Finally, the results obtained suggest the stereochemical changes diagrammed in Table II. The tetragonal pyramid structure is assigned the pentacoordinated intermediate in the one electron reactions on the basis of the following evidence. (1) Calculations by Daudel and Bucher[21] show that this stucture is possible for the dsp^3 hybridization assigned this complex. (2) K. A. Jensen and B. Nygaard[22] report that the nickel(III) complex, $NiBr_3 \cdot 2Et_3P$, has a tetragonal pyramid structure. Since nickel and platinum are members of the same group in the periodic table and have the "same" valence electronic configuration, it is believed that the platinum(III) complexes will have the same structure as do those of nickel(III). (3) The quantitative conversion of platinum(II) complexes to the analogous platinum(IV) compounds which contain the entering groups in *trans* positions suggests that rearrangement to a trigonal bipyramid structure is unlikely. (4) The fact that one electron reactions do not induce racemization is likewise consistent with the tetragonal pyramid structure. There are ten geometric isomers theoretically possible for a trigonal bipyramid structure of [Pt *i*-bn *m*-stienCl]$^{+2}$. Six of these are asymmetric but four of them are symmetrical, as for example It would therefore appear that if the pentacoördinated intermediate had such a structure then some racemization would have accompanied these reactions.

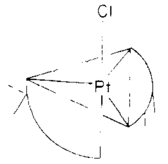
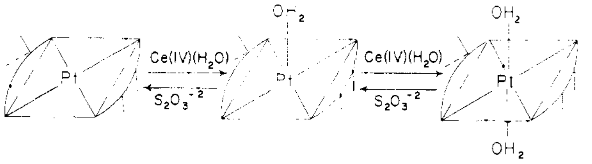
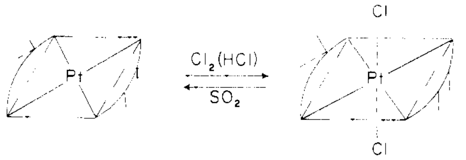


TABLE II

STEREOCHEMISTRY OF PLATINUM COMPLEXES IN OXIDATION-REDUCTION REACTIONS



One electron reagent



Two electron reagent

Finally the octahedral structure of platinum(IV) is well known and the evidence for the *trans* configuration cited for the two electron reactions has been discussed already.

Acknowledgment.—The authors wish to thank Dr. F. P. Dwyer for suggesting the use of the Mills and Quibell complex. We are also indebted to Dr. R. G. Pearson for stimulating discussions in connection with this investigation.

EVANSTON, ILL.

---

[21] R. Daudel and A. Bucher, *J. chim. phys.*, **42**, 6 (1945).

[22] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, **3**, 474 (1949).

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. III. Thermal and X-Ray Phase Diagrams of the System K_2O or K_2CO_3 with Ta_2O_5

BY ARNOLD REISMAN, FREDERIC HOLTZBERG, MELVIN BERKENBLIT AND MARGARET BERRY

RECEIVED APRIL 9, 1956

The phase diagram of the system K_2O or K_2CO_3 with Ta_2O_5 has been determined using differential and conventional thermal analysis, optical pyrometry and X-ray techniques. Four compounds corresponding to the formulas (I) $K_2O \cdot 5Ta_2O_5$, (II) $K_2O \cdot 2Ta_2O_5$, (III) $K_2O \cdot Ta_2O_5$ and (IV) $3K_2O \cdot Ta_2O_5$ have been identified. Compounds I, II and III melt incongruently at 1645, 1520 and 1370°, respectively. Within experimental limits the ferroelectric compound III occurs at a singular point between congruent and incongruent melting. The density of III has been determined as 6.96 g./cm.^{3} at 25°. Compound IV melts congruently at 1330°. The polymorphism of Ta_2O_5 has been reinvestigated from room temperature to its melting point. A low temperature form, β, melts at 1785 ± 30° and has a density of 8.18 g./cm.^{3} at 25°. At 1360 ± 5°, β transforms to a high temperature modification, α, with a melting point of 1872 ± 10°, and a density of 8.37 g./cm.^{3} at 25°. On the basis of a combination of geometric and electronic factors this system was expected to exhibit model behavior with respect to the K_2O–Nb_2O_5 system, but differed markedly. X-Ray powder data for all the anhydrous compounds have been determined and ambiguities concerning Ta_2O_5 interplanar spacings have been resolved.

Introduction

This paper is the third in a series involving a study of the high temperature reactions of alkali oxides and carbonates with the group VB pentoxides[1,2] and marks completion of that portion of the investigation in which K_2O is the basic component.

Mellor[3] reports the existence of only one anhydrous potassium tantalate, *viz.*, $KTaO_3$. This is interesting in view of the large number of anhydrous potassium niobates and vanadates listed in this treatise. Potassium metatantalate exhibits the perovskite structure with cell constant a =

---

[1] A. Reisman and F. Holtzberg, THIS JOURNAL, **77**, 2115 (1955).

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

[3] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., New York, N. Y., 1952, p. 901.

3.9885 Å.[4] Hulm, *et al.*, reported a ferroelectric transition at 13°K.[5] Attempts to grow crystals of $KTaO_3$ from melts containing K_2O and Ta_2O_5 were only successful in mixtures richer than 50 mole % K_2O. An analogous observation was made in attempting to grow potassium metaniobate in the system K_2O–Nb_2O_5, and was attributable to the meta compound maximum occurring at a singular point.

It has been demonstrated in this Laboratory that $KTaO_3$ and $KNbO_3$ form a continuous series of solid solutions, and that the introduction of Ta into the niobate lattice lowers the Curie transition approximately 7°/mole %.[6,7] Brauer[8] and Orr[9] state that according to X-ray measurements the low temperature forms of Ta_2O_5 and Nb_2O_5 are isomorphous. Schäfer, *et al.*,[10,11] report that Nb_2O_5 and Ta_2O_5 form a series of solid solutions with no detectable heterogeneous region. On the basis of the above evidence it was assumed that the niobium and tantalum "ionic radii" are approximately the same, and if this is the case then the systems K_2O–Nb_2O_5 and K_2O–Ta_2O_5 might be models for one another. It was felt that a complete investigation of the heterogeneous equilibria in the system K_2O–Ta_2O_5 would demonstrate possible model behavior, as well as define regions suitable for the growth of single crystals of $KTaO_3$.

Brauer[8] in his extensive treatise on niobium and tantalum oxides claims that from room temperature to its melting point Ta_2O_5 exists in only one structural modification, a low temperature form isomorphous with the low temperature polymorph of Nb_2O_5. However, Lagergren and Magneli[12] reported the existence of a high temperature modification of Ta_2O_5 above 1320°, with an X-ray pattern different from any of the reported forms of Nb_2O_5. Schäfer, *et al.*,[11] were not able to obtain the suspected high temperature polymorph without melting the Ta_2O_5. A reinvestigation of the allotropy of the pentoxide was deemed advisable in view of the ambiguities concerning the number of polymorphs and their transition temperatures.

Experimental Procedure

1. **Reagents.**—The Ta_2O_5 used in this study was obtained from the Fansteel Metallurgical Company. This reagent is the company's T-400 grade and is reported to contain 0.001% TiO_2 as the maximum impurity. X-Ray analysis of this material gave a pattern identical to that published by Frevel and Rinn.[13] A series of moisture determinations showed that at least 16 hours ignition at 1000° was necessary for the complete removal of water. Reagent grade Mallinckrodt potassium carbonate was dried at 400° for four hours to remove moisture. Neither chemical was subjected to any further purification prior to use.

2. **Sample Preparation.** (a) **Thermal Analysis Cooling Curves.**—Mixtures of K_2CO_3 and Ta_2O_5 were prepared so as to give 6 g. of charge after completion of reaction. The components were thoroughly mixed, then heated slowly to 1000° and held overnight at this temperature in order to prereact the charges. This treatment does not yield homogeneous mixtures, but as the charges are fused prior to actual use, the pretreatment reduces the violence of reaction when the sample is placed in the hot furnace.

(b) **X-Ray, Strip Furnace and Heating Curves.**—The charges used for X-ray analysis, strip furnace and thermal heating curves must of necessity be completely reacted and homogeneous. These samples were prepared by ball milling mixtures of the components for one hour, solid state reacting at 800° for 12 hours and then grinding. This procedure was repeated, and the sample was finally solid state reacted at 1000° for 12 hours. The reaction mixture was then ground to pass a 325 mesh screen. The hygroscopic $3K_2O \cdot Ta_2O_5$ was prepared for X-ray determination as previously described.[2]

3. **Thermal Analysis.** (a) **Differential Thermal Analysis.**—The region 50–100 mole % K_2O or K_2CO_3 was examined using differential thermal analysis with the following modifications of previously described apparatus.[1,2] The thermocouples were Pt–10Rh calibrated against the melting points of K_2SO_4, 1069°, and diopside, 1392°. The thermocouples were supported in pure alumina protecting tubes, Norton RA7232. At high temperatures the new insulators are far superior to the standard Norton RA164 formula, having considerably lower conductivity. Both temperature and differential measurements were made with an L & N Speedomax X-Y recorder. The differential e.m.f. was amplified from 5–25 times with a modified Brown Electronik null detector, and was recorded on the 2.5 mv. X axis. Zero suppression permitted centering of the pen. The Y input was also zero suppressed in order to make full use of the 10 mv. sensitivity.

(b) **Time Temperature Analysis.**—In the region 30–50 mole % K_2O, DTA was abandoned in favor of conventional time temperature methods. Above approximately 1400° the difficulty of balancing the differential circuit, because of increased conductivity and a.c. pickup, does not warrant the extra time required, provided the heat effects are unambiguously detectable with time temperature analysis. A new furnace was designed which would readily permit experimental determinations up to 1725°. A 1.5″ × 18″ alundum furnace core with $^1/_8$″ pitch was wound in the mid 12″ portion with 31 mil Pt–10Rh furnace wire. This was centered in a 4″ i.d. core wound at the top and bottom with Kanthal A-1 wire. The Kanthal winding overlapped the Pt–10Rh winding 1″ at the top and bottom. A uniform hot zone approximately 4″ long is thus obtained. In order to prolong Pt wound furnace life, several precautions were taken. Once brought to continuous operating temperature, the furnace was rarely allowed to cool below 800°. Cooling rates were seldom permitted to exceed 2°/min. To limit the diffusion of any vapors present in the furnace, an alundum insert was always placed in the core. All time temperature curves were recorded automatically on a Brown Electronik single point strip recorder with a 2 mv. full scale sensitivity. The signals were zero suppressed and a chart speed of 12″/hr. was employed.

Because it was not possible to see into the high temperature furnace, it was necessary to detect contact of the thermocouple and stirring assembly with the melt in the following manner. The ground lead of the thermocouple capsule was connected through an ohmmeter to a wire spot welded to the platinum bubbling tube. When contact was made with the melt, a large change in resistance was observed. The rate of oxygen bubbling in this apparatus was monitored with a stethoscope.

All cooling curves using DTA or time temperature techniques were run at approximately 1°/min. or slower, and the melts were seeded during a cooling cycle with small crystals obtained from preruns. All heating curves were run from 1–2°/min.[14]

In DTA experiments, in addition to the grounding techniques previously employed, the center leg of the DTA couple was also grounded, and the resulting noise level was completely innocuous. Without proper grounding neither

---

[4] P. Vousden, *Acta Cryst.*, **4**, 373 (1951).

[5] J. K. Hulm, B. T. Matthias and E. A. Long, *Phys. Rev.*, **79**, 885 (1950).

[6] A. Reisman, S. Treibwasser and F. Holtzberg, This Journal, **77**, 4228 (1955).

[7] S. Triebwasser and F. Holtzberg, *Phys. Rev.*, **98**, 1201 (1955).

[8] G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).

[9] R. L. Orr, This Journal, **75**, 2808 (1953).

[10] H. Schäfer and G. Breil, *Z. anorg. allgem. Chem.*, **267**, 265 (1952).

[11] H. Schäfer, A. Dürkop and M. Jori, *ibid.*, **275**, 19 (1954).

[12] S. Lagergren and A. Magneli, *Acta Chem. Scand.*, **6**, 444 (1952), A.S.T.M. Card #5-0258.

[13] L. K. Frevel and H. N. Rinn, *Anal. Chem.*, **27**, 1329 (1955).

[14] Heating curves were used only to determine solidus, transformation temperatures and compound melting points. It has been the authors' general experience that liquidus data obtained from heating curves are uninterpretable.

DTA nor time temperature measurements could readily be made at temperatures much above 1000°.

(c) **Strip Furnace**.—The region 0–30 mole % K_2O was examined with a strip furnace adapted from the design of Roberts and Morey.[15] Pure rhodium strip 0.001″ × 0.157″ × 1″ was used in addition to Pt–40Rh strips of the same dimensions. An L & N optical pyrometer model #8622-C, having a supplementary lens for greater magnification was used for temperature measurement. A second observer detected the melting phenomena with a 20 power telemicroscope. The rate of heating was controlled by a motor driven variable transformer in series with suitable step down transformers. Even with the modifications employed, which facilitated observation of the charges up to the m.p. of Rh, solidus points could not be determined accurately. Furthermore it has been found that measurements made under the most favorable conditions were generally reproducible to only ±10°. The factors affecting the precision of these measurements were tendency for flow of any molten material away from the remaining solid, difficulty in choosing a suitable region for reproducible temperature measurements from run to run, inability to form the U exactly the same way each time resulting in slight variation of calibration in different strips, and the subjectivity of the observer making the measurements.

The choice of calibrants for the strip furnace presented some difficulties. The majority of materials for high temperature standardization were originally reported from the Geophysical Laboratory of the Carnegie Institute of Washington.[16] In the Geophysical scale the melting point of platinum was taken as 1755°. The more widely accepted value for this m.p. as defined by the I. T. S. of 1948 is 1769°.[17] Greig[18] gave the m.p. for a 15% CaO–85% SiO_2 mixture as 1698 ± 5° based on the Geophysical scale. Employing the m.p. of diopside 1392° (I. T. S.) as a basis, the m.p. of the oxide mixture was found to be 323° higher or 1715°. This value is in excellent agreement with the corrected value, 1712°, based on the I. T. S. of 1948. Consequently the melting points of diopside, 1392°, and 15% CaO–85% SiO_2, 1712 ± 5°, were used for the calibration of the strip furnace.

In all the methods employed 2–4 runs were made at each recorded mole %.

4. **X-Ray**.—The incongruent transformation of I occurs at about the high temperature limit of the Pt–10Rh wound furnace. It was therefore difficult to establish the stoichiometry of I using thermal methods. In order to determine the composition of I, and confirm that of II obtained by thermal analysis, an X-ray phase diagram was plotted. All X-ray data was obtained using a G.E. X RD-3 diffractometer with Cu Kα radiation. The errors encountered in plotting "line intensities" as a function of composition, Fig. 3, are discussed by Klug and Alexander.[19] The compounds were determined by plotting the number of counts for selected diffraction maxima as a function of composition. Loading and reloading, as well as spinning of samples did not effect the reproducibility of line intensity measurements, indicating little or no orientation effect. The intensities shown in Fig. 2 represent the maxima of the selected reflections as determined from a plot of counts *vs.* 2θ. Plotting the appearance and disappearance of several maxima for each compound, gave results which were reproducible to 0.33 mole %. The X-ray data corroborated the stoichiometry of compound II as obtained by thermal methods.

Obtaining interplanar spacings of the moisture sensitive compound IV presented the only difficulties. The compound could not be prepared by solid state reaction. Furthermore it was necessary to quench the molten charge to reduce the contamination of the sample with platinum. The poor crystallinity of these samples gave rise to broader diffraction maxima. In addition to the previously described method,[2] for obtaining powder photographs of moisture sensitive materials, a sample holder was designed for diffractometer measurements of hygroscopic materials.

5. **Polymorphism of Ta_2O_5**.—In order to determine the number of modifications of Ta_2O_5, the pentoxide was heat treated for varying lengths of time at different temperatures. The X-ray pattern of the Ta_2O_5 obtained from Fansteel was found to be that of the reported low temperature form. Some of this material was heated to 1500° for a few days and its pattern changed completely. The heat treatments summarized in Table I were performed on both forms approaching the equilibrium temperature from two directions.

TABLE I

HEAT TREATMENTS OF Ta_2O_5

	Orig. phase	Temp. of treatment, °C.	Time of treatment, hr.	Final phase
1	β	500	48	β
2	β	720	48	β
3	β	800	67	β
4	β	920	48	β
5	β	1115	48	β
6	β	1200	57	β
7	β	1300	48	β
8	β	1346	168	β
9	β	1360	64	α + β
10	β	1362	168	α + β
11	β	1400	23	α
12	β	1426	24	α
13	β	1450 at 100°/	24	α
		hr. to 700		α + β
14	β	1420 at 100°/	65	α
		hr. to 200		α + β
15	α	1450	24	α
16	α	1400	24	α
17	α	1362	168	α + β
18	α	1360	168	α + β
19	α	1346	168	α + β

Discussion of Experimental Results

The "equilibrium" curves obtained in this investigation are shown in Figs. 1 and 2, and are based on the thermal and X-ray data tabulated in Tables II and III. The region 0–75 mole % K_2CO_3 represents equilibrium between K_2O and Ta_2O_5. The range 75–100 mole % is an entity in itself in that K_2CO_3 is one of the binary components. As K_2O and K_2CO_3 are molecularly equivalent, no discontinuity arises in going from one portion of the diagram to the other.

Figures 1 and 2 show the existence of four compounds corresponding to the formulas (I) $K_2O \cdot 5Ta_2O_5$, (II) $K_2O \cdot 2Ta_2O_5$, (III) $K_2O \cdot Ta_2O_5$ and (IV) $3K_2O \cdot Ta_2O_5$. Compounds I, II and III melt incongruently while IV exhibits a compound maximum.

The region 0–16.67 mole % K_2O represents equilibrium conditions between Ta_2O_5 and I. The melting point of Ta_2O_5 was found to be 1872 ± 10°. Tiede and Birnbauer[20] reported that Ta_2O_5 could not be fused. Ruff, *et al.*,[21] listed a melting point of 1875° for Ta_2O_5 contaminated with Nb_2O_5. Schäfer, *et al.*,[11] reported a melting point of 1880° for this oxide. X-Ray examination of the heat treated specimens, Table I, indicated conclusively that Ta_2O_5 exists in two distinct polymorphic varieties from room temperature to its melting point with a transformation temperature of 1360 ± 5°. The transformation is sluggish but completely reversible. In

---

(15) H. S. Roberts and G. W. Morey, *Rev. Sci. Instr.*, **1**, 576 (1930).

(16) R. B. Sosman, *Am. J. Sci.*, Bowen Vol. Pt. II, 517 (1952).

(17) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1948).

(18) J. W. Greig, *Am. J. Sci.*, **13**, 1 (1927).

(19) H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 422–426.

(20) E. Tiede and E. Birnbauer, *Z. anorg. Chem.*, **87**, 129 (1914).

(21) O. Ruff, H. Sheiferheld and J. Sota, *ibid.*, **82**, 373 (1913).

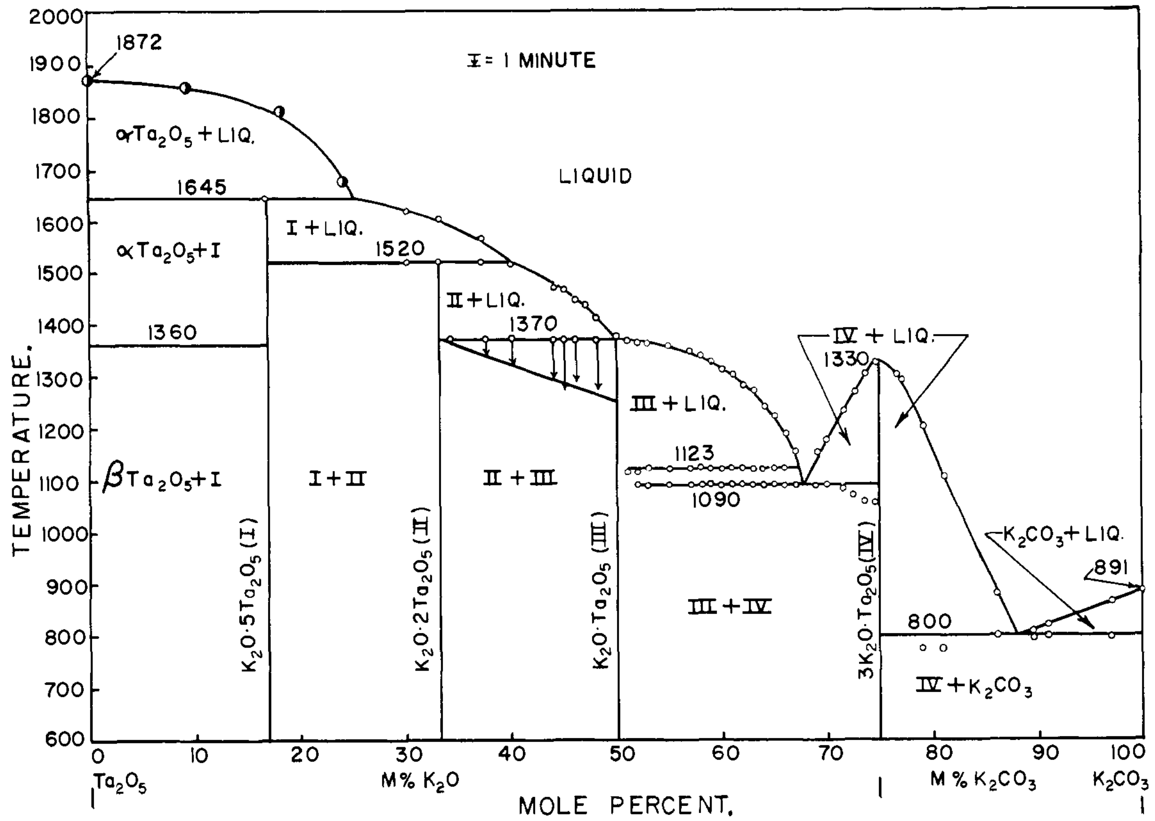


Fig. 1.—Phase diagram of system K_2CO_3–Ta_2O_5: ◑, strip furnace data; O, thermal data.

order to be certain that no other polymorphic form occurred above the limit of the Pt–10Rh wound furnace, the pentoxide was fused in a Ta_2O_5 crucible with an oxy-gas flame. The molten material was air-quenched yielding straw colored, crystalline Ta_2O_5 with an X-ray pattern characteristic of α, the high temperature form. The melting point of β-Ta_2O_5, 1785 ± 30°, was obtained using the strip furnace. The temperature was raised at approximately 50°/min. until melting was observed. This procedure was feasible only because of the sluggishness of the β to α transformation. The densities of β and α forms were pycnometrically determined as 8.18 and 8.37 g./cm.^{3} at 25°, respectively. The pycnometers were specially prepared by replacing the neck of a standard 50-cc. Pyrex volumetric flask with the scribed portion of a 10-cc. volumetric pipet. The standard taper joint was then fused to the top of the narrow column. The pycnometer could be calibrated reproducibly with water to 0.4 mg. A powdered sample was inserted into the pycnometer and 25 cc. of water added. The mixture was boiled vigorously for 3 hours to remove entrapped air and was then filled almost to mark. The pycnometer was placed in a constant temperature bath at 25°, allowed to equilibrate and diluted to mark at this temperature. Weighings could then be made at leisure. The precision obtainable was ±0.01 g./cm.^{3}.

Hahn[22] listed X-ray data for an unspecified form of Ta_2O_5. Frevel and Rinn[13] specifically determined interplanar spacings for the low temperature form of Ta_2O_5 which did not agree with the data of Hahn. Lagergren and Magneli, using a Guinier focusing camera, reported "d" spacings for the α modification which were also in disagree-

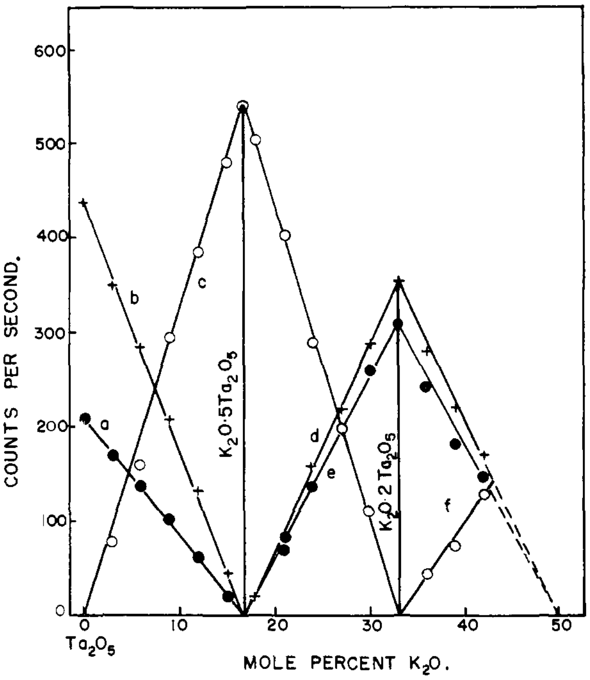


Fig. 2.—X-Ray phase diagram of system K_2CO_3–Ta_2O_5: a, 2θ = 28.79°; b, 2θ = 28.5°; c, 2θ = 14.37°; d, 2θ = 14.37°; e, 2θ = 16.98°; f, 2θ = 45.41°.

---

[22] R. B. Hahn, THIS JOURNAL, 73, 5091 (1951).

Table II

Thermal Data for the System K_2CO_3–Ta_2O_5

K_2CO_3, mole %	Ta_2O_5	Liquidus	Solidus	Transition	M.p., °C.	Primary phase
100	0				891	K_2CO_3
97	3	863	795			K_2CO_3
91	9	819	800			K_2CO_3
88.5	11.5	805	799			IV
86	14	880	799			IV
81	19	1105	773			IV
79	21	1203	775			IV
77	23	1293				IV
76.5	23.5	1300				IV
75	25				1330	IV
74.5	25.5	1325	1056			IV
73.5	26.5	1302	1058			IV
72.5	27.5	1268	1068			IV
71.5	28.5	1231	1080			IV
70.0	30.0	1177	1085			IV
69.0	31.0	1155	1088			IV
67	33	1152	1089			III
66	34	1189	1087	1121		III
65	35	1221	1092	1123		III
64	36	1239	1087	1123		III
63	37	1271	1093	1124		III
62	38	1281	1089	1123		III
61	39	1301	1090	1123		III
60	40	1312	1088	1122		III
59	41	1326	1092	1124		III
58	42	1337	1090	1122		III
57	43	1348	1090	1123		III
55	45	1357	1087	1123		III
53	47	1362	1090	1122		III
52	48	1362	1090	1114		III
51	49	1368		1114		III
50	50				1370	III
48	52	1412	1366			II
47	53	1434				II
46	54	1445	1366			II
45	55	1464	1376			II
44	56	1470	1366			II
40	60	1516	1368			II
37	63	1563	1370	1522		I
34	66		1371			I
33	67	1604	1520			I
30	70	1618	1514			I
24	76	1676				$Ta_2O_5\alpha$
18	82	1812				$Ta_2O_5\alpha$
16.67	83.33		1645			$Ta_2O_5\alpha$
9	91	1855				$Ta_2O_5\alpha$
0	100				1872	$Ta_2O_5\alpha$
					1785	$Ta_2O_5\beta$

Table III

"Intensity" Data for Selected Diffraction Maxima as a Function of Mole % K_2O

	Counts per second					
K_2O, mole %	Ta_2O_5 β 2θ = 28.25°	Ta_2O_5 β 2θ = 28.79°	Compd. I 2θ = 10.52°	Compd. II 2θ = 14.37°	Compd. II 2θ = 16.98°	$KTaO_3$ 2θ = 45.41°
0	440	209	. .			
3	349	168	77			
6	284	137	160			
9	208	100	294			
12	131	61	384			
15	44	19	479			
16.67	. .	. .	546			
18			505	20	20	
21			403	82	69	
24			288	159	140	
27			198	217	196	
30			110	287	259	
33			. .	352	312	. .
36				281	245	43
39				218	198	72
42				170	146	127

ment with Hahn's data. Lagergren and Magneli indexed the α form on the basis of an orthorhombic unit cell, whereas the low temperature form had been indexed on the basis of a monoclinic unit cell by Frevel and Rinn. Diffractometer traces[23] of the α form were obtained using a 0.02° receiving slit and high resolution Soller slits which resolved lines not reported by Lagergren and Magneli.[12] The splitting of the lines found in the present study precludes the possibility of indexing the high temperature form on the basis of an orthorhombic unit cell. The α form appears to be at least monoclinic and possibly triclinic, but thus far has not been indexed successfully from powder data. The actual departure from orthogonality is minute, and the angular deviation was not measurable with the imperfect single crystals obtainable.

In the liquidus region 0–25 mole %, α-Ta_2O_5 occurs as the primary crystallization. At 25 mole % and 1645° the Ta_2O_5 liquidus terminates incongruently. Below 1645°, the region 0–16.67 mole % represents the two phase solid equilibrium α-Ta_2O_5–I. Below 1360° α-Ta_2O_5 converts to β, and the two phase equilibrium is between β-Ta_2O_5 and I. From 25–40 mole % K_2O, I occurs as the primary crystallization, and its solubility curve also terminates in a peritectic point, at 40 mole % and 1520°. Below 1520° in the region 16.67–33.33 mole %, I and II exist in solid equilibrium. The stoichiometry of I was determined as described in section 4, see Fig. 2, and its interplanar spacings are given in Table IV. From 40–50 mole % and 1370°, II occurs as the primary solid phase and the liquidus curve terminates at the $KTaO_3$ singular point. The stoichiometry of II was determined by plotting length of the 1370° halt *vs.* time. X-Ray analysis corroborated this composition, Fig. 2, and interplanar spacings for II are given in Table IV. Below 1370°, in the region 33.33–50 mole %, the two phase solid equilibria is between II and III.

Within experimental limits III occurs at a singular point between congruent and incongruent melting, indicating that the melting point of III does not vary appreciably with pressure. This phenomenon explains the difficulty in growing crystals of III in the immediate vicinity of the singular point. As the vapor pressure of K_2O in the region 50–68 mole % is appreciable, lengthy crystal growing experiments in the region 50–52 mole % resulted in shifting the composition to the left of the singular point. The K_2O loss appears to be at the expense of the $KTaO_3$ whose solubility curve indicates extensive dissociation. Between 50 and 67.7 mole %, III is the primary solid phase. The descending curve terminates at a eutectic at 1090° and 67.7 mole %.

---

(23) The diffractometer studies were made with G. E. and N. A. Philips diffractometers.

TABLE IV

INTERPLANAR SPACINGS FOR Ta_2O_5 AND ANHYDROUS POTASSIUM TANTALATES[a]

High temp. Ta_2O_5		Compd. I		Compd. II		Compd. IV	
d, Å.	Relative intensity	*d*, Å.	Relative intensity	*d*, Å.	Relative intensity	*d*, Å.	Relative intensity
8.95	VVW	8.40	VS	6.14	M	6.36	VW
4.46	VVW	5.65	VVW	5.21	M	6.10	VW
3.776	VS	5.10	VW	4.68	VVW	5.96	VW
3.768	VS	5.00	M	3.515	VVW	5.32	M
3.754	S	4.291	VW	3.070	S	5.03	VS(B)
3.622	M	4.195	W	3.038	VS	4.61	VW
3.587	VVW	3.885	W	2.793	VS	4.27	W
3.363	VS	3.786	M	2.606	VW	4.13	VVW
3.358	VS	3.726	W	2.491	W	4.02	VW
3.351	S	3.525	W	2.341	VVW	3.92	VW
3.318	W	3.302	W	2.189	VVW	3.73	VVW
3.060	W	3.212	VS	2.047	VW	3.54	VVW
3.052	W	3.193	W	1.979	VVW	3.18	W
3.046	W	3.017	S	1.934	W	3.06	S
3.014	W	2.970	W	1.811	W	2.99	S
2.976	VS	2.840	M	1.794	VVW	2.88	M
2.748	VVW	2.788	M	1.757	VVW	2.81	W
2.741	VVW	2.695	W	1.738	VVW	2.56	VW
2.715	VW	2.654	VW	1.715	W	2.40	W
2.484	VW	2.596	W	1.665	VVW	1.88	VVW(B)
2.473	W	2.507	VW	1.601	VVW		
2.466	W	2.480	W	1.561	W		
2.456	S	2.454	W	1.557	W		
2.453	S	2.413	W	1.535	VVW		
2.434	M	2.289	VVW	1.532	VW		
2.432	M	2.256	VVW	1.521	VW		
2.241	VVW	2.217	VVW	1.503	VVW		
2.233	VW	2.196	VVW	1.492	VVW		
2.206	VVW	2.096	VW	1.466	VVW		
2.031	VVW	2.004	VVW	1.396	VVW		
2.021	VVW	1.967	VW	1.375	VVW		
1.900	W	1.962	VW				
1.890	W	1.954	VW				
1.850	VW	1.864	VVW				
1.841	VW	1.849	VW				
1.837	W	1.775	VW				
1.824	VW	1.766	W				
		1.762	W				
		1.747	W				
		1.737	W				
		1.707	W				
		1.694	VW				
		1.672	VVW				
		1.628	W				
		1.562	VVW				
		1.524	VW				
		1.515	VVW				
		1.485	VVW				
		1.470	VVW				
		1.449	VW				
		1.446	VW				
		1.427	VW				

[a] Data for $KTaO_3$ and βTa_2O_5 are in agreement with the previously reported interplanar spacings of references 4 and 13, respectively, and therefore are not included in the table.

In the $KTaO_3$ liquidus field a sharp exothermic heat effect was observed at 1123° in cooling curves for all compositions between 51 and 67 mole %. This was indicative of either a phase transformation involving pure $KTaO_3$ or solid solution. The 1123° heat effect was spontaneous, and if a high temperature form of $KTaO_3$ exists it could not be quenched in. Furthermore, pure $KTaO_3$ gave no such heat effect. Quenches of 64 mole % mixtures gave $KTaO_3$ X-ray patterns which showed slight line shifts. This is not conclusive proof for the existence of solid solution because the crystallites were undoubtedly strained. Of further interest is the observation that even at very high amplifications neither the 1123° nor 1090° heat effects were observable below 51 and 52 mole % K_2O, respectively. This again indicates the presence of limited solid solution except that the 1123° heat effect reaches a maximum value at 64 to 66 mole %. The possibility of another compound occurring in the 50–68 mole % region is precluded by the data obtained. As no thermodynamically acceptable diagram could be drawn to correlate all of the observations, the $KTaO_3$ field is drawn directly from the experimental data. The density of $KTaO_3$ was pycnometrically determined as 6.96 g./cm.^{3} at 25° as compared to the X-ray density of 7.00 g./cm.^{3} at 25°. From 68 to 88 mole %, IV occurs as the primary crystallization. The melting point of IV was determined as 1330°. The shape of the liquidus curve is surprising in that practically no liquid dissociation is indicated as was the case for the analogous niobate. The same reaction behavior was observed in the IV field as occurred in the vanadate system. The reaction mixtures would melt, partially resolidify and finally melt again at higher temperatures after a final CO_2 evolution. The region 75–100 mole % represents the only region of stability of K_2CO_3. The ratio of the amount of CO_2 evolved to the amount of Ta_2O_5 present is constant. In the range 88.7–100 mole %, K_2CO_3 crystallizes as the primary phase, and at temperatures below 800°, IV and K_2CO_3 are in equilibrium.

Comparison of Systems K_2O with Ta_2O_5, Nb_2O_5 and V_2O_5.—Contrary to the literature none of these systems generate more than 5 anhydrous compounds. None of the systems exhibits model behavior with another. The 3:1 compounds of the three systems show marked moisture sensitivity. Attempts at producing fine crystals of $KTaO_3$ in a manner analogous to the method developed for $KNbO_3$[24] were unsuccessful because $3K_2O{\cdot}Ta_2O_5$ could not be held in solution. All of the other niobates and tantalates are extremely water insoluble and are attacked only by HF. In the vanadate series the 1:1 compound is slightly water soluble, the 16:9, 2:1 and 3:1 compounds are extremely hygroscopic and the 1:4 compound is insoluble in water, and soluble in acids.

One wonders in view of the apparent similarity in size of the Nb^{5+} and Ta^{5+} ions why deviation from model behavior is so marked. Periodic trends would predict the similarity in size on the basis of the intervening Lanthanide contraction. Ta has an ionization potential of approximately 6 e.v. which is slightly lower than the 7 e.v. listed for Nb.[25] Therefore, one might expect that the Ta–O bond would be more ionic and consequently smaller than the Nb–O bond, this in spite of the fact that Ta^{5+} is conceivably slightly larger than the Nb^{5+}. If such is the case then the $KTaO_3$ cubic lattice parameter should be smaller than the cubic parameter for $KNbO_3$ at the same temperature. Figure 3 is a 450° isotherm showing the variation of lattice constant in the continuous series of solid solutions for the system $KNbO_3$–$KTaO_3$. The lattice constant can be seen to decrease with increasing tanta-

---

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

(25) E. S. Gould, "Inorganic Reactions and Structures," Henry Holt and Co., New York, N. Y., 1955, pp. 454–5.

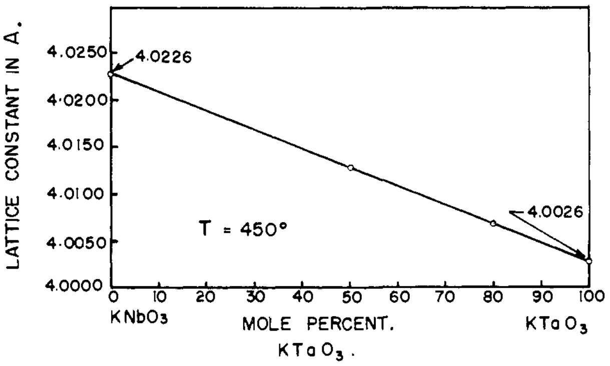


Fig. 3.—Variation of lattice constant of $KNbO_3$ with mole % $KTaO_3$ at 450°.

lum concentration. This decrease in lattice constant can only be attributed to an increase in the ionic character of the heavy metal atom–oxygen bond. Using the data of Shirane, *et al.*,[26] for cubic $KNbO_3$ at various temperatures above the Curie point, one obtains a straight line relationship between cubic lattice parameter and temperature. The extrapolated value obtained for $KNbO_3$ at room temperature is 4.0033 Å. As the $KTaO_3$ parameter is 3.9885 Å. this further substantiates the belief that the Ta–O bond is more ionic than the Nb–O bond.

A qualitative application of the Huggins relationship[27] indicates that "effective" ionic characters of the Ta–O and Nb–O bonds are essentially the same. The equation was applied, assuming that the contribution of K would be the same for both systems. What is most apparent, however, is that the combination of geometric and electronic factors is not significantly different for Ta and Nb indicating that the Goldschmidt theory[28] is extremely sensitive to this combination. Therefore one would rarely expect to encounter model behavior relationships.

Acknowledgment.—The authors wish to acknowledge the invaluable assistance given by S. Triebwasser during his many helpful discussions and to thank Miss S. Silverman for preparation of samples, and the North American Philips Company for making available equipment for several experiments.

NEW YORK, NEW YORK

---

[26] G. Shirane, R. Newnham and R. Pepinsky, *Phys. Rev.*, **96**, 581 (1954).

[27] M. L. Huggins, THIS JOURNAL, **75**, 4123, 4126 (1953).

[28] J. M. Goldschmidt, *Skrift Norske, Vid. Akad. Oslo. Mat. Nat. Kl.*, No. 8, 7 (1926).

[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY]

The Thermodynamics of Indium Sulfate Solutions[1]

BY M. H. LIETZKE AND R. W. STOUGHTON

RECEIVED MARCH 26, 1956

E.m.f. data are presented for the cell In, $In_2(SO_4)_3(m)$, Ag_2SO_4(sat), Ag for $In_2(SO_4)_3$ concentrations of 0.01 to 2.3 m and temperatures of 15 to 70°. The log of the activity of $In_2(SO_4)_3$ is approximately proportional to the molality at any given temperature. E.m.f., conductivity and solubility data all strongly indicate considerable ionic association in $In_2(SO_4)_3$ solutions.

Introduction

The cell In, $In_2(SO_4)_3(m)$, Hg_2SO_4, Hg was studied by Hattox and DeVries[2] as a function of $In_2(SO_4)_3$ concentration at 15, 25 and 35°. They calculated activity coefficients of $In_2(SO_4)_3$ on the assumption of complete dissociation into In^{+++} and SO_4^{--} ions at the lower concentrations and by making the usual extrapolation using the Debye-Hückel equation. The current study began as an attempt to extend the useful range of the In, $In_2(SO_4)_3(m)$ electrode to higher temperatures. Because of the lesser tendency of Ag_2SO_4 than Hg_2SO_4 to hydrolyze as the temperature is raised and the acidity lowered and the consequently greater reliability of the Ag, Ag_2SO_4 electrode under these conditions,[3] the cell In, $In_2(SO_4)_3(m)$, Ag_2SO_4(sat), Ag was used. The $In_2(SO_4)_3$ concentration was varied from about 0.01 to 2.3 m and the temperature from 15 to 70°. The lower limit in concentration and the upper limit in temperature were fixed by the ability to obtain reproducible results.

The relatively highly solubility of Ag_2SO_4 (0.02676 m in water at 25°) combined with the necessity of keeping it out of the In, $In_2(SO_4)_3$ electrode compartment imposed a further restriction on the lower limit of useful $In_2(SO_4)_3$ concentrations as far as interpreting the data was concerned, because of the problem of liquid junction potentials.

Experimental

The Ag_2SO_4 used in all the measurements was prepared according to the method described by Archibald,[4] while the $In_2(SO_4)_3$ was prepared by the method suggested by Hattox and DeVries.[2]

E.m.f. Measurements.—The Ag, Ag_2SO_4 electrode consisted of a pure silver wire dipping into the desired $In_2(SO_4)_3$ solution saturated with Ag_2SO_4. The indium electrode consisted of a platinum spiral plated with indium metal as previously described.[2] Both electrodes were contained in 10 mm. o.d. glass tubes which were drawn down to capillary size at the lower end and then bent up in the form of a *U*. The $In_2(SO_4)_3$ solution and electrodes were contained in a Pyrex tube fitted with a Teflon cover having holes to admit the electrode compartments. The entire electrode assembly was sealed in a steel bomb fitted with electrically insulated leads. As shown previously,[5] this type of electrode as-

---

[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] E. M. Hattox and T. DeVries, THIS JOURNAL, **58**, 2126 (1936).

[3] M. H. Lietzke and R. W. Stoughton, *ibid.*, **75**, 5226 (1953).

[4] E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1932.

[5] M. H. Lietzke and J. V. Vaughen, THIS JOURNAL, **77**, 876 (1955).