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SOLUBILITY OF IRON, NICKEL, AND COBALT IN LIQUID POTASSIUM AND EFFECT OF OXYGEN GETTERING AGENTS ON IRON SOLUBILITY

by James H. Swisher

Lewis Research Center
Cleveland, Ohio

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SUMMARY

The solubility of iron, nickel, and cobalt in potassium was studied in the temperature range 941° to 1328° K. The cobalt solubility was less than 5 parts per million at the highest temperature. The equilibrium solubility obtained for alpha iron and nickel can be described by the following equations:

$$\log \text{ppm alpha iron} = 8.193 - \frac{6166}{T}$$

$$\log \text{ppm nickel} = 3.89 - \frac{3040}{T}$$

where T is the temperature in °K.

The solubility data were determined by sampling the potassium at the test temperature using a dissimilar metal cup. The equation for iron was determined by using molybdenum sampling cups; however, the observed iron solubility was found to be strongly dependent on the cup material. This dependence was correlated with the oxygen gettering ability of various cup materials.

INTRODUCTION

The containment of liquid alkali metals is a serious problem in the development of space power systems. Solubility data are needed to aid in the selection of materials that will be compatible with liquid metal heat-transfer media and working fluids. This report describes the determination of the solubility of iron, nickel, and cobalt in potassium for the temperature range 941° to 1328° K.

Previous work in this area has been limited primarily to solubility in liquid lithium and liquid sodium. The solubility of several elements in
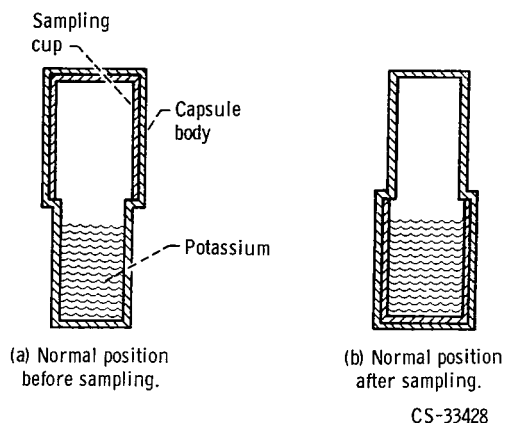
Sampling
cup

Capsule
body

Potassium

(a) Normal position
before sampling.

(b) Normal position
after sampling.

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Figure 1. – Schematic illustration of test procedure.

lithium is reported in reference 1. In reference 2, the existing data for niobium, tantalum, molybdenum, and tungsten in lithium and sodium are summarized. Additional data for the solvents lithium and sodium are given in references 3 to 10.

The only available data for the solubility of high-melting-point metals in potassium are for the potassium-molybdenum system (ref. 11). For temperatures up to 1352° K (1975° F), the solubility of molybdenum is reported to be less than 0.2 parts per million for potassium containing about 50 parts per million of oxygen. Reported also, however, is the fact that the apparent solubility of molybdenum increases linearly with the oxygen content of the potassium.

APPARATUS AND PROCEDURE

The experimental method used was to sample the potassium at the test temperature using an invertible solubility capsule. A schematic diagram of the solubility capsule is given in figure 1, and the capsule parts are shown in figure 2. In most cases, the solubility capsule was machined from the material whose solubility was to be determined, and the sampling cup was made of molybdenum; however, a modification was required for the tests with cobalt and with nickel at temperatures of 1144° K and above. Columbium capsules were used because of the poor fabricability of cobalt and the poor creep strength of nickel at high temperatures. The potassium was equilibrated in cobalt or nickel cups, and the samples were taken in the lower section of the columbium capsules. For the modified procedure figures 1(a) and (b) should be reversed.

To check for possible interaction effects in solution, other metals were substituted for molybdenum as the sampling cup material in a series of iron solubility tests. The other metals used were zirconium, columbium, tantalum, and nickel. Chemical analyses of the container materials used are given in table I.

Prior to the experiments, the solubility capsules were filled with about 1.5 grams of potassium and sealed by electron-beam welding. Both steps were accomplished without interruption in a single vacuum chamber (10^{-5} torr). The potassium contained less than 20 parts per million of oxygen, as measured by a mercury amalgamation method (ref. 12).

The solubility experiments were performed in the vacuum furnace (10^{-5} torr) shown schematically in figure 3(a); a photograph of the furnace is shown in figure 3(b). The capsules were held in a close-fitting molybdenum holder that aided in minimizing temperature gradients in the capsules. Preliminary tests showed that the equilibrium solubility was achieved in a few
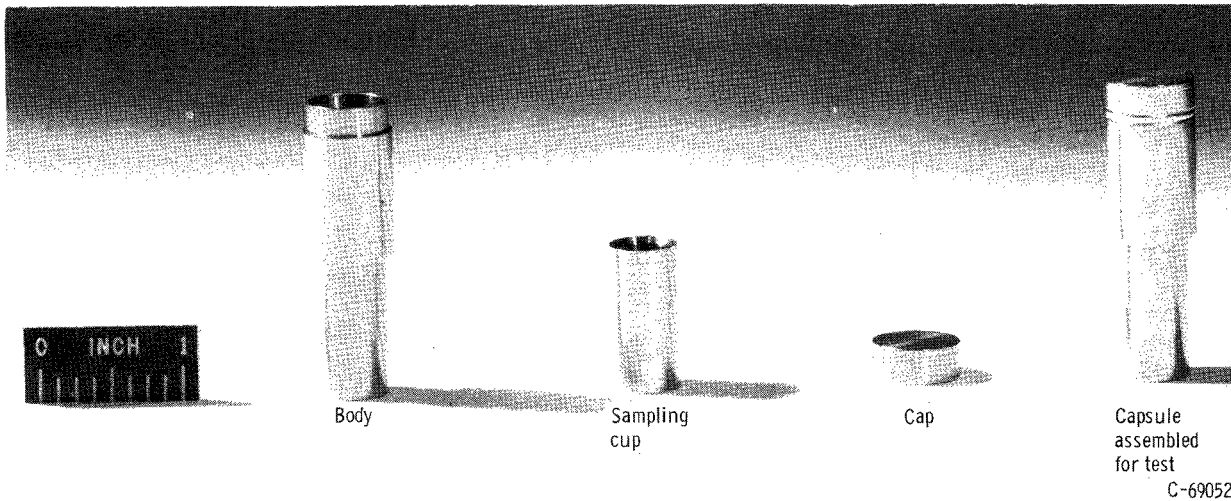
Figure 2. – Solubility capsule.

TABLE I. – CHEMICAL ANALYSES OF CONTAINER MATERIALS

[Dashes indicate no analysis was obtained for impurity element.]

Impurity	Concentration of impurity in container material, ppm						
	Iron	Nickel	Cobalt	Molybdenum	Columbium	Tantalum	Zirconium
Carbon	150	50	-----	20	100	21	125
Oxygen	510	---	-----	16	90	51	~800
Nitrogen	68	---	-----	4	110	29	35
Hydrogen	----	---	-----	2	2	----	-----
Cobalt	----	2	-----	----	----	----	-----
Sulfur	160	10	-----	----	----	----	-----
Phosphorus	40	---	-----	----	----	----	-----
Silicon	20	5	-----	<10	----	21	65
Manganese	400	<10	-----	<10	----	----	<200
Copper	700	<10	-----	<10	----	<1	<10
Calcium	----	---	-----	40	----	----	-----
Magnesium	----	---	-----	<10	----	----	<200
Tin	----	---	-----	<10	----	----	<200
Aluminum	----	---	-----	10	----	25	-----
Iron	----	4	-----	20	----	25	400
Nickel	----	---	-----	<10	----	<5	<200
Chromium	----	5	-----	<10	----	<5	<200
Tungsten	----	---	-----	30	----	<40	-----
Zirconium	----	---	-----	----	<100	----	-----
Columbium	----	---	-----	----	----	80	-----
Total	2048	<96	<1000	<212	<402	<303	<2435
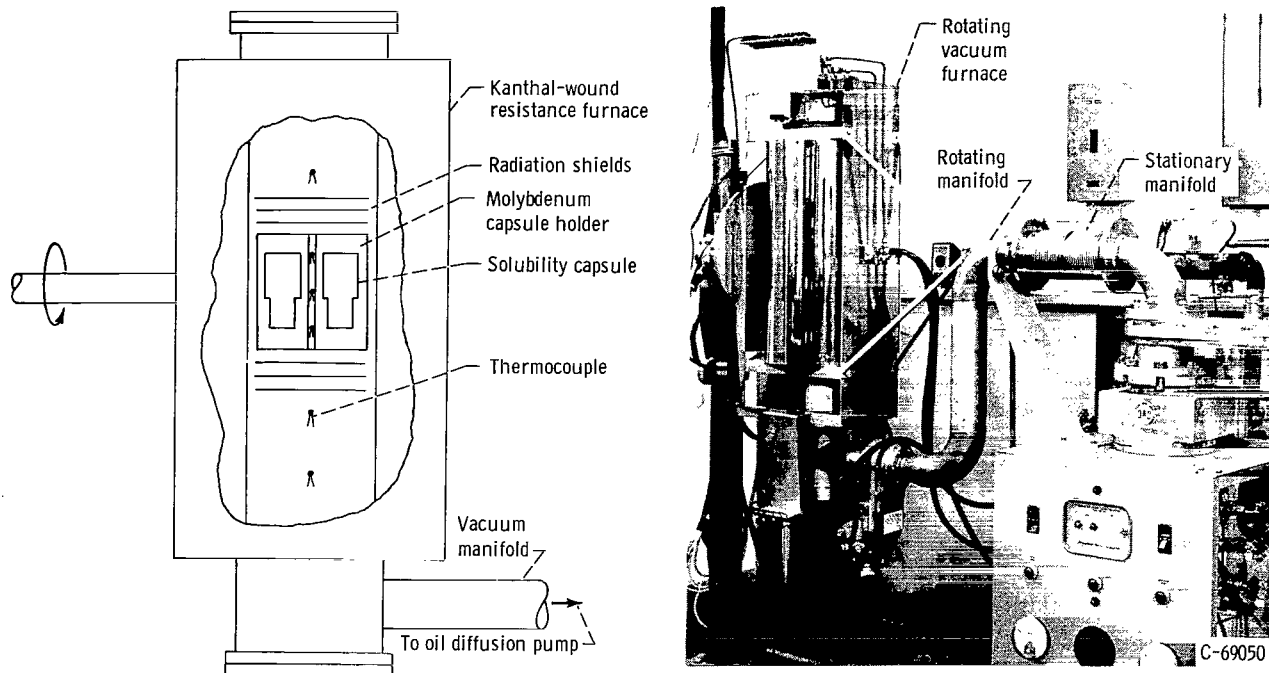
(a) Schematic of vacuum furnace.

(b) Overall view.
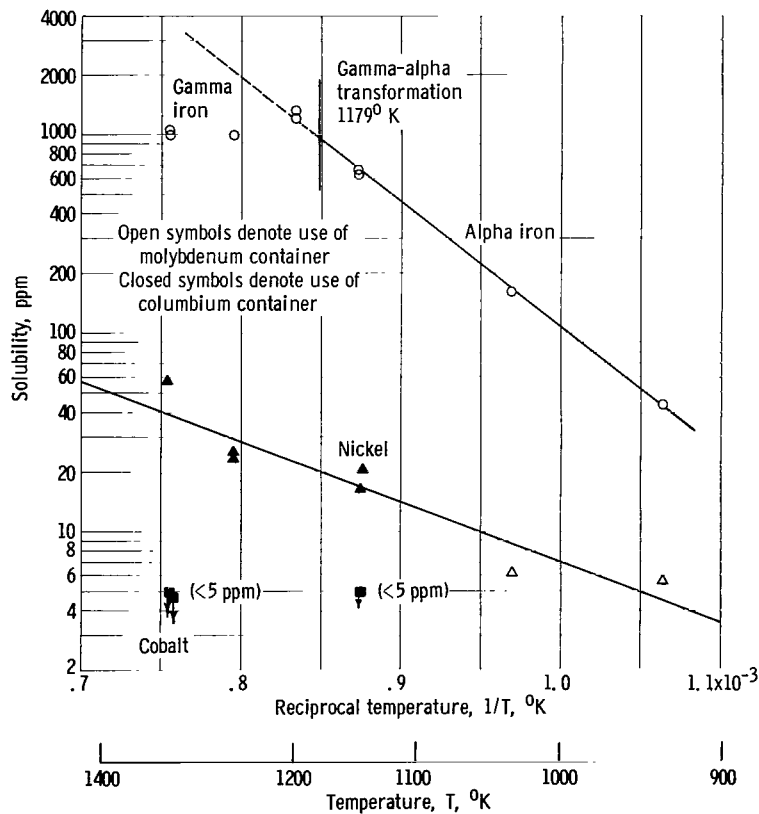
Figure 3. – Solubility apparatus.

Figure 4. – Solubility of iron, nickel, and cobalt in potassium.

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hours at the experimental temperature. Temperatures were measured with platinum - platinum-13-percent-rhodium thermocouples positioned at the center of the capsule holder. The thermocouples were accurate to within 3° K, and the temperature fluctuation in the hot zone of the furnace was $\pm 1^{\circ}$ K.

Sampling at the test temperature was accomplished by inverting the furnace, which allowed the potassium to flow into the sampling cups. After cooling to room temperature, the capsules were cut open and the potassium samples dissolved in butyl alcohol. The sampling cups then were leached with hydrocloric acid to remove the material that had precipitated during cooling. Colorimetric methods were used to determine the concentrations of iron, nickel, and cobalt (refs. 13 to 15) in the alcohol and acid solutions; the amount of potassium present in the alcohol solutions was determined gravimetrically.

RESULTS AND DISCUSSION

Experimental

The solubility data for iron, nickel, and cobalt in potassium are shown in figure 4. Least squares calculations led to the following analytical equations for the iron and nickel data:

$$\log \text{ ppm alpha iron} = 8.193 - \frac{6166}{T}$$

$$\log \text{ ppm nickel} = 3.89 - \frac{3040}{T}$$

where T is the temperature in $^{\circ}$K.

In figure 4 the data points for iron that correspond to the highest test temperatures of 1257° and 1328° K do not fall on the line drawn through the other points. Although a change in slope of the solubility line is to be expected at the alpha to gamma transformation temperature, this change should be too small to be observed in the experimental plot. (The enthalpy change accompanying the transformation is only 0.2 kcal/mole as shown in ref. 16, p. 397.) An explanation of this anomaly in the iron data will be presented later in connection with an oxygen gettering effect.

From the solubility-temperature dependence, the apparent heats of solution of alpha iron and nickel in potassium were found to be 28.2±0.3 and 13.9±2.1 kilocalories per mole, respectively. Standard deviations in solubility values averaged over the experimental temperature range were ±2.3 percent for alpha iron and ±27.8 percent for nickel. The large uncertainty in the nickel values was mainly due to a blank correction for the leaching step. The blank weight of 15 micrograms was nearly as large as the total weight of nickel in the samples. In the cobalt tests, the concentrations of cobalt were detectable, but the analyses were not sufficiently accurate to specify values for the cobalt solubility.

The concentrations of iron, nickel, and cobalt obtained in the solubility tests are typical of data reported for alkali metal solvents (refs. 1 to 11)

TABLE II. - RELATIVE SOLUBILITIES OF IRON, NICKEL,

AND COBALT IN POTASSIUM, SODIUM, AND LITHIUM

[Comparisons made on atomic rather than weight basis.]

(a) Relative solubility in alkali metal solvents

Solute	Alkali metal solvent
Iron Nickel Cobalt	Potassium > sodium > lithium Lithium > sodium > potassium Potassium ≈ sodium

(b) Relative solubility of iron, nickel, and cobalt

Alkali metal solvent	Solute
Potassium Sodium[a] Lithium	Iron > nickel > cobalt Iron ≈ cobalt > nickel Nickel > iron

[a]Disagreement exists between investigators on reported
values for iron and nickel in sodium (refs. 5, 6,
and 8).

TABLE III. - EFFECT OF VARIOUS CONTAINER MATERIALS

ON OBSERVED SOLUBILITY OF IRON IN POTASSIUM

Sampling cup material	Observed iron solubility at 1144° K, ppm
Nickel	3540
Molybdenum	639, 655
Columbium	194, 257, 358
Tantalum	117
Zirconium	44
Molybdenum with zirconium coupons	77, 129

but very low in comparison to other liquid metal solvents, such as copper, tin,
and aluminum (ref. 17). The results are not unexpected because the generally
recognized effects that govern solubility (atomic size, electronegativity, and
valency) are unfavorable for producing high solubility in alkali metals
(ref. 16, p. 79).

It should be noted that the relative solubilities of iron, nickel, and
cobalt in potassium, sodium, and lithium are not the same. A comparison is
given in table II. This difference in relative solubilities is not consistent
with current theoretical principles (ref. 16, p. 79).

Effect of Oxygen Impurity on Solubility

The solubility data for iron obtained by using various sampling cups are
given in table III. A variation of two orders of magnitude was observed in the
solubility of iron at 1144° K (1600° F) as the sampling cup metal was varied
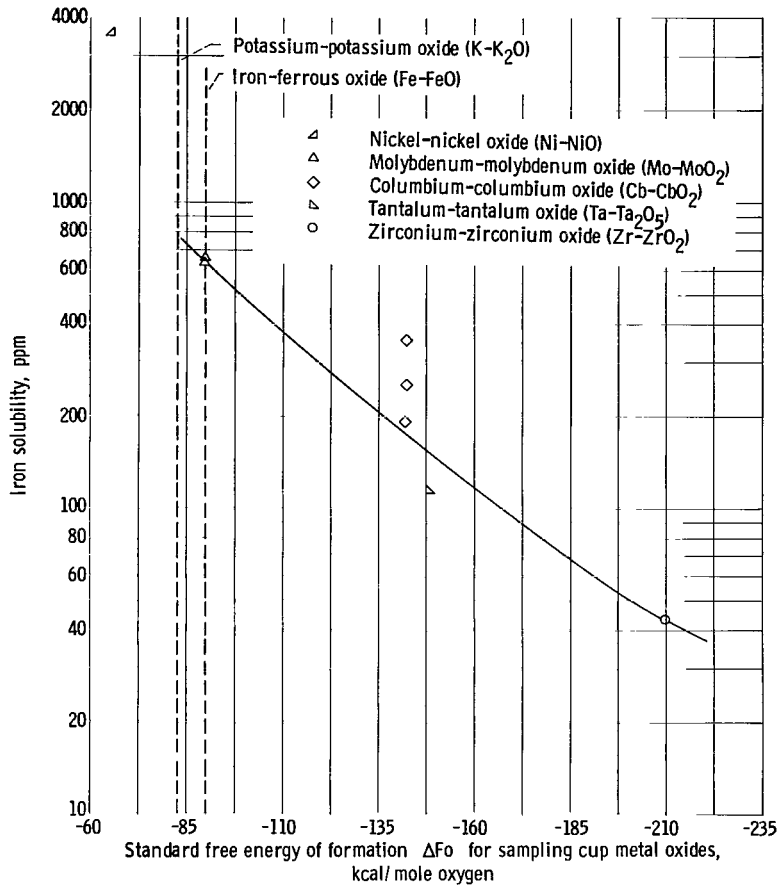
Figure 5. – Effect of oxygen gettering agents on observed solubility of iron in potassium. Temperature, 1144° K (1600° F).

through the following series: nickel, molybdenum, columbium, tantalum, and zirconium. These results can best be explained by assuming that the solubility of iron is a function of the oxygen concentration in the potassium, which in turn is controlled by the gettering action of the cup materials.

A general correlation was made in figure 5 between the observed iron solubility and the standard free energy of formation (ΔFo, a measure of gettering potential) of the sampling cup metal oxides (ref. 18). The solubility of iron can be seen to increase in a regular manner with decreasing -ΔFo of the sampling cup metal oxides. The use of standard free-energy data was considered valid because, even though complete saturation of the sampling cups with oxygen did not occur, the surfaces of the cups were believed to be saturated during the course of the tests, and the principle of local equilibrium was believed to apply (ref. 19).

An interesting parallel can be seen in dynamic corrosion tests of steels with sodium, where it was found that the corrosion rate varied with the oxygen content of the sodium (ref. 20). It was subsequently proposed that a sodium ferrate, $(Na_2O)_2 \cdot FeO$, isolated in the sodium-iron-oxygen system (ref. 21),
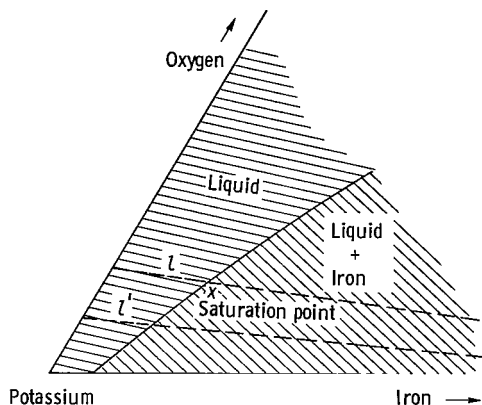
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Figure 6. – Potassium corner of proposed potassium-iron-oxygen phase diagram at constant temperature.

could act as an intermediary species in the iron mass-transfer process. A comparable entity, potassium ferrate, could be the species that accounts for the dependence of the solubility of iron in potassium on oxygen content.

Figure 6 shows the potassium corner of a proposed potassium-iron-oxygen phase diagram. Here the oxygen concentration in the potassium, established by a particular gettering agent, is represented by line l, which intersects the iron apex of the diagram when extended. Iron will dissolve along line l until saturation is reached at point x. Since the position of line l varies with each gettering agent, the observed solubility will also vary. In the event that more than one gettering agent is present, the position of the line will be governed by the most effective gettering material present.

This latter contention was tested in two iron capsules with molybdenum sampling cups and zirconium coupons placed in the potassium. Since molybdenum is a poorer getter than zirconium, the iron solubility should be the same as that obtained when using a zirconium cup (table III and fig. 5). The values obtained were 77 and 129 parts per million, compared to a value of 44 parts per million resulting from the original test with the zirconium cup. Qualitative agreement was obtained because the values were closer to the zirconium value in figure 5 than to the molybdenum values. An oxide film observed on the zirconium coupons after the test could have reduced the effectiveness of the zirconium gettering agent by reducing the rate of transport of oxygen into the metal. Thus, the test time may not have been long enough to reach the equilibrium concentration of oxygen in the potassium.

In figure 5, the point obtained using the nickel sampling cup should be independent of the ΔF_O of NiO. Since potassium and iron are stronger gettering agents than nickel, the oxygen content of the potassium and hence the observed iron solubility should depend primarily on the total oxygen content of the system. In other words, line l in figure 6 cannot be fixed by the cup material when it is a weaker gettering agent than potassium or iron.

The apparently anomalous high-temperature iron points presented earlier in figure 4 can also be explained in terms of the oxygen impurity effect. For these points it is suggested that there was not sufficient oxygen present in the system to reach the partial pressure of oxygen that would be in equilibrium with the gettering material at the test temperature. The iron solubility, therefore, would correspond to a lower than equilibrium concentration of oxygen in the potassium and the solution process would follow a line l' (fig. 6), which lies below line l established by the gettering agent used (molybdenum).

It should be noted (see fig. 4, p. 4) that the solubility of nickel in potassium appeared to be independent of the container material. (Molybdenum and columbium were used.) Thus, for nickel, it may be inferred that the oxygen interaction effect is small. This behavior is consistent with oxygen-catalyzed mass-transfer results obtained for nickel in sodium, which yielded lower values than those for iron in sodium (refs. 22 to 24).

CONCLUDING REMARKS

The results of this investigation indicate that iron-rich alloys could have limited use as containment materials for liquid potassium. A significant amount of mass-transfer of iron could occur in a liquid metal loop because the the liquid is circulated through a temperature gradient. The experimentally determined factors that support this conclusion are the relatively high iron solubility, the high temperature coefficient of solubility, and the enhancement of solubility with oxygen contamination. The successful use of iron-base alloys would depend to a large extent on how well the oxygen level in the potassium is controlled. On the other hand, the data determined for nickel and cobalt in potassium indicate that their use in space power systems should not be seriously limited by solubility criteria when potassium is the heat-transfer medium or working fluid.

Lewis Research Center,
     National Aeronautics and Space Administration,
          Cleveland, Ohio, January 5, 1965.

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