0.99 e.u. at 56.2°K., using a combined Debye–Einstein type extrapolation. Our results give a value of 1.10 e.u. at this temperature. In the case of MoO_3 the previously published data[16] showed a value of 2.966 e.u. at 70.05°K. which is to be compared with our result of 2.50 e.u. at 70°K. Using the Bureau of Standards Compilation[19] for the heat of formation of molybdenum trioxide and the entropies of molybdenum and oxygen we derive for the reaction

$$Mo(c) + 3/2O_2(g) = MoO_3(c)$$

at 298.15°K. these values: $\Delta S_f^0{}_{298.15} = -61.75$ e.u. and $\Delta F_f^0{}_{298.15} = -161.92$ kcal./mole.

It is now evident that a number of anisotropic substances fail to follow the Debye T^3 law in the range between 15 and 60°K. The low temperature heat capacity results reported here show that it is quite important for measurements to extend well below 50°K. and preferably into the helium range if one is to derive satisfactory values for the entropy. In particular, extrapolations from 50°K. in the case of heavy substances may be subject to serious error.

OAK RIDGE, TENNESSEE

[19] "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, D. C., 1952.

[CONTRIBUTION FROM THE WATSON LABORATORY OF INTERNATIONAL BUSINESS MACHINES]

Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. II. Phase Diagram of the System K_2CO_3–V_2O_5

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

RECEIVED NOVEMBER 12, 1955

The high temperature equilibrium between V_2O_5 and K_2O or K_2CO_3 has been reinvestigated using thermal and X-ray analysis. Five compounds have been found corresponding to the formulas (I) $K_2O \cdot 4V_2O_5$, (II) $K_2O \cdot V_2O_5$, (III) $16K_2O \cdot 9V_2O_5$, (IV) $2K_2O \cdot V_2O_5$, and (V) $3K_2O \cdot V_2O_5$. II and IV melt congruently at 520 and 910°, respectively. IV undergoes an α- to β-transformation at 740°. Compounds I and III melt incongruently at 520 and 696°, respectively. Within experimental limits, I appears to occur at a singular point between congruent and incongruent melting. V melts at approximately 1300°. X-Ray powder data have been obtained for all the anhydrous compounds of this system, and are available through the A.D.I. Thermal and X-ray analysis failed to reveal the presence of previously reported allotropic modifications of V_2O_5.

Introduction

This paper is the second in a series involving the study of the high temperature reactions of K_2O and K_2CO_3 with the group VB pentoxides.[1] Many compounds having the molecular formula $(K_2O)_x \cdot (V_2O_5)_y$ have been reported in the literature. Mellor[2] abstracts the methods for the preparation of the following anhydrous potassium vanadates, with x to y ratios 4:1, 3:1, 2:1, 1:1, 1:3 and 2:9. Ephraim[3] also lists a 3:5 compound without a method of preparation. In 1928, Canneri[4] studied the reactions of the alkali oxides with V_2O_5. The results of his partial investigation of the system K_2O–V_2O_5, Fig. 1, indicated the formation of only 3 anhydrous potassium vanadates with x to y ratios 1:1, 2:1, and 3:1. Canneri also showed that the equilibrium pressure of oxygen varied with composition, exhibiting a maximum O_2 evolution at approximately 44 mole % K_2O. There was no apparent attempt to relate the results of the oxygen loss experiments to the effect it might have in the determination of the phase diagram.

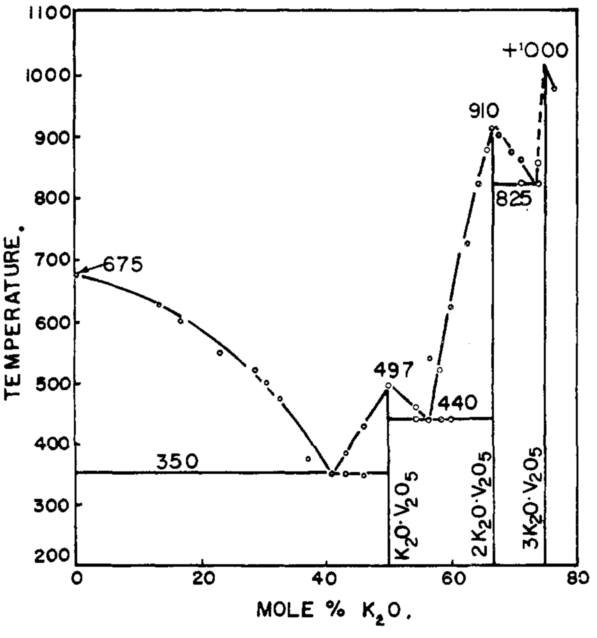

Fig. 1.—Partial phase diagram of the system K_2O–V_2O_5 reconstructed from Canneri's data.

In editorial comment both Ephraim and Mellor express some doubt as to the actual existence of all the compounds reported. It was felt that an examination of the complete phase diagram, using techniques of thermal and X-ray analysis, might help clarify the uncertainties concerning the actual number of compounds in this system.

In addition to the confused state of the V_2O_5–K_2O chemistry, the question of allotropic modifications of V_2O_5 arises. Ditte[5] reported the existence of three allotropic modifications of V_2O_5, each having different color and different water solubility. Brauer,[6] and Frevel and Rinn[7] reported on the structural modifications of the low and high temperature forms of Nb_2O_5 and Ta_2O_5. A survey of

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

[2] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., New York, N. Y., 1952, pp. 764–765.

[3] F. Ephraim, "Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1949, pp. 505–506.

[4] G. Canneri, *Gazz. chim. ital.*, **58**, 6 (1928).

[5] A. Ditte, *Compt. rend.*, **101**, 498 (1885).

[6] Von G. Brauer, *Z. anorg. allgem. Chem.*, **248**, No. 1, 1 (1941).

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

the literature failed to reveal any comparable study of the allotropes of V_2O_5, and it was decided to repeat Ditte's experiments using X-ray analysis for identification of the V_2O_5 allotropes.

Experimental

I. **Reagents.**—The V_2O_5, containing a minimum of 99.94% V_2O_5, and a purified grade of ammonium vanadate were purchased from the Fisher Scientific Company. The K_2CO_3 was Mallinckrodt analytical grade reagent dried at 300° for one hour to remove moisture. None of the reagents were subjected to further purification.

II. **Preparation of Charges for Thermal Analysis.**—If a mixture of V_2O_5 and K_2CO_3 is heated rapidly, the ensuing reaction is violent, and the losses due to spattering are large. In order to avoid loss of material, all charges were prepared and treated as follows: quantities of V_2O_5 and K_2CO_3 were weighed to give 5 g. of charge after CO_2 evolution. After thorough mixing, the samples were placed in platinum or gold crucibles and heated to the solidus temperature, as determined in preruns, at 100°/hr. The reacted charges were cooled in a desiccator and the CO_2 loss determined.

In the region 0–75 mole % K_2O the number of moles of CO_2 evolved is equivalent to the number of moles of K_2CO_3 in the reaction mixture. From 75 to 100 mole % K_2CO_3, the ratio of the number of moles of CO_2 lost to the number of moles of V_2O_5 present, was found to be constant. Consequently the completeness of reaction could be checked throughout the diagram. Gold crucibles were used in the region 87–100 mole % K_2CO_3, because the platinum ware was attacked by the molten alkali.

III. **Thermal Analysis.**—The data were plotted on a time-temperature scale with a Brown Electronik single point strip recorder. Zero suppression in series with the thermocouple output permitted use of the 2 mv. full scale sensitivity. Pt 10 Rh thermocouples, calibrated against the melting points of sodium chloride, 800.4°, and potassium sulfate, 1069°, were used to measure temperatures. Design of the furnace, thermocouple assembly and stirring mechanism have been previously described.[1] Oxygen stirring provided excellent agitation of the melts and prevented partial reduction of the vanadium compounds.

A motor-driven variable transformer was used to raise and lower reproducibly the furnace temperature. 2–4 runs were made at each recorded mole % at rates of 1–3°/min. All liquidus and simple eutectic transitions were obtained from cooling curves. In regions where several successive transitions occurred, heating curves were also employed. All melts were seeded because of the tendency for supercooling in most regions.

IV. **Weight Loss Determination.**—Weight loss experiments were performed in order to establish the stoichiometry of V. Heat effects in this region were small, even with the large charges employed. Furthermore, at the high temperatures necessary to ensure completeness of reaction, volatilization of the melts was appreciable. Because the ratio of the number of moles of CO_2 evolved to the number of moles of V_2O_5 present is constant in the region 75–100 mole % K_2CO_3, it is possible to avoid the high temperature of the 75 mole % region in determining the stoichiometry of V. Therefore, the low temperature region from 90–94 mole %, in which volatilization from the melts is insignificant, was chosen to perform weight loss experiments. V_2O_5 was fused in a gold crucible to which a calculated amount of K_2CO_3 was added, and the crucible was loosely capped. The charges were placed in a furnace 10° above the liquidus temperature and allowed to react for 15 minutes. This procedure was repeated until no further weight loss occurred.

V. **Chemical and Heat Treatments of NH_4VO_3 for X-Ray Analysis.**—A. Charges of NH_4VO_3 were placed in furnaces at 150 and 440° for seven days and were then quenched in liquid nitrogen.

B. NH_4VO_3 was heated in a closed Pt crucible at 440° for three hours. The residue was treated with HNO_3; the acid evaporated, and the residue heated at 440° for one hour, cooled and weighed. A rust colored powder was obtained.

C. NH_4VO_3 was heated at 440° for four hours in a stream of oxygen. A rust colored powder slightly darker than B was obtained.

D. NH_4VO_3 was boiled with 1:1 HNO_3. This treatment was followed by evaporation of the acid and ignition of the residue at 350–440° for one hour. An orange powder resulted.

E. NH_4VO_3 was heated out of contact with air for two hours at 440° and then treated with HNO_3. The acid was evaporated and the residue fused. The material before fusion is a yellow brown and becomes purple after fusion with the formation of needle-like crystals. When powdered this material was a brown-green. Table I lists average weight loss in each experiment.

TABLE I

WEIGHT LOSS OF NH_4VO_3 DURING VARIOUS TREATMENT

Theor. wt. loss	A at 440°	B	C	D	E
22.26%	22.18%	22.17%	22.14%	22.10%	22.40%

VI. **X-Ray Analysis. Preparation of Pure Compounds.**—Charges were prepared to give two-gram samples. Wherever possible different methods of preparation were used for a given compound, the conditions for preparation having been established by the phase diagram. All charges were air quenched from 350° in a desiccator to prevent moisture pick up.

(a_1) $K_2O{\cdot}4V_2O_5$.—The charges were brought to 450° at 10°/minute and held eight hours. The temperature was increased to 550°. Samples were air-quenched and placed in a desiccator.

(a_2) $K_2O{\cdot}4V_2O_5$.—Charges were heated at 10°/minute to 500° and held at this temperature for 24 hours. They were quenched, ground in a dry-box and the procedure was repeated two more times. After the third firing the sample was cooled at 1°/min. to 350°.

(b_1) KVO_3.—Same procedure as a_1.

(b_2) KVO_3.—Same procedure as a_2.

(c_1) $16K_2O{\cdot}9V_2O_5$.—Charges were heated at 10°/minute to 800° and held for eight hours. The temperature was then rapidly raised to 920° and the samples air-quenched and ground in a dry-box. The charges were then placed in a furnace at 620° and held for 24 hours. They were then air-quenched, ground and placed in a furnace at 670° and cooled at 1°/min. to 350°, and then air-quenched.

(c_2) $16K_2O{\cdot}9V_2O_5$.—Charges were heated slowly to 670°, held 12 hours, air-quenched, and ground in a dry-box. The procedure was repeated two more times with a final cooling rate of 1°/min. to 350°.

(d_1) $2K_2O{\cdot}V_2O_5\alpha$.—Charges were heated slowly to 800°, held eight hours, and then the temperature was increased to 950°. Charges were quenched in liquid nitrogen and placed in a dry-box.

(d_2) $2K_2O{\cdot}V_2O_5\beta$.—Same as d_1 except air-quenched. Samples were then ground in a dry-box, heated to 700°, and held 24 hours, then cooled 1°/min. to 350° and air-quenched.

(e_1) $3K_2O{\cdot}V_2O_5$.—Charges were slowly heated to 650°, held eight hours, then heated to 1350°, air-quenched and placed in a desiccator.

(e_2) $3K_2O{\cdot}V_2O_5$.—Samples were placed in a cold furnace and the temperature was raised at 20°/min. to 750° at which time the charges became molten. They were then air-quenched and placed in a desiccator.

VII. **Sample Preparation for X-Ray Powder Camera.**—All the compounds present in the system are extremely deliquescent except $K_2O{\cdot}4V_2O_5$ and KVO_3. Special techniques were devised for loading samples into thin walled soft glass capillaries. The specimens were handled in a dry-box and all equipment was thoroughly dried at 130°. 0.2 mm. thin walled soft glass capillaries obtained from the Caine Sales Company, were fused to 6 mm. i.d. soft glass tubing to enable easier handling and subsequent evacuation of the capillaries. The charges were ground and loaded into the capillaries. A rubber pressure hose was fastened to the glass tubing and pinched closed with a screw clamp. The capillaries were removed from the dry-box and evacuated. They were supported vertically with a small weight attached to the sample end of the tube. A single loop of B & S #28 platinum wire was placed around the capillary and the wire was electrically heated until the capillary dropped free. The thin fiber remaining at the seal was beaded in a micro-flame.

All photographs were taken with a Debye–Scherrer Camera, radius 114.6 mm., using nickel filtered copper radiation at 35 kv. 15 ma. Exposures were of the order of eight hours.

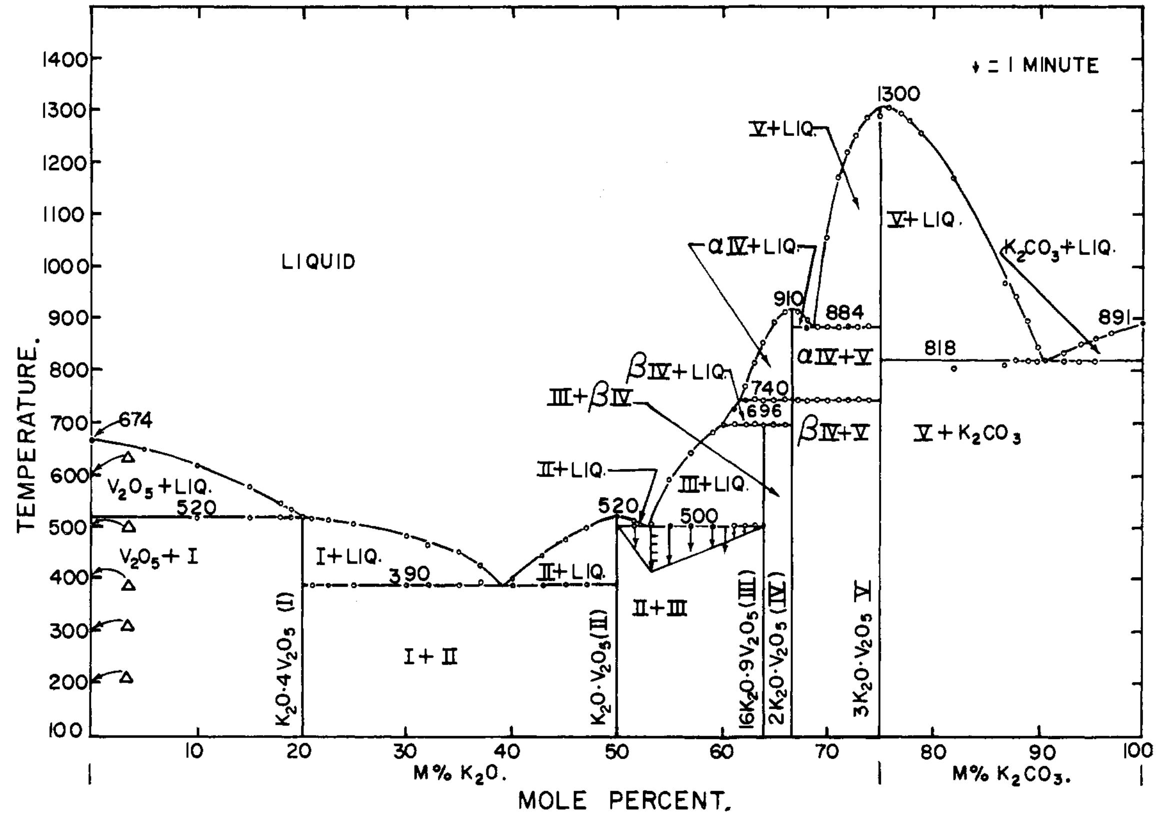

Fig. 2.—Phase diagram of the system K_2O or K_2CO_3 with V_2O_5 Δ, quenching expts.

Discussion of the Phase Diagram

The "equilibrium" curves obtained in this study are shown in Fig. 2 and are based on the thermal analysis data tabulated in Table II. The region 0–75 mole % K_2CO_3 represents equilibrium between K_2O and V_2O_5. Above 75 mole %, K_2CO_3 is one of the binary components. No discontinuity occurs in going from one region to the other since K_2O and K_2CO_3 are equivalent.

Figure 1 reveals the presence of five compounds corresponding to the formulas (I) $K_2O{\cdot}4V_2O_5$, (II) $K_2O{\cdot}V_2O_5$, (III) $16K_2O{\cdot}9V_2O_5$, (IV) $2K_2O{\cdot}V_2O_5$ and (V) $3K_2O{\cdot}V_2O_5$. Compounds I and III melt incongruently, and II, IV and V melt congruently. In addition IV exists in low and high temperature forms.

The region 0–20 mole % K_2O represents equilibrium between V_2O_5 and I. The melting point of V_2O_5 as determined in this study was found to be 674 ± 5°. The values previously reported were 675°,[4] 658°, 690°[8] and 800°.[9] The descending V_2O_5 solubility curve intersects the ascending $K_2O{\cdot}4V_2O_5$ curve at 20 mole % and 520°. Within experimental limits the intersection occurs at the congruent melting point of I, and represents a singular point between congruency and incongruency of melting. As atmospheric pressure need not represent a special case, it is probable that the m.p. of I does not vary appreciably with pressure.

One would expect that thermal analysis would reveal the presence of the reported allotropes of V_2O_5. If an enantiomorphic transition occurs during solid-liquid equilibrium in the 0–20 mole % K_2O region, the slope of the liquidus curve would show a break. Furthermore the maximum heat effect of such a transition would occur at 100 mole % V_2O_5. If phase transformations occur beneath the solidus, then solid state heat effects would be observed. The possibility exists that the transformations are sluggish. In this case extended heat soakings of V_2O_5 followed by quenching and X-ray analysis might reveal the presence of allotropes.

Since the liquidus curve in the region 0–20 mole % K_2O shows no discontinuity, and since no solid–solid heat effects were observed down to room temperature, it was decided to re-examine the previously reported evidence.

Samples of V_2O_5 were heat treated for one week at temperature increments of 100 degrees from room temperature to the m.p. of V_2O_5. The samples were quenched in liquid nitrogen and examined with X-rays. The products of the various treatments of NH_4VO_3, as described in the experimental portion of this paper were also examined with X-rays. All traces gave results in excellent agreement with the A.S.T.M. card #3-0206 for V_2O_5. It would appear that Ditte's modifications represent various states of subdivision of the pentoxide. It was found that if the pentoxide was fused and then ground, the color varied from purple for the fused oxide to tan for the finely ground material.

The region from 20–50 mole % K_2O represents equilibrium conditions between I and II. In the

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(8) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., New York, N. Y., 1952, p. 749.

(9) "Lange's Handbook of Chemistry," Eighth Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 308.

TABLE II

THERMAL DATA FOR THE SYSTEM K_2O AND K_2CO_3–V_2O_5 TEMPERATURE OF HEAT EFFECTS, °C.

Compn. K_2CO_3	Mole % V_2O_5	M.p., °C.	Liquidus	Solidus	Transition	
0	100	674				
5	95		650			
10	90		622		520	
15	85		580		517	
18	82		548		519	
19	81		533		522	
20	80	520				
21	79		521	392		
22.5	77.5		518	390		
25	75		510	388		
30	70		488	391		
32	68		469	389		
35	65		455	393		
37	63		429	399		
40	60		405	392		
43	57		446	390		
45	55		474	390		
47	53		500	387		
50	50	520				
51.5	48.5		512	500		
53	47		505			
54	46		594	500		
57	43		642	500		
59	41		680	499		
60	40		693	500		
61	39		721	498	696	
62	38		765	500	694	740
63	37		811	499	695	740
64	36		857		697	742
65	35		890		696	741
66	34		905		696	742
66.67	33.33	910				740
68	32		892	884		740
69	31			887		741
70	30		1051	881		740
71	29		1120	883		740
72	28		1214	884		741
73	27		1250	881		740
74	26		1284	881		770
75	25	1300				
76	24		1300			
77	23		1290			
78	22		1281			
79	21		1254			
82	18		1167	800		
87	13		959	812		
88	12		939	819		
89	11		890	818		
90	10		840	816		
91	9		822			
92	8		828	817		
94	6		845	816		
95.5	4.5		860	818		
97	3		868			
100	0	891				

region 20–39 mole %, I occurs as the primary crystallization. The eutectic composition is fixed at 390° and 39 mole %. From 39–50 mole %, II is in equilibrium with the liquid down to the solidus at which point I and II crystallize simultaneously.

The region from 50–64 mole % represents equilibrium between II and III. II melts congruently at 50 mole % and 520°. The liquidus curve from 50 to 52.9 mole % represents the region in which II occurs as the primary crystallization. From 52.9 mole % to the peritectic intersection at 60.4 mole % and 696° the liquidus curve shows equilibrium between III and liquid. At the 696° transition, III decomposes to give the β-modification of IV + liquid and absorbs energy in the process. The β- to α-transformation of IV occurs at 740° with the absorption of energy. The 740° peritectic intersection occurs at 61.5 mole % K_2O. Compound IV was determined by plotting the duration of the 500° eutectic halt as a function of composition from 50–65 mole %.

In order to prevent supercooling at the α- to β-transformation of IV, it was necessary to continue seeding through the transition. It is believed that the seeding induces formation of the β-modification from the remaining liquid and this triggers the α- to β-transformation of the initially crystallized form.

The α-phase was quenched with liquid nitrogen as described in procedure d_1. The X-ray pattern was obtained as soon as the sample could be prepared. The pattern obtained on the following day from the same capillary was that of the β-form which showed that the successfully quenched α-modification could not be retained at room temperature for long periods.

The region from 64–$66^{2}/_{3}$ mole % K_2O represents equilibrium between III and β-IV and then between β- and α-IV. IV melts congruently at 910°. From $66^{2}/_{3}$–75 mole % K_2O, equilibrium exists between IV and V. In the region $66^{2}/_{3}$–69 mole % K_2O, α IV occurs as a primary crystallization. The eutectic is at 69 mole % and 882°. The liquidus curve ascends steeply from the eutectic to the compound peak of V. As the attack of the platinum crucibles in the immediate vicinity of the compound peak is rapid the exact m.p. of V was difficult to determine, but is in the vicinity of 1300 ± 20°. The stoichiometry of V was determined by means of weight loss experiments as described in procedure IV.

In preparing charges of V, mixtures of the components were solid state reacted at 650° for 12 hours. Upon heating these charges it was noted that at approximately 700° the charge became completely molten. As the temperature was further increased the melt resolidified and did not become molten again until 1300°. The process was not reversible once the initial liquid solidified, and this was indicative of a monotropic system. However X-ray analysis showed that the apparent metastable monotrope gave a pattern identical with that of β-IV. Furthermore it was observed that if the charge was quenched immediately after the first liquefication, and then plunged into a furnace at 1350°, a violent reaction occurred. It appears that at low temperatures the reaction does not proceed to completion and only β-IV forms. Weight loss experiments performed at 75 mole % and solid state reacted at 650° confirmed the results of the X-ray analysis since the CO_2 loss corresponded to a compound formed at $66^{2}/_{3}$ mole %. The low temperature reaction takes several days to reach completion. Above 750–800°, however, the reaction goes to completion in a matter of minutes with the formation of V. Interplanar spacings for all anhydrous compounds are presented elsewhere.[10]

Comparison of Figs. 1 and 2 indicates a number of basic differences. In addition to the presence of two more compounds in Fig. 2, and the existence of an α,β-modification of $2K_2O \cdot V_2O_5$, large discrepancies exist in m.p. data. In the region 0–50 mole % K_2O Canneri observes that there are always three thermal arrests present. The first represents the liquidus, the second oxygen liberation referred to as "spitting," and finally a eutectic arrest. Our data in this same region never shows more than two arrests. Furthermore, careful weight loss experiments in this entire region are always in excellent agreement with theoretical weight loss corresponding to CO_2 evolution from the carbonate in the reaction mixture. It was observed that if oxygen stirring was dispensed with, then the phenomenon of "spitting" did indeed occur. Canneri attributes this O_2 evolution to the partial reduction of the V_2O_5. As the molten charges he examined were not maintained in an oxygen rich atmosphere it is undoubtedly the case that all of the charges employed for thermal analysis were strongly reduced. Thus his thermal analysis charges were not binary in character having relatively large quantities of reduced vanadic oxides which would most probably lower liquidus and eutectic data.

NEW YORK, N. Y.

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[10] These data have been deposited as Document number 4760 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[CONTRIBUTION NO. 431 FROM THE INSTITUTE FOR ATOMIC RESEARCH, DEPARTMENT OF CHEMISTRY AND VETERINARY RESEARCH INSTITUTE, IOWA STATE COLLEGE]

The Kinetics of the Ce(IV)–Ce(III) Exchange Reaction in Perchloric Acid[1]

BY FREDERICK R. DUKE AND FRANK R. PARCHEN

RECEIVED SEPTEMBER 1, 1955

The rate of the Ce(IV)–Ce(III) exchange reaction is found to be first order in Ce(III), first and second order in Ce(IV) and complex order in $[H^+]$. At high acidities, the Ce(IV) and $[H^+]$ dependencies are best explained by the reaction of Ce(III) with the species $Ce(OH)_2^{+2}$, $Ce(OH)_3^+$ and $[CeOCeOH]^{+5}$. At low $[H^+]$ more highly hydrolyzed and polymerized species appear to be involved.

Gryder and Dodson[2] demonstrated that the cerium(III)–cerium(IV) exchange rate could be determined when an ether extraction procedure was employed to effect separation of the reactants. This opened the way for further investigations on the exchange reaction.[3,4] They[3a] found that, in perchloric acid solution, the exchange rate was first order in cerium(III), but a fractional order between zero and one in cerium(IV). They also observed that the rate decreased as the acid concentration was increased.

Hornig and Libby[3b] found that both fluoride and chloride catalyzed the exchange reaction in nitric acid. The chloride catalytic effect was observed to be of lesser magnitude.

Experimental

Cerium Tracer.—Radioactive Ce^{144}, 275 day half-life, was obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. It was purified according to the method of Boldridge and Hume.[5] The final cerium oxalate precipitate was fumed with perchloric acid to destroy the oxalate ion. The cerium(III) perchlorate solution in concentrated perchloric acid was then diluted to give a cerium(III) perchlorate in *ca.* 6 *f* perchloric acid.

Measurement of Radioactivity.—All radioactive measurements were made using a dipping Geiger–Müller tube. Presumably the principal radiation being measured was the 3 mev. β-radiation of the 17.5 minute half-life Pr^{144} daughter. All solutions were allowed to stand at least three hours before counting to permit the daughter product to grow into equilibrium concentration. All samples were counted long enough to reduce the statistical counting error to 1.0% standard deviation or less.

Chemicals.—Stock reagent solutions were prepared from G. F. Smith Chemical Company hydrated cerium(IV) perchlorate (approximately 0.5 *f* cerium(IV) in 6 *f* perchloric acid) and 70% perchloric acid. The cerium(III) and cerium (IV) concentrations were determined by titration with standard iron(II), after oxidation of cerium(III) with persulfate in sulfuric acid. The acid solutions were analyzed by titration with standard alkali.

The *n*-butyl phosphate used was obtained from Commercial Solvents Corporation.

Separation of Reactants.—The separation of reactants was accomplished by extraction with *n*-butyl phosphate.[6] An aliquot of the exchange mixture was added to a solution 1 *f* each in nitric acid and ammonium nitrate. The cerium(IV) was then extracted with *n*-butyl phosphate. After separation the cerium(IV) was re-extracted with water from the solvent, first reducing cerium(IV) with hydrogen peroxide. Preliminary work on the extraction procedure indicated that the solvent caused very little reduction of cerium(IV). It was also determined that the cerium(IV) was quantitatively recovered from the solvent and that cerium(III) was not extracted.

Procedure.—Cerium(IV) perchlorate, perchloric acid and appropriate reagents were added to the exchange vessel. All solutions used in the exchange run were placed in a large refrigerated constant temperature bath at 0.1 ± 0.05°. The exchange was started by the rapid addition of tagged cerium(III) perchlorate to the exchange vessel. The exchange solution was further agitated by the removal and reinjection of an aliquot plus gentle swirling of the exchange

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[1] Work was supported in part by the Ames Laboratory of the Atomic Energy Commission.

[2] J. W. Gryder and R. W. Dodson, THIS JOURNAL, **71**, 1894 (1949).

[3] (a) J. W. Gryder and R. W. Dodson, *ibid.*, **73**, 2890 (1951); (b) H. C. Hornig and W. F. Libby, *J. Phys. Chem.*, **56**, 869 (1952).

[4] G. E. Challenger and B. J. Masters, THIS JOURNAL, **77**, 1063 (1955).

[5] W. F. Boldridge and D. N. Hume, National Nuclear Energy Ser., Division IV, 9, "Radiochem. Studies: The Fission Products," Book **3**, 1693 (1951).

[6] J. C. Warf, THIS JOURNAL, **71**, 3257 (1949).