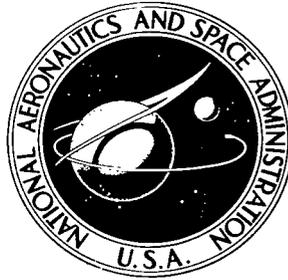


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# SOLUBILITIES OF VANADIUM, TITANIUM, AND ZIRCONIUM IN LIQUID POTASSIUM

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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## ABSTRACT

The solubility of vanadium in liquid potassium containing less than 20 wt ppm of oxygen between 1012 and 1341 K is about 6 and 70 wt ppm, respectively. The heat of solution for the vanadium solubility is  $21 \pm 4$  kilocalories per mole (87.9 kJ/mole). Titanium and zirconium solubilities in liquid potassium between 1020 and 1341 K are less than 4 and 10 wt ppm, respectively. Vanadium, titanium, and zirconium solubilities were studied in potassium doped with potassium nitrate ( $\text{KNO}_3$ ). The data suggest that  $\text{KNO}_3$  is not a good doping agent for determining the effect of oxygen on the solubilities of transition metals in liquid potassium.

# SOLUBILITIES OF VANADIUM, TITANIUM, AND ZIRCONIUM IN LIQUID POTASSIUM

by Stephan Stecura  
Lewis Research Center

## SUMMARY

Solubilities of vanadium, titanium, and zirconium were studied in liquid potassium containing less than 20 parts per million by weight (wt ppm) of oxygen between 1012 and 1341 K. Vanadium solubility is described by the relation

$$\log \text{ wt ppm V} = 5.18 - \frac{4500}{T}$$

where  $T$  is the absolute temperature. The heat of solution for the vanadium solubility in potassium is  $21 \pm 4$  kilocalories per mole (87.9 kJ/mole).

Titanium solubility in liquid potassium over the entire temperature range is less than 4 wt ppm and that of zirconium is less than 10 ppm by weight.

Vanadium, titanium, and zirconium solubilities were studied in potassium doped with potassium nitrate ( $\text{KNO}_3$ ) in order to determine the effect of oxygen on the solubilities of these metals in liquid potassium. The data suggest that  $\text{KNO}_3$  is not a good doping agent for determining the oxygen effect on the solubilities of transition metals in liquid potassium because of the interfering effect of nitrogen.

## INTRODUCTION

In advanced power systems, alkali metals such as sodium, potassium, and lithium are of interest as heat-transfer and thermodynamic working fluids. In some advanced Rankine type of space-power systems the use of potassium at temperatures up to about  $1200^\circ \text{C}$  (1473 K) (refs. 1 and 2) is contemplated. At such high temperatures alloys of the refractory metals (tantalum, niobium, molybdenum, or tungsten) are required for the

containment of liquid metals. Vanadium and the reactive metals, titanium and zirconium, are common alloying additions to the refractory metals.

Although several studies of the corrosion resistance of refractory metals and alloys to liquid potassium have been made (refs. 3 to 6), few quantitative data on their solubilities in liquid potassium are available. Solubility data are needed to properly interpret the results of corrosion tests and to assist in predicting the corrosion behavior under test conditions that have not yet been studied. Solubility data for the following refractory and reactive metals in liquid potassium have been reported: molybdenum (refs. 7 and 8), niobium (refs. 7 and 8), tantalum (refs. 8 and 9), titanium, and zirconium (ref. 9).

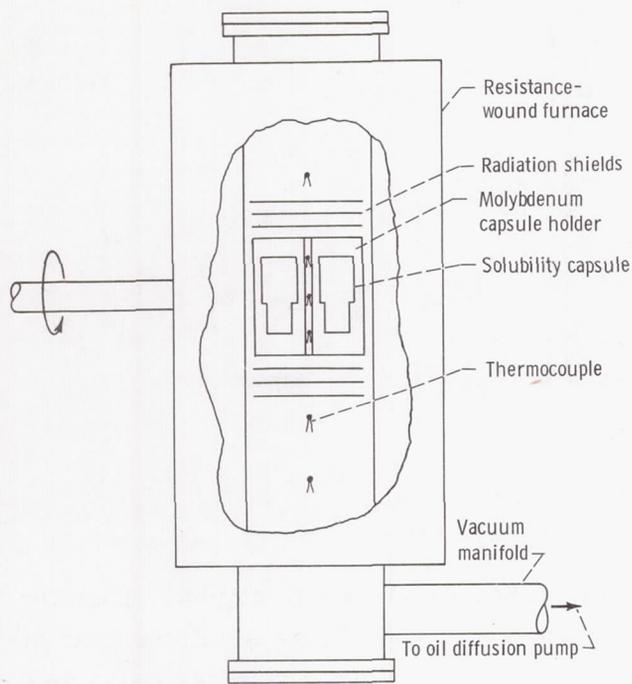
There is considerable disagreement and scatter in the reported solubility data. This may be attributed, in part, to the effects of interstitial impurities ( $O_2$ ,  $N_2$ , and C) present in either the refractory metal or potassium or both. Recently published data indicate that the solubilities of refractory metals or alloys in liquid potassium are most significantly affected by the presence of oxygen (refs. 3, 7, and 9 to 11). Nitrogen and carbon are believed to have lesser effects than oxygen.

The primary purpose of this study was to determine the solubilities of vanadium, titanium, and zirconium in liquid potassium at high temperatures. Solubilities of these three metals in liquid potassium between  $739^{\circ}$  and  $1068^{\circ}$  C (1012 and 1341 K) were determined by a rotatable-capsule method using equipment and techniques similar to those reported by Swisher (ref. 10).

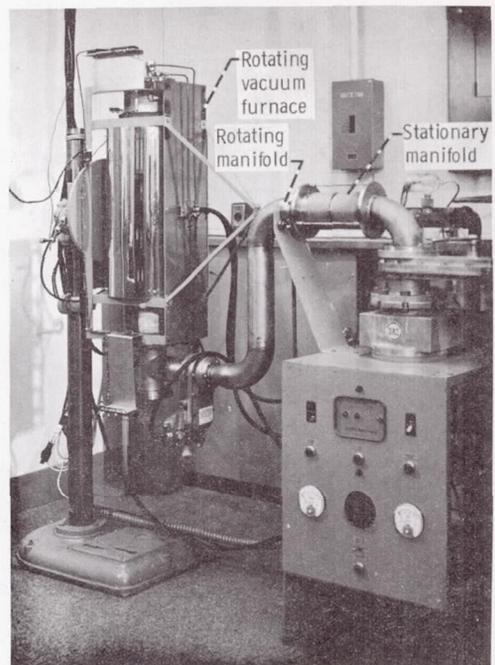
An attempt was also made to determine the oxygen effect on the solubilities of these three metals in oxygen-doped potassium. The doping agent was potassium nitrate ( $KNO_3$ ). As discussed in appendix B, interfering effects from the nitrogen precluded an accurate assessment of the effect of oxygen alone.

## MATERIALS, APPARATUS, AND PROCEDURE

The solubilities of vanadium, titanium, and zirconium in liquid potassium were determined by allowing crucibles of these three metals to be in contact with liquid potassium for 24 hours at a desired temperature. Figure 1 shows a photograph of the equipment used and a schematic diagram of the solubility furnace. The potassium and the crucibles were sealed in capsules made of either niobium or tantalum. After 24 hours, the capsules were inverted at the test temperature and the potassium containing the solutes was allowed to flow from the crucibles into the empty parts of the capsules. The furnace was then cooled to room temperature, the capsules opened, and the solute-containing potassium removed for analysis.



(a) Schematic of vacuum furnace.



(b) Overall view.

Figure 1. - Solubility apparatus.

## Materials

The potassium used in this study contained less than 20 ppm by weight of oxygen as determined by the vacuum amalgamation method.

The vanadium, titanium, and zirconium crucibles, which were the sources of solutes, were machined from 1/2-inch (1.27-cm) diameter polycrystalline rods. Tantalum and niobium capsules were machined from 5/8-inch (1.59-cm) diameter polycrystalline rods. The capsules were used as the containers for the crucibles and potassium and, also, as the collectors for the solute-containing potassium at the end of a test run. The dimensions and the relative positions of the crucibles and capsules during a test run are given in figure 2.

Before the crucibles and capsules were analyzed for impurities, they were first cleaned to remove surface contaminants. After they had been ultrasonically degreased

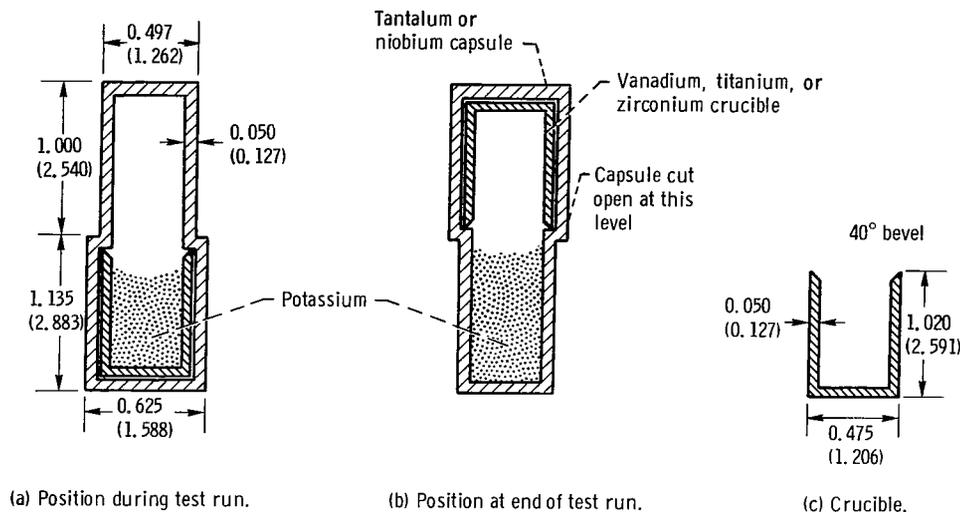


Figure 2. - Solubility capsule and crucible. (All units are in inches (cm).)

in a fluorinated hydrocarbon, they were ultrasonically cleaned in a detergent. Then the crucibles and capsules were etched for 10 to 15 seconds. The etching solutions used are given in table I. Finally, the crucibles and capsules were rinsed in distilled water and then in absolute ethyl alcohol and dried in an oven at about 75<sup>o</sup> C (348 K).

Analyses of the impurities were done on two crucibles and one capsule selected at random for each metal. As indicated in table II, the vanadium, titanium, and zirconium crucibles had a maximum total impurity of about 0.2 weight percent. The tantalum and niobium capsules had a total impurity of less than 0.1 weight percent. The impurities in these crucibles were determined by wet chemical and optical spectrographic analyses.

## Apparatus

The solubility furnace used in this study (fig. 1) was the same as that used in the study reported in reference 10. To minimize the temperature variation along the capsules, they were placed in a molybdenum holder. The largest temperature variation along the length of the capsule walls, inside the 4-inch (10.16-cm) long molybdenum holder over a period of 24 hours, was  $\pm 4^{\circ}$  C at 1068<sup>o</sup> C ( $\pm 4$  K at 1341 K). The temperature was measured with five platinum - platinum-13-percent-rhodium thermocouples spaced about 1 $\frac{1}{2}$  inches (3.81 cm) apart. The estimated accuracy of the temperature measurement is about  $\pm 8^{\circ}$  C at 1068<sup>o</sup> C ( $\pm 8$  K at 1341 K).

TABLE I. - ETCHANT SOLUTIONS

Metal	Etchant solution	Composition by volume
Nb	HF: HNO <sub>3</sub> : H <sub>2</sub> O	20: 20: 60
Ta	HF: HNO <sub>3</sub> : H <sub>2</sub> SO <sub>4</sub>	20: 25: 55
Zr	HF: HNO <sub>3</sub> : PB(NO <sub>3</sub> ) <sub>2</sub>	30: 30: 40
Ti	HF: HNO <sub>3</sub> : H <sub>2</sub> O	5: 35: 60
V	HF: HNO <sub>3</sub> : H <sub>2</sub> O	3: 30: 67

TABLE II. - IMPURITY CONTENT OF CRUCIBLE  
AND CAPSULE METALS

Impurity	Concentration of Impurity, wt ppm				
	Zirconium	Titanium	Vanadium	Niobium	Tantalum
Carbon <sup>a</sup>	97	62	119	40	40
Oxygen <sup>a</sup>	722	587	675	50	13
Nitrogen <sup>a</sup>	66	46	570	35	8
Hydrogen <sup>a</sup>	9	44	12	3	2
Aluminum	10	60	ND <sup>b</sup>	10	10
Cadmium	ND <sup>b</sup>	ND <sup>b</sup>	300	5	ND <sup>b</sup>
Calcium	ND	ND	ND	10	10
Cobalt	10	10	ND	10	10
Chromium	10	15	10	10	10
Copper	300	30	10	10	10
Iron	180	220	100	15	20
Hafnium	100	100	ND	ND <sup>b</sup>	50
Magnesium	60	30	ND	10	10
Manganese	10	450	ND	ND	ND
Molybdenum	10	10	100	30	55
Nickel	ND	ND	10	10	20
Niobium	ND	ND	ND	High	65
Silicon	10	10	100	10	30
Tantalum	100	500	37	600	High
Tin	10	10	10	10	10
Titanium	70	High	150	10	10
Tungsten <sup>a</sup>	6	8	ND	100	100
Vanadium	10	380	High	1	ND
Zirconium	High	10	468	20	10

<sup>a</sup>Results obtained by chemical analyses. All other data were obtained by optical spectrographic method.

<sup>b</sup>Not detected.

At the end of a solubility run, this furnace can be inverted. The rotation of the furnace into the upside-down position is necessary because the potassium containing vanadium, titanium, or zirconium must be collected at the end of a test run in the tantalum or niobium capsules and not in the crucibles. The solutes that precipitate during cooling the furnace to room temperature can only be recovered for analysis if the potassium is in the capsules.

## Procedure

The experimental technique used in this study is similar to that described in reference 10. Tantalum capsules were used in determining the solubility of vanadium, and niobium capsules were used in determining the solubilities of titanium and zirconium in liquid potassium.

The handling of potassium was carried out in a vacuum chamber at about  $5 \times 10^{-6}$  torr. Each of the capsules was filled with about 1.2 grams of potassium. The crucibles, made of the metal whose solubility was to be tested, were placed into the capsules. Capsules were capped and electron beam welded. After welding, the capsules were removed from the chamber and leak checked.

The capsules containing the crucibles and potassium were put into the molybdenum holder and then placed in the furnace with the crucibles at the bottom of the capsules as shown in figure 2(a). The furnace was evacuated to  $10^{-6}$  torr and heated to the desired temperature. As the temperature increased, the potassium melted and flowed into the crucible. After 24 hours at the desired temperature, the furnace was rotated upside-down and the solute-containing potassium flowed into the smaller section of the capsule (fig. 2(b)).

After cooling to room temperature, the capsules were removed from the furnace and cut open at almost the middle as shown in figure 2(b). The potassium was then dissolved in butyl alcohol. The inside wall of the smaller-diameter capsule section was leached with hydrochloric acid (HCl) to remove the solute that precipitated on cooling. Butyl alcohol and acid solutions were combined. Potassium present in the combined solution was converted to potassium chloride (KCl) by acidifying the combined solution with HCl and evaporating the solvent. The weight of potassium chloride was determined gravimetrically. The concentrations of vanadium, titanium, and zirconium in potassium chloride samples were determined primarily by the optical spectrographic method. Graphite electrodes were used. Wet chemical analytical methods were used whenever the concentrations of solutes were high enough to give meaningful results (refs. 12 to 14).

## RESULTS AND DISCUSSION

### Solubility in Pure Potassium

The solubility of vanadium in pure liquid potassium is about 6 parts per million by weight (wt ppm) at 739° C (1012 K) and about 70 wt ppm at 1068° C (1341 K) (fig. 3). The solubility data for vanadium in pure liquid potassium were obtained by the optical spectrographic method. The accuracy of these data was determined by comparing the results obtained by the optical spectrographic method against the results obtained by the wet chemical method. The accuracy of the wet chemical analysis for greater than 30 wt ppm of vanadium in a sample is about  $\pm 6$  percent (ref. 14). Below a vanadium concentration of 30 wt ppm, the accuracy is unknown but undoubtedly lower based on the poor reproducibility of the data in this range.

The results from the optical spectrographic and wet chemical analyses did not differ by more than  $\pm 12$  percent. Because the vanadium solubility data were obtained by the optical spectrographic method, their estimated accuracy is about  $\pm 18$  percent above 30 wt ppm of vanadium. Below 30 wt ppm of vanadium, the data are probably less accurate.

Vanadium solubility data reported in figure 3 can be represented by the relation

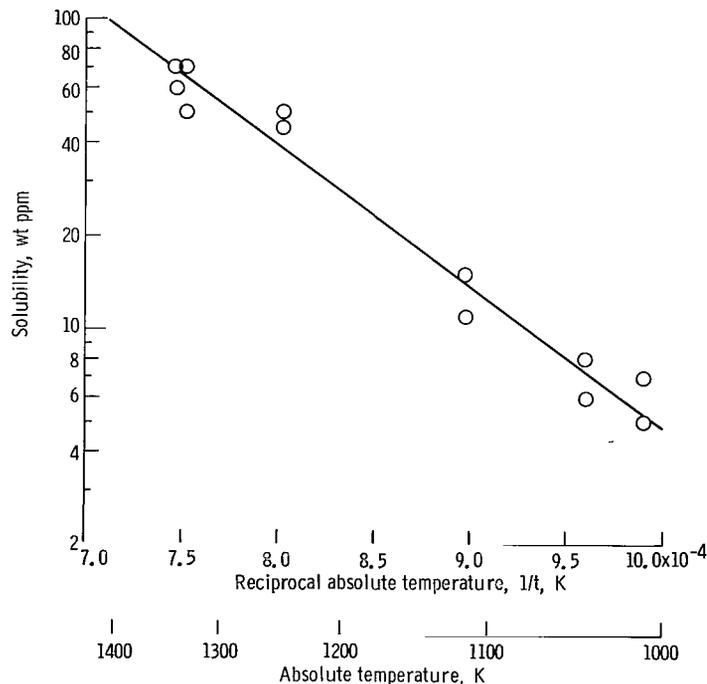


Figure 3. - Solubility of vanadium in high-purity potassium.

$$\log \text{ wt ppm V} = 5.18 - \frac{4500}{T, \text{ K}}$$

where T is the absolute temperature. The apparent heat of solution of vanadium in liquid potassium, calculated from a plot of log wt ppm V against 1/T, is 21±4 kilocalories per mole (87.9 kJ/mole).

The solubilities of titanium and zirconium in pure liquid potassium are so low that the optical spectrographic and wet chemical methods (refs. 12 and 13) could not give quantitatively reproducible data. Therefore, the solubilities of titanium and zirconium between 747° and 1067° C (1020 and 1340 K) are reported as being less than the limits of analyses, 4 and 10 wt ppm, respectively (table III).

TABLE III. - SOLUBILITIES OF TITANIUM AND ZIRCONIUM  
IN HIGH PURITY LIQUID POTASSIUM

[Data obtained by optical spectrographic analyses.]

Temperature, °C	Titanium, wt ppm	Zirconium, wt ppm	
1068	<4	10	
1068	↓	<10	
1059			
1059			
972			
972			
842			
842			
747		4	↓
747		<4	

From the theoretical considerations, the solubilities of vanadium, titanium, and zirconium in pure liquid potassium would be expected to be low. Low solubilities are expected because of the large atom sizes, electronegativities, and valency differences of these transition metals with respect to potassium (ref. 15). The theoretical treatment of the data in appendix A and the experimental data in appendix B suggest that the small amount of oxygen present in pure potassium had little or no effect on the solubilities of these transition metals in liquid potassium.

On the basis of these data presented in this report, it is concluded that the true solubility values for vanadium, titanium, and zirconium should not be higher than those presented in figure 3 and table III.

## Solubility in Nitrate-Doped Potassium

An attempt was made to determine the effect of oxygen on the solubilities of vanadium, titanium, and zirconium in liquid potassium between 747<sup>o</sup> and 1069<sup>o</sup> C (1020 and 1342 K). Potassium was doped with potassium nitrate. However, the true total oxygen effect could not be determined because of the interfering effect of nitrogen. Therefore, the discussion on the solubilities of these three metals in the nitrate-doped potassium is presented in the appendix B.

## SUMMARY OF RESULTS

The solubilities of vanadium, titanium, and zirconium were determined in liquid potassium containing less than 20 wt ppm of oxygen. The primary results of this study are

1. The solubility of vanadium in liquid potassium between 739<sup>o</sup> and 1068<sup>o</sup> C (1012 and 1341 K) varies with the temperature as described by the relation,  $\log \text{ppm by weight V} = 5.18 - 4500/T$ . At 739<sup>o</sup> and 1068<sup>o</sup> C (1012 and 1341 K) the solubility of vanadium is about 6 and 70 ppm by weight, respectively. The heat of solution for vanadium in liquid potassium is 21±4 kilocalories per mole (87.9 kJ/mole).

2. Over the entire temperature range (1020 to 1341 K), the solubilities of titanium and zirconium were below the limits of quantitative reproducibilities of the optical spectrographic and wet chemical methods. The solubilities were less than 4 and 10 ppm by weight for titanium and zirconium in liquid potassium, respectively.

An attempt was made to determine the effect of oxygen on the solubilities of vanadium, titanium, and zirconium in liquid potassium. Oxygen was added to potassium as potassium nitrate. Unfortunately, the apparent solubilities of these three metals in liquid potassium appear to have been affected by the presence of nitrogen which reacted with the metals and formed metal nitrides on the metal surfaces as described in appendix B. These nitrides seem to be inert to liquid potassium.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, December 18, 1968,  
129-03-03-01-22.

## APPENDIX A

### CONSIDERATION OF POSSIBLE EFFECT OF OXYGEN ON TRUE SOLUBILITIES OF VANADIUM, TITANIUM, AND ZIRCONIUM IN PURE LIQUID POTASSIUM

The author believes that 20 wt ppm of oxygen present in the high-purity potassium used in this study had a negligible effect on the measured solubilities of vanadium, titanium, and zirconium (V, Ti, and Zr) in liquid potassium. Vanadium, titanium, and zirconium picked up oxygen from the potassium (appendix B, table IV), as would be predicted from the relative free energies of formation of the oxides of these three metals and potassium. The free energies of formation per oxygen atom for  $V_2O_5$ ,  $TiO_2$ ,  $ZrO_2$ , and  $K_2O$  are -49.6, -84.8, -101.4, and -29.8 kilocalories (-207.6, -355.0, -424.4, and -124.7 kJ), respectively (ref. 16). On the basis of these free energies and the high oxygen solubility in vanadium, titanium, and zirconium (refs. 17 to 20) the following reaction should occur



where  $M = V, Ti, \text{ or } Zr$ . However, the formation of an oxide on the metal surface would also result if the rate of oxygen chemisorption is greater than the rate of oxygen diffusion into the metal matrix. The oxide present on the metal surface may then react with potassium or potassium oxide and form a ternary oxide according to the following equations (ref. 21):



where  $M = Ti \text{ or } Zr$ . The presence of reactions (2) and (3) or (4) would be expected to increase significantly the apparent solubilities of vanadium, titanium, and zirconium in liquid potassium. However, data indicate that the solubilities of vanadium, titanium, and zirconium in pure liquid potassium are very low (fig. 3 and table III). Therefore, reactions (2), (3), and (4) do not appear to occur. Consequently, the author concluded that, under the experimental conditions described in this report, the solubility data presented in figure 3 and table III are representative of the true solubilities of vanadium, titanium, and zirconium in high-purity liquid potassium.

## APPENDIX B

### SOLUBILITIES OF VANADIUM, TITANIUM, AND ZIRCONIUM IN OXYGEN-NITROGEN DOPED POTASSIUM

The solubilities of vanadium, titanium, and zirconium were studied in liquid potassium doped with potassium nitrate ( $\text{KNO}_3$ ) in order to determine the oxygen effect on the solubilities of these three metals in liquid potassium. Potassium nitrate as well as potassium carbonate ( $\text{K}_2\text{CO}_3$ ) have been previously used in studying the oxygen effect on the solubilities of transition metals in liquid alkali metals (ref. 7).

The present study indicates that the true total effect of oxygen on the solubilities of vanadium, titanium, and zirconium in liquid potassium could not be determined using potassium nitrate as the dopant. Nitrogen present in potassium reacted with these transition metals and formed inert nitrides which interfered with the oxygen effect. This led to unusual relations among temperature, oxygen-nitrogen concentrations, and the apparent solubilities of these three metals.

A detailed discussion of the observed effects of potassium nitrate on the apparent solubilities of these three metals is presented because

(1) Even though the true total effect of oxygen could not be determined, some of the results from the doped potassium study presented in this appendix support the solubility data for these three metals in pure potassium given in the main body of this report.

(2) The data from the doped potassium study emphasize the need for using high-purity liquid metals in the solubility studies, such as those described in this report. Solubility data are needed to interpret the corrosion test results. Meaningful interpretations can only be made when the interpretations are based on the data obtained from unambiguous tests.

(3) The data from the doped potassium study clearly indicate the danger of using  $\text{KNO}_3$  or  $\text{K}_2\text{CO}_3$  in the evaluation of the true total effect of oxygen on the solubilities of metals in liquid alkali metals.

#### Oxygen Doping of Pure Potassium

Pure potassium containing less than 20 wt ppm of oxygen was doped with potassium nitrate ( $\text{KNO}_3$ ) to the following oxygen and nitrogen levels:

- (1) Low-nitrate-level potassium containing 560 wt ppm of oxygen and 163 wt ppm of nitrogen
- (2) Medium-nitrate-level potassium containing 2500 wt ppm of oxygen and 730 wt ppm of nitrogen

(3) High-nitrate-level potassium containing 5000 wt ppm of oxygen and 1460 wt ppm of nitrogen

The doping procedure was as follows: Three different potassium nitrate concentration solutions were prepared by dissolving different quantities of  $\text{KNO}_3$  in aqueous ethyl alcohol. The concentration of each of these three solutions was such that 0.2 cubic centimeter of solution was equivalent to the oxygen-nitrogen concentrations stated previously. Using a microburette, 0.2 cubic centimeter of one of the nitrate solutions was measured into each of the several crucibles. The crucibles were then placed in a drying chamber and left there for 48 hours at a 15-micron ( $2 \text{ N/m}^2$ ) pressure. After this, the crucibles (containing only  $\text{KNO}_3$ ) and an equivalent number of capsules were transferred to an electron-beam welding chamber. The crucibles and capsules remained in the chamber for at least 24 hours at  $10^{-6}$  torr. Then 1.2 grams of pure potassium were added to each capsule, the crucibles were placed into the capsules, and the capsules were capped and electron-beam welded. The rest of the procedure is like that described in the main text.

## Special Analyses

X-ray diffraction analyses. - Samples for the X-ray diffraction analyses were recovered from the inside walls of the crucibles (crucibles were the sources of the solutes). When the capsules were opened, the crucibles were removed from the capsules and put into the vials containing ethyl alcohol for about 5 minutes. Only crucibles that contained no potassium or showed no reaction with ethyl alcohol were used. The crucibles were then washed with acetone and dried. The inside walls of the crucibles were scraped with a spatula. The samples were put into the X-ray capillaries and X-ray diffraction patterns were obtained.

The author was able to index completely all X-ray diffraction patterns obtained for the various vanadium and titanium samples. These X-ray diffraction results are discussed in this appendix in the sections entitled: Apparent Solubility of Vanadium and Apparent Solubility of Titanium.

Oxygen and nitrogen analyses. - Whenever possible, the crucibles were analyzed for the oxygen and nitrogen before and after they were exposed to doped liquid potassium. The crucibles used in oxygen and nitrogen analyses were those that, after being exposed to doped liquid potassium, showed no reaction with ethyl alcohol. Oxygen in vanadium crucibles was determined by the inert-gas fusion method. Oxygen concentration in the vanadium crucibles before exposure to doped liquid potassium was assumed to be about the same as that reported in table II. Oxygen concentrations in the titanium and zirconium crucibles were determined by the neutron activation analysis.

Nitrogen concentrations in vanadium, titanium, and zirconium crucibles were determined by the Kjeldahl method. The original nitrogen concentrations in these crucibles were assumed to be the same as those reported in table II.

### Apparent Solubility of Vanadium

The apparent solubility of vanadium in low-nitrate-level potassium at the lowest temperature (747° C or 1020 K) is significantly higher than the solubility of vanadium in pure potassium (figs. 3 and 4). With temperature increase, this significant difference decreases until, at the highest test temperature (1069° C or 1342 K), there is no significant difference between the solubility in pure and low-nitrate-level potassium. The higher solubility in low-nitrate-level potassium is probably due to the formation of  $V_2O_5$  on the inside wall of the crucible. Vanadium pentoxide reacted with potassium (ref. 21) and formed a ternary oxide which accounted for the increased solubility in doped potassium. As the temperature increases, the amount of  $V_2O_5$  decreases because of the greater rate of oxygen diffusion into the metal matrix and the more rapid nitrogen chemisorption from the potassium which results in the formation of an inert nitride on the metal surface. At

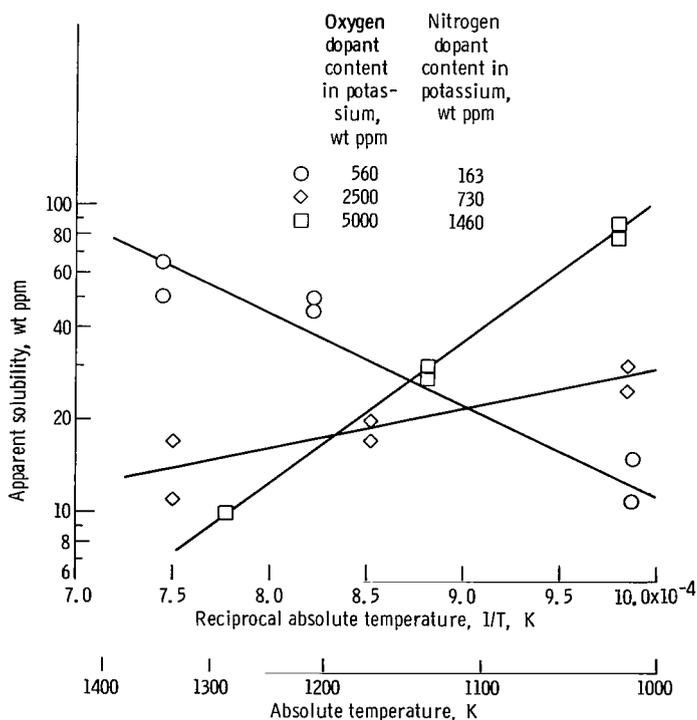


Figure 4. - Apparent solubility of vanadium in oxygen-nitrogen doped potassium.

high temperature ( $1069^{\circ}$  C or  $1342$  K),  $V_2O_5$  is not formed and the ternary oxide is absent. Therefore, at high temperature, oxygen in doped potassium had little or no effect on the apparent solubility of vanadium.

The apparent solubility of vanadium in medium- and high-nitrate-level potassium is significantly influenced by the presence of oxygen and nitrogen in potassium (fig. 4). At low temperature ( $747^{\circ}$  C or  $1020$  K), the higher apparent solubility is again due to a ternary oxide formed from  $V_2O_5$  and potassium (ref. 21). Vanadium pentoxide forms because the oxygen concentration in liquid potassium is high and vanadium metal picked up about all the oxygen added to pure potassium, particularly from the medium-nitrate-level potassium (table IV). The author believes that it is only  $V_2O_5$  that reacts with potassium to form a ternary oxide and not  $VO_{0.9}$ , which was recovered from the crucible wall and identified by the X-ray diffraction analysis.

The decrease in the apparent solubility of vanadium with the temperature increase is probably due to a more rapid formation of a nitride layer on the walls of the crucibles and the increased rate of oxygen diffusion into the vanadium metal. The formation of a nitride layer on the inside walls of the crucibles was confirmed by the X-ray diffraction data obtained for the samples removed from the crucible walls. This nitride layer consisted of trivanadium nitride ( $V_3N$ ). The nitride layer decreases the rate of oxygen chemisorption and this results in the decrease of  $V_2O_5$  formed. Consequently, less ternary oxide is formed and the apparent solubility decreases with the temperature increase. In addition, as the inert nitride layer covers more and more of the inside wall of the crucible, the solubility of vanadium decreases below that in pure potassium. This probably is due to the lack of equilibrium between vanadium and potassium. The nitride layer is inert and acts as a barrier. It decreases the rate of solution of vanadium into potassium. Because of this decrease in the rate of solution and because of the increasingly greater coverage of the vanadium metal surface by the nitride, equilibrium in the vanadium - potassium system was not established.

Because  $VO_{0.9}$  and  $V_3N$  were recovered from the crucible walls,  $VO_{0.9}$  and  $V_3N$  are either inert or are negligibly affected by the liquid potassium.

## Apparent Solubility of Titanium

The apparent solubility of titanium in low- and medium-nitrate-level potassium between  $747^{\circ}$  and  $1067^{\circ}$  C ( $1020$  and  $1340$  K) is less than 4 wt ppm (fig. 5). Titanium chemisorbed about all the oxygen and some nitrogen added to potassium (tables IV and V). The formation of  $Ti_2O$ ,  $TiO$ ,  $Ti_2N$ , and  $TiN$  was confirmed by the X-ray diffraction data obtained for the samples that were scraped from the inside walls of the crucibles. These crucibles were exposed to medium-nitrate-level potassium at  $747^{\circ}$  C ( $1020$  K) for

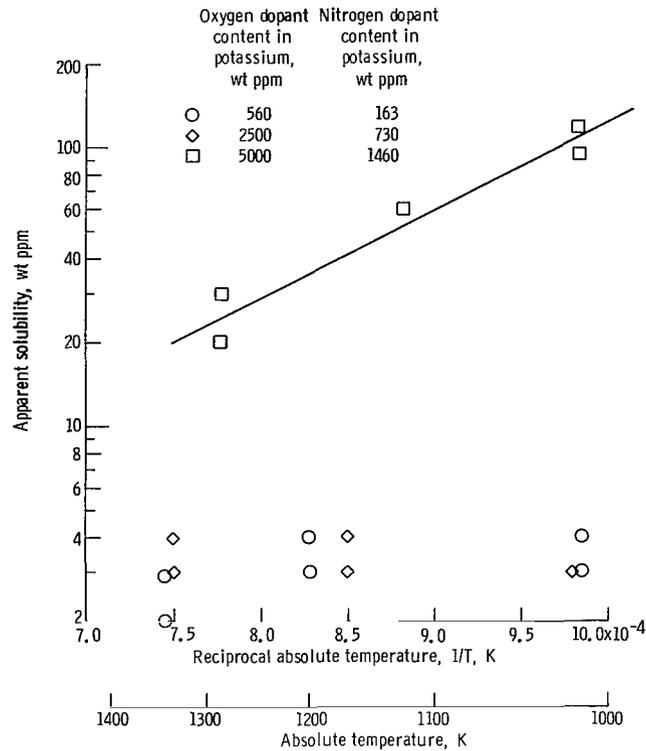


Figure 5. - Apparent solubility of titanium in oxygen-nitrogen doped potassium.

TABLE IV. - AMOUNT OF OXYGEN PICKED UP BY VANADIUM, TITANIUM, AND ZIRCONIUM FROM OXYGEN-NITROGEN DOPED POTASSIUM<sup>a</sup>

Crucible	Temperature, <sup>b</sup> °C	Milligrams oxygen added per gram of potassium	Milligrams of oxygen picked up by crucible
V-1	1061	2.5±0.1	2.5±0.2
V-14	747	2.5	2.2
V-18	1013	5.0±0.2	3.2
V-21	859	5.0	3.3
V-22	850	5.0	3.5
Ti-1	1061	2.5±0.1	3.0±0.5
Ti-2	1061	2.5	2.1
Ti-3	899	2.5	3.4
Ti-13	747	2.5	3.1
Zr-1	1061	2.5±0.1	2.9±0.5
Zr-4	899	2.5	2.9
Zr-6	747	2.5	2.7

<sup>a</sup>Oxygen in vanadium metal was determined by inert-gas fusion method and the oxygen in titanium and zirconium metals by the neutron activation method.

<sup>b</sup>Temperature at which crucible was exposed to oxygen-nitrogen doped potassium for 24 hr.

TABLE V. - AMOUNT OF NITROGEN PICKED UP BY VANADIUM, TITANIUM, AND ZIRCONIUM FROM THE OXYGEN-NITROGEN DOPED POTASSIUM<sup>a</sup>

Metal and crucible	Temperature, <sup>b</sup> °C	Milligrams of nitrogen added per gram of potassium	Milligrams of nitrogen picked up by crucible
V-18	1013	1.4±0.06	0.70±0.04
V-21	859	1.4	.73
Ti-18	1013	1.4	.53
Zr-16	1013	1.4	.49

<sup>a</sup>Nitrogen was determined by the Kjehdahl method.

<sup>b</sup>Temperature at which crucible was exposed to oxygen-nitrogen doped potassium for 24 hr.

24 hours. These two oxides were formed because the rate of oxygen chemisorption was greater than the rate of oxygen diffusion into the titanium matrix. The overall oxygen solubility limit in titanium was not exceeded (ref. 17).

Even the presence of Ti<sub>2</sub>O and TiO on the inside walls of the crucibles did not increase the solubility of titanium in liquid potassium above that in pure potassium. This suggests that the presence of 20 wt ppm of oxygen in pure potassium probably had no effect on the solubility of titanium in pure liquid potassium. Therefore, the solubility of titanium in pure liquid potassium should not be greater than the experimentally determined values reported in table III.

The apparent solubility of titanium in high-nitrate level potassium is greater than for lower nitrate-level potassium (fig. 5). It decreases with the temperature increase. The higher apparent solubility of titanium at 747° C (1020 K) than at 1060° C (1333 K) is probably due to a greater amount of TiO<sub>2</sub> formed on the inside walls of the crucibles at low temperatures. The TiO<sub>2</sub> is believed to have reacted with potassium or potassium oxide and formed a ternary oxide which accounted for the increased titanium solubility. As the temperature increases, the decrease in the apparent solubility is due to a more rapid formation of the titanium nitride layer which decreases the rate of oxygen chemisorption from the potassium. These conclusions can be drawn on the bases of the X-ray data obtained for the samples scraped off the crucible walls which were exposed to the high-nitrate-level potassium at 747° and 859° C (1020 and 1132 K). The sample from the 747° C (1020 K) run contained Ti<sub>2</sub>O, TiO, Ti<sub>2</sub>N, and TiN, and the sample from the 859° C (1132 K) run contained only TiN. The only way TiN could have formed from the Ti<sub>2</sub>N is that the increase in the rate of nitrogen chemisorption was greater than the increase in the rate of nitrogen diffusion into the titanium matrix. The absence of the oxides at 859° C (1132 K) is due to the decrease in the rate of oxygen chemisorption which is due to the formation of the nitride layer on the crucible surface. Under these con-

ditions, the apparent solubility of titanium should decrease with the temperature increase. This is supported by the data presented in figure 5.

### Apparent Solubility of Zirconium

The apparent solubility of zirconium in low-, medium-, and high-nitrate-level potassium between 747<sup>o</sup> and 1060<sup>o</sup> C (1020 and 1333 K) is less than 10 wt ppm over the range of these temperatures. Zirconium chemisorbed significant quantities of oxygen and nitrogen from the potassium (tables IV and V). However, the lack of change in the apparent solubility of zirconium in oxygen-nitrogen doped potassium as compared with the solubility in pure potassium is probably due to the absence of zirconium dioxide and the presence of the nitride layer on the inside walls of the crucibles. Zirconium probably behaves very similarly to titanium.

The solubility of zirconium was not affected by the presence of high concentrations of oxygen and nitrogen in potassium. Therefore, the author assumed that the 20 wt ppm of oxygen present in pure potassium would have little or no effect on the solubility of zirconium in pure liquid potassium. Consequently, the solubility of zirconium in pure liquid potassium should not be greater than that reported in table III.

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