TABLE II

SPECTRAL DATA AND DISSOCIATION CONSTANTS FOR CYCLIC SULFIDE DIIODIDES

	Thiacyclobutane		Thiacyclopentane		Thiacyclohexane	
λ (mμ)	ϵ	$K \times 10^3$	ϵ	$K \times 10^3$	ϵ	$K \times 10^3$
420	1690	12.0	2310	5.46	2570	8.85
430	1855	11.6	2500	5.30	2810	9.30
440	1920	11.7	2460	5.41	2620	8.98
450	1680	10.7	2130	5.38	2330	9.16
Av. K	11.5 ± 0.5		5.39 ± 0.06		9.07 ± 0.17	
λ_{max} (mμ)	437		431		431	

The iodine absorptivities are also taken from that work.

Too little is known at the present time about dissociation constants of compounds of the type R_2SI_2 to discuss the results in terms of either structure or $\lambda_{max.}$ values. It is interesting to note that, although the constants are all comparable to that for dimethyl sulfide diiodide, there is no systematic relationship among the cyclic sulfide diiodides with respect to ring size. The accuracy of the present determination is, without doubt, high enough to state that the order of stability of the diiodides is definitely thiacyclopentane > thiacylohexane > thiacyclobutane > dimethyl sulfide.

The position of the four-membered ring compound (Tcb) in this series is at variance with the results of Tamres and Hudson[5a,b] on the stabilities of cyclic ether–iodine complexes in *n*-heptane solution.

The order of the stabilities of the ether–iodine complexes was found to be trimethylene oxide > tetrahydrofuran > tetrahydropyran. As a check on the dissociation constant of the Tcb–I_2 compound, a sample of Tcb was redistilled *in vacuo* in an all-glass system to minimize the possibility of Tcb polymer or other impurities being present. A new series of solutions was prepared and measured and the results were in excellent agreement with the previous findings for Tcb–I_2.

Polymerization of Thiacyclobutane.—In the preliminary work on the Tcb-I_2 compound it was found that the more concentrated solutions (*i.e.*, those with formalities of Tcb and I_2 both above 3×10^{-3} F) deposited a brown material on the container walls. This material was insoluble in the common organic solvents but was bleached white by aqueous sodium metabisulfite, probably by removal of iodine. The white residue was also insoluble in acetone, ether, alcohol, etc. Solutions with the compositions in Table I show no deposits, even after several weeks. However, there is a slow decrease in the absorbances with time over the range 400–550 mμ. For this reason, all data used in the final computations were obtained within a few hours after mixing the solutions. No deposits were evident in any of the Tcp and Tch solutions. Further studies of the Tcb polymer are in progress.

Acknowledgments.—The authors gratefully acknowledge the financial assistance of the National Science Foundation under Research Grant NSF-G2354 and the kindness of the Petroleum Experiment Station, Bureau of Mines, United States Department of Interior for supplying the cyclic sulfides through American Petroleum Institute Research Project 48A. We also wish to thank Miss Donna Karasek for making the final measurements on the Tcb compound.

LOS ANGELES, CALIF.

(5) (a) M. Tamres and M. Hudson (to be published). (b) Sister Mary Brandon Hudson, Ph.D. thesis, University of Michigan, June 1957.

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Metastability in Niobate Systems

BY ARNOLD REISMAN, FREDERIC HOLTZBERG AND MELVIN BERKENBLIT

RECEIVED JULY 2, 1958

Experiments are described which together with previous information[2] elaborate on one of the metastable equilibria in the interaction K_2O–Nb_2O_5. Quenched samples having an initial composition of 49.9 mole % K_2O were found to consist of fibrous insoluble and non-descript soluble fractions. The fibrous phase was found to contain 76.55 ± 0.15 weight % Nb_2O_5 corresponding to approximately $6K_2O \cdot 7Nb_2O_5$. On the basis of DTA and X-ray analysis, the recrystallized water-soluble fraction appeared to be identical to the $7 \cdot 6 \cdot 27H_2O$ compound reported in the early literature. It is believed that the metastable system 6:7–7:6 exists at the expense of the 2:3–1:1 and 1:1–3:1 fields and that such behavior in intermediate composition ranges is directly related to deviations from model behavior and shows a possible extension of the ternary aqueous, into the anhydrous system.

Introduction

In studying "equilibrium" interactions of the type M_2O–$M_2'O_5$, two problems have been encountered with disturbing regularity. The first involves metastable field formation, and the second relates to the dissimilarity between the aqueous and anhydrous systems. In a recent paper,[1] model relationships among several niobate systems have been qualitatively explained on the basis of the relative structural stability of the end members. Subsequent re-evaluation of certain data pertaining to intermediate composition metastability in the system K_2O–Nb_2O_5[2] indicated that the problem was directly related to the model system hypothesis and that a possible correlation existed between the aqueous and anhydrous systems *via* this metastability.

Discussion of Experimental Results

Because the experiments are best described in context, a separate Experimental section has been omitted. The techniques of measurement re-

---

(1) A. Reisman and F. Holtzberg, THIS JOURNAL, **80**, 6503 (1958).

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

ferred to have been described in earlier papers and were employed without modification.

In the Na_2O–Nb_2O_5 study,[3] data were obtained which signified a metastable equilibrium in the join, 75–100 mole % carbonate. Similar evidence of metastability was found in all the other systems studied.[1,2,4,5] Since the 75–100 mole % interactions appeared identical, to a first approximation, they are probably carbonate controlled. Furthermore, as these regions are not continuations of the oxide–oxide equilibria, they are not of direct concern in the present discussion and are mentioned only because the behavior observed in them tended to obscure the significance of a second type of metastability encountered in only two systems. In one of these, K_2O–V_2O_5, metastable field formation in pentoxide compositions as great as 40 mole % was noted, but pending studies of the remaining alkali oxide–V_2O_5 diagrams nothing more can be said. In the sequence of interactions Li_2O-, Na_2O-, Ag_2O- or K_2O–Nb_2O_5, coincident with the deterioration of model behavior, regions of metastability are observed in the last member of the series. The affected portions of the diagram include, amongst others, the $K_2O{\cdot}3Nb_2O_5$–$2K_2O{\cdot}3Nb_2O_5$ and the $2K_2O{\cdot}3Nb_2O_5$–$K_2O{\cdot}Nb_2O_5$ fields.

In the absence of seeding techniques,[2] cooling curves for compositions containing 35–50 mole % K_2O, showed an initial liquidus crystallization followed by a sharply rising spike and at a lower temperature the final solidification, Fig. 2, ref. 2. It was postulated that the initial crystallization involved the formation of a metastable phase and that the ensuing spike represented transformation of the metastable phase into the stable species. Attempts were made to quench several compositions in the range 45–50 mole % K_2O in order to isolate the metastable system. The appearance of the rapidly cooled samples served as a guide in estimating the degree to which the metastable phases had been frozen in. For poor quenches the specimens exhibited a microcrystalline surface, and with better quenches the samples acquired a characteristic fibrous habit. The greatest success was achieved in the range 49.9–50.1 mole %, and diffraction studies of samples quenched in this region failed to reveal $KNbO_3$ maxima.

Samples containing 49.9 mole % K_2CO_3 were fused in platinum crucibles using an oxy-gas hand torch. A small quantity, 0.1–0.5 g. of melt was poured onto a 10 mil thick platinum foil which was heated to remelt the partially quenched bead and flicked to remove excess material. The thin film which adhered was then quenched by applying a stream of oxygen to the undersurface of the foil, and the sample obtained by repeating this process many times was stored in an airtight vial. In all, *ca.* 1.5 g. of quench product were obtained for each separate quenching series. In the region involved, $KNbO_3$ tends to lose oxygen and exhibit a blue color. The quench product contained minute agglomerates of blue material randomly distributed in the otherwise white fibrous matrix. The blue material, subsequently confirmed as the meta salt, was removed by hand picking under the microscope, and the remaining fibrous mass was examined using DTA, X-ray and chemical analysis.

The quench product was heated at 2°/minute in the DTA apparatus.[6] At 520° a sharp, non-reversible exotherm occurred. Subsequent heating and cooling curves showed only the phase transformations associated with the structural changes in $KNbO_3$, at 416 and 214°. X-Ray powder photographs of the quench product prior to thermal treatment were not well resolved but the diffraction pattern was distinctly different from that of any known equilibrium potassium niobate.[2] X-Ray examination of the specimen after the exothermic evolution showed only $KNbO_3$ diffraction maxima indicating that the 520° heating exotherm represented the process metastable phases → stable phases. Since the indications of a metastable equilibria were observed in the liquidus regions of the diagram, the 520° temperature observed in this study is probably unimportant, depending critically on the heating rate, completeness of quench and thermal excitation of the atoms. A similar phenomenon was observed in studying the transformation amorphous $Nb_2O_5 \rightarrow$ crystalline Nb_2O_5,[6] in which the temperature of transformation was found to be critically time dependent.

In the 0–50 mole % Nb_2O_5 region of the diagram, the equilibrium potassium niobates are extremely insoluble in water.[7] The quenched samples, 49.9 mole % K_2O, which had been exposed to air for several hours caked slightly and leaching with water showed the presence of a soluble alkaline fraction. The entire quench sample was then extracted with water, and the insoluble fibrous fraction dried at 100° for 1 hr. was examined using DTA. The pattern was identical to that given by the original total quench product, and X-rays now showed the presence of $2K_2O{\cdot}3Nb_2O_5$ in addition to $KNbO_3$. The soluble fraction was recrystallized from water yielding a colorless crystalline material.

The fibrous material prepared from melts having the composition 49.9 mole % K_2O was chemically analyzed using the method previously reported,[8] and the results of four analyses performed on two separate samples prepared at different times were 76.55 ± 0.15% Nb_2O_5, corresponding to a stoichiometry of 46.37 mole % K_2O. The closest whole small number ratio for the compound is $6K_2O{\cdot}7Nb_2O_5$, 46.15 mole % K_2O. It would appear from what has been found that this compound exists metastably with respect to the binary system $2K_2O{\cdot}3Nb_2O_5$–$K_2O{\cdot}Nb_2O_5$ at all temperatures in the interval, room temperature to the liquidi in the range 40–50 mole % K_2O. It is believed that the 6:7 niobate has no stable field of existence for the following rea-

---

[3] A. Reisman, F. Holtzberg and E. Banks, THIS JOURNAL, **80**, 37 (1958).

[4] F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *ibid.*, **78**, 1536 (1956).

[5] A. Reisman, F. Holtzberg, M. Berkenblit and M. Berry, *ibid.*, **78**, 4514 (1956).

[6] F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *ibid.*, **79**, 2039 (1957).

[7] It is for this reason that samples containing more than 50 mole % Nb_2O_5 were studied. Since fusion mixtures containing ~50 mole % K_2O lose as much as 0.05 mole % K_2O due to volatility, the final composition of the samples examined is estimated to have contained between 49.8 and 49.9 mole % K_2O.

[8] A. Reisman, F. Holtzberg, S. Triebwasser and M. Berkenblit, THIS JOURNAL, **78**, 719 (1956).

sons: (1) upon heating, the compound transforms exothermally. If the material was part of the stable diagram, an endothermic transformation would be most probable. (2) The compound has been formed only by quenching from the molten state. (3) The 2:3 and 1:1 compounds prepared *ca.* 5 years ago and heat treated on numerous occasions have shown no evidence of conversion.

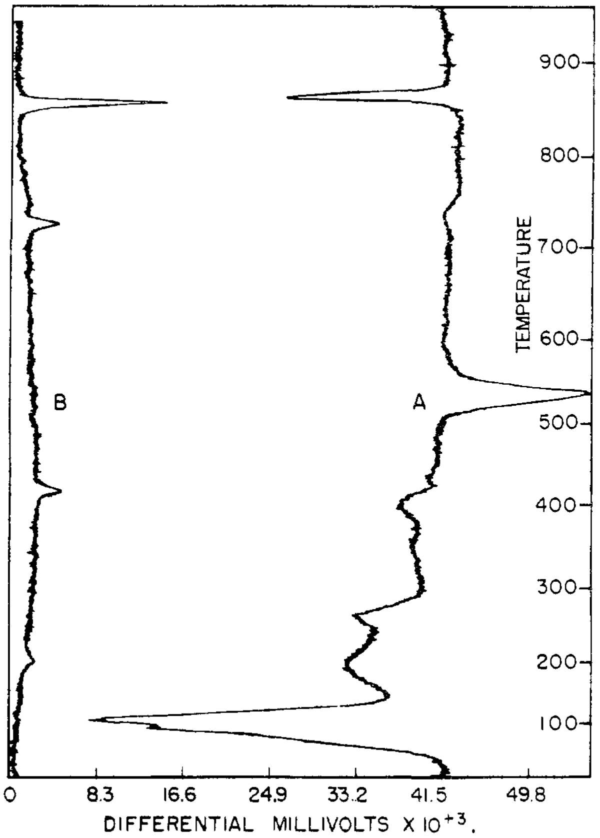

Fig. 1.—DTA trace of the 7:6·27H_2O hydrate.

The Water-soluble Fraction.—All of the anhydrous systems evaluated thus far are reported to generate hydrated compounds in the ternary interaction. While the stoichiometries of the hydrates have been the subject of considerable controversy, it is interesting that in the majority of cases they have no known counterparts in the anhydrous systems, *viz.*, no 7:6, or 4:3 base:acid anhydrous compounds exist stably. Yet it is apparent that when dehydrated, the aqueous derived compounds are part of some anhydrous, metastable interaction. An attempt was made to determine the temperature interval of stability of the dehydrated potassium niobate hydrates and perhaps show a link between the hydrated and anhydrous systems.

The methods employed by Balke and Smith[9] were utilized in preparing compounds purported to have stoichiometries of $7K_2O·6Nb_2O_5·27H_2O$ and $4K_2O·3Nb_2O_5·16H_2O$, the former obtainable only by addition of an alcohol to a solution of the 4:3·16 hydrate. These chemicals were each recrystallized 10–15 times from "CO_2-free water" *in vacuo.* Between each recrystallization the solutions were centrifuged to remove small quantities of Nb_2O_5 resulting, it is believed, from the hydrolysis of the niobates in the presence of traces of CO_2. For each reagent, the products of successive recrystallizations gave essentially the same X-ray and DTA traces. While there appears to be no doubt that two distinct hydrates exist, their stoichiometries could not be established beyond certain limits, because of the general difficulty in preparing stoichiometric hydrates which are not stable under ambient aqueous partial pressures and whose vapor pressure temperature relationships are unknown and because of the limits of accurate Nb_2O_5 analysis. Thus analysis of the two dehydrated niobates showed Nb_2O_5 wt. % of *ca.* 68 and 71 corresponding to mole ratios of 4:3 and either 7:6 or 8:7. The water contents of each are much more uncertain and this problem is being investigated.

Figure 1a represents a DTA heating curve of what we shall call the "7:6·27H_2O" compound. The lower, endothermic peaks represent the isobaric dissociation of the hydrate. There appear to be four, and possibly five dehydration stages, if the endotherm at *ca.* 100° is not attributable to a decomposition. In the neighborhood of 510°, a sharp, non-reversible, exotherm occurs; followed at 730° by a small endotherm and at a still higher temperature by the eutectic melting in the 50–75 mole % join of the K_2O–Nb_2O_5 system. Once the 510° exotherm has occurred, the cooling curve, Fig. 1b, shows in addition to the two high temperature effects, the phase transformations associated with $KNbO_3$. Subsequent heating curves are mirrors of Fig. 1b, and X-ray analysis confirmed that the transformation at *ca.* 510° is due to the process dehydrated hydrate $\rightarrow KNbO_3 + 3K_2O·Nb_2O_5$.

When the water-soluble phase of the quenched sample was examined with X-rays and DTA, it gave the patterns of the 7:6 hydrate. This is interesting since the 7:6 hydrate is not obtained directly from the solution of an equilibrated fusion mixture of K_2CO_3 and Nb_2O_5 in the region 50–100 mole % K_2O. This indicates that the 7:6 compound forms directly in the quenched sample and not after treatment with water. Of further interest is the fact that the exotherms exhibited by the 6:7 and 7:6 compounds occur at about the same temperature which explains why two separate thermal anomalies are not observed in a heating curve of the complete quench product. It is probable that the compound $7K_2O·6Nb_2O_5$ is metastable with respect to the system $K_2O·Nb_2O_5$–$3K_2O·Nb_2O_5$ using the same reasoning as for the 6:7 compound. Of related interest is the observation that the 4:3 hydrate is probably metastable with respect to some system involving the 7:6 hydrate since once the latter compound has formed, the 4:3 compound cannot be generated except by a fusion and solution process.

On the basis of the experiments described, it is believed that even though one of the hydrates may exist metastably with respect to a system involving the other, both, when dehydrated, form part of met-

---

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

astable systems in the interaction K_2O–Nb_2O_5 and represent an extension of the ternary, aqueous, into the binary anhydrous diagram.

Further experiments were conducted with the 4:3·16 hydrate which also exhibited a non-reversible exotherm at *ca.* 510° resulting in the formation of the stable anhydrous system.

NEW YORK, NEW YORK

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

Constitution of Aqueous Oxyanions: Perrhenate, Tellurate and Silicate Ions

BY JOSEPH E. EARLEY, DONALD FORTNUM, ANDREW WOJCICKI AND JOHN O. EDWARDS

RECEIVED OCTOBER 10, 1958

Evidence is presented which indicates that the predominant form of the perrhenate ion in aqueous solution is tetrahedral, but that forms of higher coördination number are possible under extreme conditions of acidity and basicity. From Raman spectral data, the silicate ion is shown to be $SiO_2(OH)_2^=$. Equilibrium constants for the first two ionizations of telluric acid have been measured by potentiometric and spectrophotometric techniques and have been found to be $K_1 = 2.0 \times 10^{-8}$ and $K_2 = 9.2 \times 10^{-12}$. Spectrophotometric evidence has been found for a third ionization; the value $K_3 = 3 \times 10^{-15}$ has been estimated. The ultraviolet absorption spectra of telluric acid and its mono- and di-negative ions have been measured. The stability constant of the peroxytellurate ion has been found to have the value $K_s = 0.68$. Potentiometric evidence for the existence of polytellurate ions is given. The coördination number of tellurium in tellurate species is shown to be six in aqueous solutions.

Introduction

It has been realized for some time that the central atoms of oxyanions in aqueous solution may not have the same coördination number (hereafter c.n.) at all *p*H values. For example, tetravalent carbon can be in either c.n. two or c.n. three and heptavalent iodine can be in c.n. four or c.n. six. In this study, perrhenate, tellurate and silicate ions have been investigated by various experimental methods to see if any change in c.n. could be detected.

Experimental

Equipment.—The Raman spectra were taken on a Photoelectric Recording Raman Monochromator. Infrared spectra were taken using the pellet technique. The ultraviolet spectra were taken with a Beckman DU Spectrophoto and quartz cells. *p*H data were obtained with the Beckman models G and GS meters. All equilibrium measurements were made at 25°. The limits of error for measurements are indicated in appropriate sections.

Materials.—For the perrhenate studies, Re_2O_7 samples from A. D. Mackay, Inc., and The University of Tennessee were used. In the silicate studies, B. & A. sodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$, and ACS reagent sodium hydroxide were the compounds mostly used; other silicate samples gave similar results. Na_2PO_3F was obtained from Ozark-Mahoning Co. Reagent grade salts were used whereever available; other salts were recrystallized. Telluric acid was prepared by oxidizing impure metal with nitric acid to TeO_2 and then oxidizing the dioxide with permanganate.[1] Purification was effected by one recrystallization from nitric acid, followed by from seven to nine recrystallizations from water. Some telluric acid samples were prepared by alternative methods[2] or were purchased. All of the telluric acid samples were recrystallized from water. Solutions of the acid were standarized by *p*H titration in the presence of glycols.[4] The well-known colloid-forming property of hexavalent tellurium was often encountered. Solutions containing more than 0.04 *M* of KH_5TeO_6 were observed to form opalescent suspensions on standing; therefore the highest concentration used was 0.03 *M*.

Hydrogen peroxide solutions were made from 90% reagent material donated by ·BECCO. Other solutions were made from reagent materials and were analyzed by standard procedures.

Procedures.—Measurements of optical absorbancy as a function of *p*H were made as follows: Two hundred ml. of telluric acid solution of the desired concentration and ionic strength was placed in a beaker in a water-bath. The *p*H of this solution was repeatedly adjusted by the addition of very small quantities of 2.5 *M* base from a microburet. After each addition, the *p*H of the solution was measured and a 5-ml. sample withdrawn and placed in a closed container. When samples covering the desired *p*H range had been withdrawn, the absorbancy of each sample was measured and the entire procedure then repeated. For *p*H values greater than 12, samples were made up individually with concentrated KOH; H_0 values were calculated from the hydroxyl ion concentrations.

Optical density measurements at 275 mm. (mμ) were corrected for absorption due to hydroxyl ion using 0.017 as the appropriate molar extinction coefficient. Tellurate buffer solutions were prepared by adding the calculated amount of base to acid solutions and then diluting to the desired volume.

The effect of μ (ionic strength) on the *p*H of these buffers was studied as follows. Two equal portions of the buffer were diluted, one with stock electrolyte ($NaClO_4$ or NaCl) and the other with water; both were thermostated and one portion titrated into the other with the *p*H being measured after each addition. The effect of concentration of buffer was studied in a similar manner, isotonic salt solutions being mixed with the buffer and the *p*H measured after each mixing.

Extinction coefficients for the tellurate ions were measured on solutions prepared by diluting telluric acid stock solutions with buffers (borate and phosphate) of the appropriate *p*H. Polymerization experiments were performed by measuring the *p*H of solutions prepared by diluting concentrated telluric acid solutions. Peroxide systems were made up using tellurate buffers as previously described and 3.0 *M* hydrogen peroxide.

Results

Perrhenate Ion.—The majority of the perrhenate salts found suggest an anion of tetrahedral symmetry; however, there is a hint that the rhenium atom can take on a higher c.n. Raman and infrared data in solution are consistent with the tetrahedral structure,[5–7] although the results at

---

(1) F. C. Mathers, C. M. Ric, H. Broderick and R. Forney, in "Inorganic Syntheses," Vol. II, L. F. Audrieth, Ed., McGraw-Hill Book Co., New York, N. Y., 1950, p. 145.

(2) In this Laboratory, Mr. H. A. Chopoorian found it difficult to obtain good results with the method of Horner and Leonard.[3]

(3) H. J. Horner and G. W. Leonard, Jr., THIS JOURNAL, **74**, 3694 (1952).

(4) J. O. Edwards and A. L. Laferriere, *Chemist-Analyst*, **45**, 12 (1956).

(5) L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 615 (1956).

(6) R. Fonteyn, *Naturw. Tijdschr.* (*Belg.*), **20**, 20 (1938).

(7) H. H. Claasen and A. J. Zielen, *J. Chem. Phys.*, **22**, 707 (1954).