mono or dihydrate had been reported.[6] The choice of the Li_2O and Ag_2O 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 $LiNbO_3$ or $AgNbO_3$; the fact that the "ionic radius" of Ag^+ lies between that of Na^+ and K^+ presented a distinct possibility that $AgNbO_3$ would exhibit dielectric properties not unlike $NaNbO_3$ or $KNbO_3$; 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 Li_2CO_3 dried in CO_2 at 400°, in gold–20% palladium and Fisher certified Ag_2SO_4 dried at 200° in silver served as basic components in all reactions. The "High Purity" Nb_2O_5 purchased from the Fansteel Co. was dried at 1100° 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°/hr. until the sample

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(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).

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

(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).

melted, and cooling curves were subsequently recorded. Density, X-ray and heating curve specimens were weighed to yield 15 g. of reacted material. The mixed components were solid-state reacted for three 24-hour periods at appropriate temperatures; 1200° for the range 0–20 mole % Li_2O, 990° for the range 50–75 mole % Li_2O and 800–1000° in O_2 for the range 0–50 mole % Ag_2O. The charges were pulverized in a mullite mortar after each heat treatment.

X-Rays.—All X-ray analyses were made with a N. A. Philips diffractometer or a Debye Scherrer camera using Ni filtered Cu radiation generated at 40 KV. and 20 ma.

DTA.—The cooling curve furnace previously described[2,4] was further modified by replacing the outer, Kanthal, ballast winding with a platinum one. All cooling experiments were conducted in 10-cc. platinum crucibles, and the melts were stirred with oxygen and seeded with crystallites obtained from preruns. Heating experiments were conducted in 1 cc. gold–20% palladium or platinum crucibles. These studies were made in the unmodified low heat capacity furnace,[7] using a differential sensitivity of 5 μv./inch. The differential sensitivity used in monitoring cooling curves was varied between 5 and 15 μv/inch. Heating rates of the order of 2°/minute and cooling rates of 2–4°/minute were employed.

Density Measurements.—The technique described in earlier publications[3,4] was used without modification.

Discussion of Experimental Results

a. The System Li_2O-Nb_2O_5.—Former studies have included descriptions of the binary joins, 75–100 mole % alkali carbonate, even though such regions are not continuations of the oxide–oxide diagrams. They do, however, represent the only fields in which the carbonates are stable in the systems M_2CO_3—M'_2O_5 under atmospheric conditions. In the present work, resolution of the carbonate portion of the diagram was not feasible, because of the great reactivity of the melts with all containers used.

Survey experiments conducted with 90–100 mole % Li_2CO_3 showed that the strange reaction behavior previously noted[1–4] and attributed to metastability reoccurred; the Nb_2O_5 partially reacted and then became passive, requiring that the samples be heated to higher temperatures, *ca.* 1300°, in order to drive the reactions to completion. This temperature was at least 500° above that expected for the liquidi. The Nb_2O_5 passivity was more pronounced with increasing Li_2CO_3 concentration, a phenomenon also observed in the other systems. In view of the violence of interaction in the lower alkali regions and the great reactivity of molten alkali carbonates, the discussed behavior is quite unexpected. Metastable equilibria in the systems M_2O-Nb_2O_5 and M_2O-Nb_2O_5-H_2O are considered in another paper.[8]

The thermal and density data obtained in this study are listed in Table I and the proposed "equilibrium" curves are depicted in Fig. 1 and 2.

αNb_2O_5 occurs as the primary crystallization in the liquidus field extending from 0–25 mole % Li_2O. At 1268°, in the region 0–6²/₃ mole %, the pentoxide partially reacts with liquid, forming $Li_2O \cdot 14Nb_2O_5$. From 6²/₃ to the 25 mole % peritectic, all of the Nb_2O_5 is converted to compound I + liquid. During the dynamic DTA experiment it is impossible to maintain equilibrium through successive incongruent transformations. Consequently, the stoichiometry of compound I was established with density measurements on a series of solid state reacted homogeneous samples. The intersection of the density curves, Fig. 2, occurs at 6.60 mole % Li_2O. The nearest small whole number ratio to this value is $Li_2O \cdot 14Nb_2O_5$.

TABLE I

THERMAL DATA FOR THE SYSTEM Li_2O–Nb_2O_5

Mole % Li_2O	Liquidus	Solidus	Transition	M.p., °C.	Primary phase
0				1491	αNb_2O_5
10	1427	1225	1265		αNb_2O_5
15	1386	1230	1268		αNb_2O_5
17.5	1361	1228	1267		αNb_2O_5
20	1331	1222	1269		αNb_2O_5
25	1274	1186	1231		αNb_2O_5
30	1234	1193			I
35	1204	1200			II
40	1226	1190			III
45	1247	1181			III
50				1253	III
55	1228	1153	1054		III
57.5	1201	1153			III
60	1166	1160	1056		III
62.5	1202	1153			IV
65	1251	1160	1057		IV
67.5	1296	1129			IV
70	1342		1056		IV
72.5	1376		1056		IV
75				1408	IV
77.5	1391				IV

DENSITY DATA FOR THE SYSTEM Li_2O–Nb_2O_5

Mole % Li_2O	Density, g./cm.³ at 25°
0	4.554
3	4.577
6	4.603 ± 0.004
9	4.653
12	4.724 ± 0.008
15	4.784

In the 25–30 mole % liquidus region, compound I occurs as the primary crystallization. In the interval 6²/₃ to 20 mole %, at 1228°, compound I partially reacts with liquid generating compound II, and in the 20–30 mole % range, compound I reacts completely with liquid forming the compound II secondary liquidus field. The stoichiometry of II was established by extrapolating the 1200° eutectic halt to zero differential peak height.[3,4] Additional confirmation was obtained with X-ray examination of samples at 17.5, 20 and 22.5 mole % Li_2O. The 17.5 mole % sample gave a pattern containing maxima of compounds I and II. The 22.5 mole % pattern showed the presence of compounds II and III. The 20 mole % pattern gave only the compound II lines.

The $Li_2O \cdot 4Nb_2O_5$ primary liquidus field extends from 30–36 mole %, and its solid field covers the region 20–50 mole % in association with III. The liquidus curve for the congruently melting $LiNbO_3$ ascends from 36 mole % to the melting point at 1253 ± 2° and 50 mole % Li_2O. It then descends to the eutectic at 60.5 mole % and 1160°. High gain, 5 μv./inch, DTA traces of $LiNbO_3$ in the range room temperature to the melting point failed to reveal any first-order anomalies.

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

(8) A. Reisman, F. Holtzberg and M. Berkenblit, *ibid.*, **81**, in press.

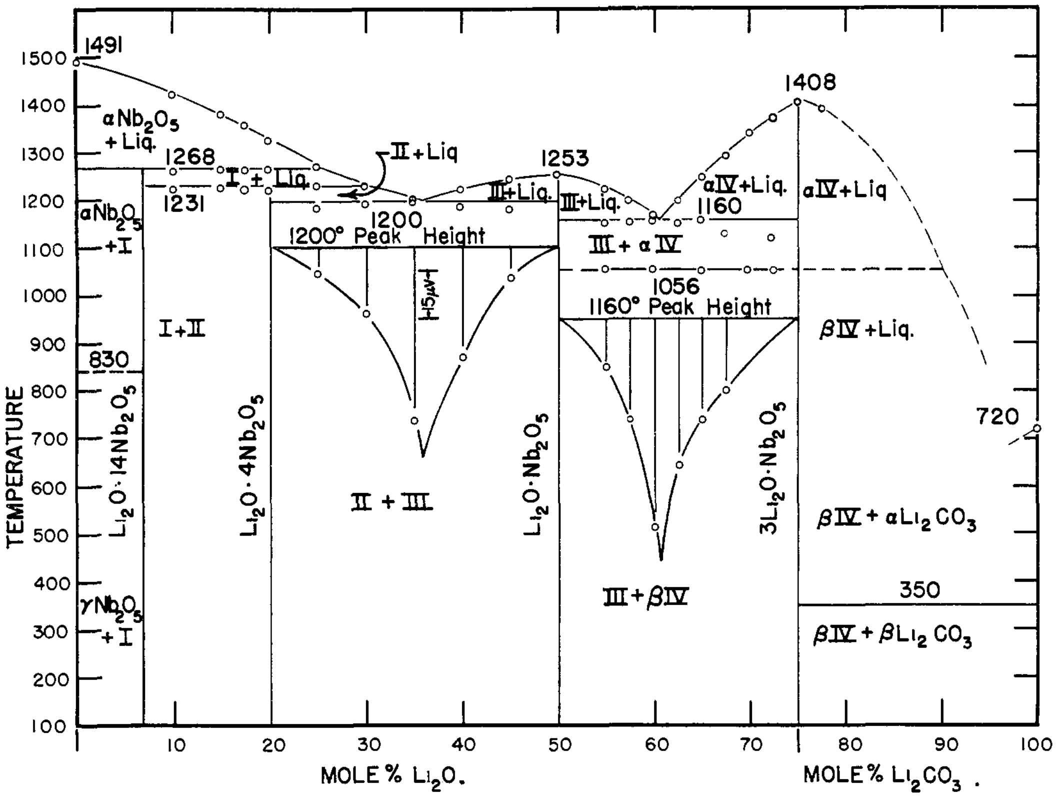

Fig. 1.—Thermal phase diagram of the system Li_2O–Nb_2O_5.

Compound IV melts congruently at 1408°. In the solid region 50–75 mole %, IV is in equilibrium with III and from 75–100 mole % with Li_2CO_3.[9] The great reactivity of molten Li_2CO_3 with the reaction vessels is almost sufficient to define the high alkali isoplethal boundary of the compound III-compound IV solid field. In the region around pure $LiNbO_3$ the samples are brown due to some oxygen loss. This brown color changes to a pale yellow after a 24 hour anneal at 1100° in an oxygen atmosphere. As the carbonate concentration is increased, the reduction of $LiNbO_3$ decreases, and the reaction mixtures become almost white. This color persists to 75 mole % Li_2O. At 75.5 mole % Li_2CO_3 the reaction mixtures become black or brown depending on whether the fusions are conducted in platinum or gold–20% palladium, respectively, and treatment of the cooled sample with acid results in the liberation of CO_2.

In the solid region 50–75 mole %, an anomalous reversible heat effect was observed at 1007 ± 3° on cooling and 1056 ± 0.5° on heating. The size of the anomaly, as measured on cooling curves, increased from a minimum at 50 mole % to a maximum between 65 and 70 mole % and then disappeared by 75 mole %. This suggested that III + IV reacted, yielding $2Li_2O \cdot Nb_2O_5$ at $66^2/_3$ mole %. In order to test this possibility, a series of samples reacted in the solid state were examined with X-rays and DTA. The X-ray series showed a progressive line intensity decrease of the $LiNbO_3$ pattern with a simultaneous line intensity increase of a new pattern from 50–75 mole % Li_2O, in complete contradiction to the cooling curve traces obtained with DTA. The same series of samples examined twice with heating experiments gave inconsistent results. The first series essentially duplicated the cooling experiments. The second series showed persistence of the anomaly up to but not including 75 mole %. Since the CO_2 loss of the samples corresponded to the theoretical amount and the identical samples gave non-reproducible DTA and reproducible X-ray results, the only plausible interpretation seems to be that the anomaly represents a phase transformation in $3 Li_2O \cdot Nb_2O_5$, which is sluggish in the absence of impurities. In order to account for the apparently reproducible, normal se-

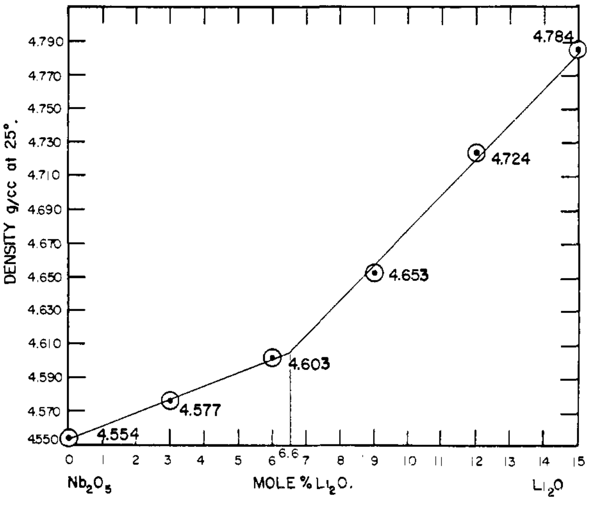

Fig. 2.—Density phase diagram of the system Li_2O–Nb_2O_5.

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(9) A. Reisman, THIS JOURNAL, **80**, 3558 (1958).

quence of line intensity variations, it is assumed that the transformation has gone to completion by the time the samples have been pulverized and X-ray examination is made.

Unfortunately the matter could not be unequivocally resolved because of the 900° upper limit of the X-ray diffractometer high temperature furnace. None of the compounds except $LiNbO_3$ could be readily indexed from powder data.

Despite the low water solubility of Li_2CO_3 as compared with the other alkali carbonates, all of the compounds generated in the system exhibited some degree of solubility, as evidenced by an alkaline reaction when any of the compounds were leached with water. Such behavior was not observed in any of the previous systems studied, where the alkali oxides were more alkaline in nature. It would appear that the combination of the most "acidic" alkali oxide with the acidic pentoxide results in slightly less stable niobate formation.

b. The System Ag_2O–Nb_2O_5.—Liquidus data could not be obtained for this system because of the decomposition with formation of free silver, at temperatures in excess of 1000°.

The phase diagram consequently was determined with X-rays using samples which had been prepared as described in the Experimental section. It was noted immediately that the patterns given by compositions corresponding to $6^2/_3$, 20, 50 and 75 mole % Ag_2O were the same as those obtained in the Na_2O–Nb_2O_5 system with minor displacement in "*d*" spacings and slight intensity variations. Samples on either side of these compositions were examined, and in all cases the traces showed the pattern of the next lower or high compound. Thus additional samples at 5, 6, 7.5, 10, 19, 21, 30, 40, 49, 51 and 60, and 74 mole % Ag_2O were studied, and the room temperature phase diagram was found to be equivalent to that of Fig. 1.

DTA examination of $AgNbO_3$ showed anomalies at 292 and 578°, and ceramic samples were then prepared in order to examine the dielectric properties of the compound. A plot of the dielectric constant *versus* temperature showed anomalies at 60 and 292°, the latter being more distinct. Polarization–electric field experiments were performed at temperatures up to 453°. Considering that ceramic specimens were employed, remarkably clean "loops" were observed in most samples examined. The nominal switching fields needed were of the order 1.7–2.3 kv./cm. Although all of the described experiments indicate that $AgNbO_3$ is ferroelectric up to 450° at least, the results may not be considered definitive in view of the following. X-Ray examination of the $AgNbO_3$ phase at 25° indicated that it was isostructural with the orthorhombic phase of $NaNbO_3$. Detailed X-ray examination of the variation of lattice parameters as a function of temperature is in progress and will be reported in a separate publication. Preliminary measurements indicate that the meta salt is cubic above 578°, the temperature of the upper specific heat anomaly. The diffraction pattern of $AgNbO_3$ at 25° showed the presence of lines which could not be accounted for by assuming a simple unit cell. In order to prove that the "extra lines" are attributable to $AgNbO_3$ and not to an impurity, the diffraction pattern given by the meta salt at 620° was examined. It was found that the "extra lines" were absent from the cubic phase pattern. The sample was cooled to 25° and the "extra lines" reappeared in the powder photograph indicating that they are $AgNbO_3$ diffraction maxima. Structurally therefore, solely on the basis of analogy with $NaNbO_3$, the material appears to be antiferroelectric, but as the atomic displacements which give rise to the "extra lines" are unknown, the question of the dielectric nature of the silver salt consequently is unresolved.

As is the case with the lithium niobates the complex diffraction patterns given by the other silver salts could not be indexed. Whereas the silver niobates are apparently isostructural with the sodium niobates, the equivalent lithium niobates gave diffraction patterns not obviously related to their sodium and silver analogs.

Comparison of the $AgNbO_3$ and $NaNbO_3$ diffraction patterns showed the absence of certain groups of lines in the $AgNbO_3$ trace. In the cubic phase the absences are those of a body centered structure except that the 111 reflection is observed. On the basis of structure factor calculations the absences were shown to be accidental, and similar in origin to those in KCl. Although the computations require that all reflections *hkl*, all odd, have finite intensity, their absence, except for the 111 can probably be attributed to the fact that they are weak reflections and that the powder specimens were of relatively poor crystallinity. The room temperature form of $AgNbO_3$ was indexed on the basis of a non-multiple monoclinic unit cell with $a = c = 3.943$ Å.; $b = 3.917$ Å., $\beta = 90°34'$.

c. Model System Relationships in the Sequence Alkali Oxide Group-VB Pentoxide.—On the basis of Goldschmidt's criteria[10] for model system behavior, the systems K_2O–Nb_2O_5[2] and K_2O–Ta_2O_5[4] should be almost perfect subjects, because the ionic radii and polarizabilities of the heavy metal ions are similar. It has, however, been adequately demonstrated that the compounds generated in the regions 0–50 mole % alkali oxide do not have the same stoichiometries, the niobate system giving rise to 2:33, 1:3, 2:3 and 1:1 compounds and the tantalate system to 1:5, 1:2 and 1:1 compounds.

Considering now the substitution of Li^+ for any of its congeners in the interaction alkali oxide–Nb_2O_5 and applying the radius ratio test, it is apparent that the possibility of the lithium containing systems modeling any of the others is extremely remote since even in comparison with Na^+ the radius ratio $Na^+/Li^+ \simeq 1.66$ is extremely unfavorable.

Thus, two extreme situations have been described, both of which are ideally suited to testing the applicability of the Goldschmidt hypothesis, since single ion substitution is involved. In the tantala–niobia case the criteria are satisfied, but the systems do not generate equivalent compounds. In the case of the alkali metal and silver ion substitutions where model behavior is forbidden, it is observed.

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[10] V. M. Goldschmidt, *Skrift Norski Vid. Akad. Oslo, Mat. Nat. Kl.*, **8**, 7 (1926).

It is apparent that in complex reactions of the type discussed involving high melting oxides, one cannot use radius ratios in order to predict or prohibit model relationships between different systems. In general, the Goldschmidt hypothesis when employed in the past, has proved valid in isolated regions of diagrams, if at all, indicating that its prediction of model behavior is fortuitous.

On the basis of the above, an alternative approach to explain model or non-model behavior suggests itself. In the systematic study of the substitution of the series of ions Li^+, Na^+, Ag^+ and K^+, in reactions of the type M_2O–Nb_2O_5, one observes the interaction between end members having different structural stabilities. The M–O bond is extremely labile, relative to the Nb–O bond. X-Ray examination of almost all the alkali niobates, studied thus far, shows a persistence of interplanar spacings attributable to an O–Nb–O configuration. This strongly suggests that the preferred stoichiometries of generated compounds, and to a first approximation their structures, are determined by the NbO_6 octahedral arrangement. It is believed that the addition of increasing concentrations of M_2O causes changes in the inter-octahedral coördination from face sharing to edge sharing, etc., in a manner analogous to that observed in silica systems where the stable structural entity is the SiO_4 tetrahedron.

It is interesting to note that in the systems Li_2O–SiO_2[11] and Na_2O–SiO_2[12] compounds of equivalent stoichiometries are formed while marked deviations are again observed in the K_2O–SiO_2[13] interaction. Unfortunately, the literature dealing with binary reactions involving TiO_2, P_2O_5, GeO_2 and Be_2O_3 amongst others is either incomplete or contradictory and, therefore, these systems could not be evaluated.

It would appear therefore that radius ratio tolerances must be supplanted by a consideration of the hole size created by the packing of the stable structural unit. The "hole" apparently can accommodate ions up to a critical size with minor perturbations in the preferred structure which are reflected ultimately in the compound stoichiometries. The failure of the niobia–tantala systems to model one another can be resolved on the basis of the structural dissimilarities of the stable pentoxides. The results of a study of the interaction Nb_2O_5–Ta_2O_5 show that these materials do not form an uninterrupted series of solid solutions.[14]

Pending the accumulation of quantitative structural data of compounds studied and more extensive investigation of other congener series, a preliminary hypothesis for predicting model system behavior in oxide–oxide systems can be stated as follows:

1. In the interactions being compared, the end members must consist of one stable or structural determining factor and one labile member.

2. (a) If in the interactions being compared, the stable end members of each are structurally similar, model behavior should be observed.

(b) If the stable, structurally dissimilar end members do not form an uninterrupted series of solid solutions, model behavior is prohibited.

3. In a sequence of interactions in which the cationic size of the labile end member increases, deviation from model behavior is observed when the ionic radius of the cation approximates that of oxygen, *viz.*, $r_{K^+} \sim r_O$.

4. (a) In comparing interactions of stable-stable or labile-labile end members, model behavior cannot be predicted. Furthermore such systems cannot be expected to model labile-stable interactions.

The enumerated conditions are seen to severely restrict the possibility of observing model behavior between different systems. The limited number of verified models reported in the literature supports this contention.

NOTE ADDED IN PROOF.—After receipt of galley proof, an article by M. H. Francombe and B. Lewis, *Acta Cryst.*, **11**, 175 (1958), came to the attention of the authors. Data for $AgNbO_3$ are presented which approximate those reported herein.

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(11) F. C. Kracek, *J. Phys. Chem.*, **34**, 2645 (1930).

(12) F. C. Kracek, *ibid.*, **34**, 1588 (1930); THIS JOURNAL, **61**, 2869 (1939).

(13) F. C. Kracek, N. L. Bowen and G. W. Morey, *ibid.*, **41**, 118 (1937).

(14) To be published.