

The Fe-K (Iron-Potassium) System

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Equilibrium Diagram

The assessed Fe-K binary phase diagram is shown in Fig. 1. The system is virtually completely immiscible both in the solid and the liquid states. In Fig. 1, it is assumed that the solubility of K in solid (Fe) is negligible. The solubility of Fe in liquid K is taken from the compilation of [67Ant], but these values are only approximate. Not shown in Fig. 1 is the gas phase, which at 1 bar protrudes from the K side at 759 °C (the boiling point of K [Melt]).

Little solubility of K in (Fe) would be expected at ordinary pressures because the melting points of the elements differ by more than 1400 °C. K was described as "insoluble" in (Fe) [29Wev1, 29Wev2], but no supporting evidence was given. Fe was heated in liquid K at 1000 to 1300 °C [34Jon] and examined microscopically for K diffusion into the metal, but none was detected.

Data on the solubility of Fe in K were reviewed by [67Ant] and [82Kub]. There are significant discrepancies among the data from different sources that apparently derive from the contamination of liquid K with oxygen, nitrogen, and carbon. [67Ant] argued that the data of [65Swi] should be preferred, because the

"...high-temperature vacuum centrifuge technique of [66Gin] and [65Gin] appears incapable of yielding reliable solubility data," and because the data of [66Mck] exhibit so much scatter. These evaluators agree with [67Ant].

Coefficients for the solubility relationship:

$$\log(\text{solubility, wt. ppm}) = a + b/T, K$$

reported both by the original authors and by the reviewers are given in Table 1. The experimental data and the linear relationships are plotted in Fig. 2, which shows that the uncertainty at a given temperature is up to two orders of magnitude.

[65Swi] used half capsules of Fe that were machined from a rod that contained 510 ppm O, 68 ppm N, and 150 ppm C (all "ppm" units are presumed to be by weight, but it should be noted that the original sources failed to specify wt. ppm or at. ppm). The Fe capsules were filled with K and electron beam welded to receiver capsules of nickel, molybdenum, tantalum, niobium, or zirconium under vacuum ($\sim 10^{-5}$ torr, $\sim 1.3 \times 10^{-8}$ atm). The liquid K was gettered with titanium sponge at 1243 °C and distilled into a stainless steel container. This procedure yielded liquid K with less than 20 ppm O as measured by mercury amalgamation. Samples were heated for several hours with opening of the Fe capsule facing down, and then they were inverted and cooled in the furnace. Loading and unloading of the capsules was done in a glove box ($\sim 10^{-5}$ torr, $\sim 1.3 \times 10^{-8}$ atm). Liquid K products were analyzed for Fe (colorimetrically), but not for oxygen, nitrogen, or carbon. The effect of sampling cup material was determined at 871 °C, and the range of measured solubility values was 44 to 3540 wt. ppm; this is shown in Fig. 2 as an error bar. According to [82Kub], the most reliable measurements appear to be those in

Table 1 Coefficients for Fe-K Solubility
 $\log(\text{solubility wt. ppm}) = a + b/T, K$

Reference	Temperature, °C	Coefficient	
		a	b
[65Swi].....	670 to 910	8.2	-6170
[66Mck].....	800 to 1000	3.4	-1700
[67Ant](a).....	670 to 910	5.3	-4170
[82Kub].....	670 to 925	8.6	-6600

(a) Recommended values.

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Table 2 Solubility of Fe in Liquid K

Reference	Solubility		Temperature, °C	Equilibration time, h
	wt. ppm Fe	at. % Fe		
[65Swi](a).....	43	0.0030	670	...
	250	0.0175	760	...
	650	0.0455	870	...
	1300	0.0910	930	...
	1000	0.0700	1000	...
	1000	0.0700	1060	...
[66Gin].....	457	0.0320	925	3
	447	0.0313	925	3
	555	0.0389	1000	3
	444	0.0311	1000	3

(a) As reported in [Shunk].

which molybdenum receiver capsules were used; a regression analysis of these data yields:

$$\log X_{\text{Fe}} = 0.5310 - 4.5724 \times 10^3 (1/T)$$

where X_{Fe} is the mole fraction of Fe and T is in K.

[65Gin], [65Tei], and [66Gin] used L-shaped Nb-1 at.% Zr capsules with an Fe sample cup in one leg, a tungsten receiver cup in

the other, and an Fe pouring spout that connected them. Initially, the Fe sample cups ("99.97% Puron-Fe") contained 30 ppm C and an unspecified concentration of O. The tungsten receiver cup contained <30 ppm O and 5 ppm C. The oxygen content of the Nb-1 at.% Zr capsules was not reported. Samples were loaded under purified argon ("passed over 50-50 Zr-Ti alloy chips at 900 °C") in a dry box. Analysis of the dry box exhaust gas during operation

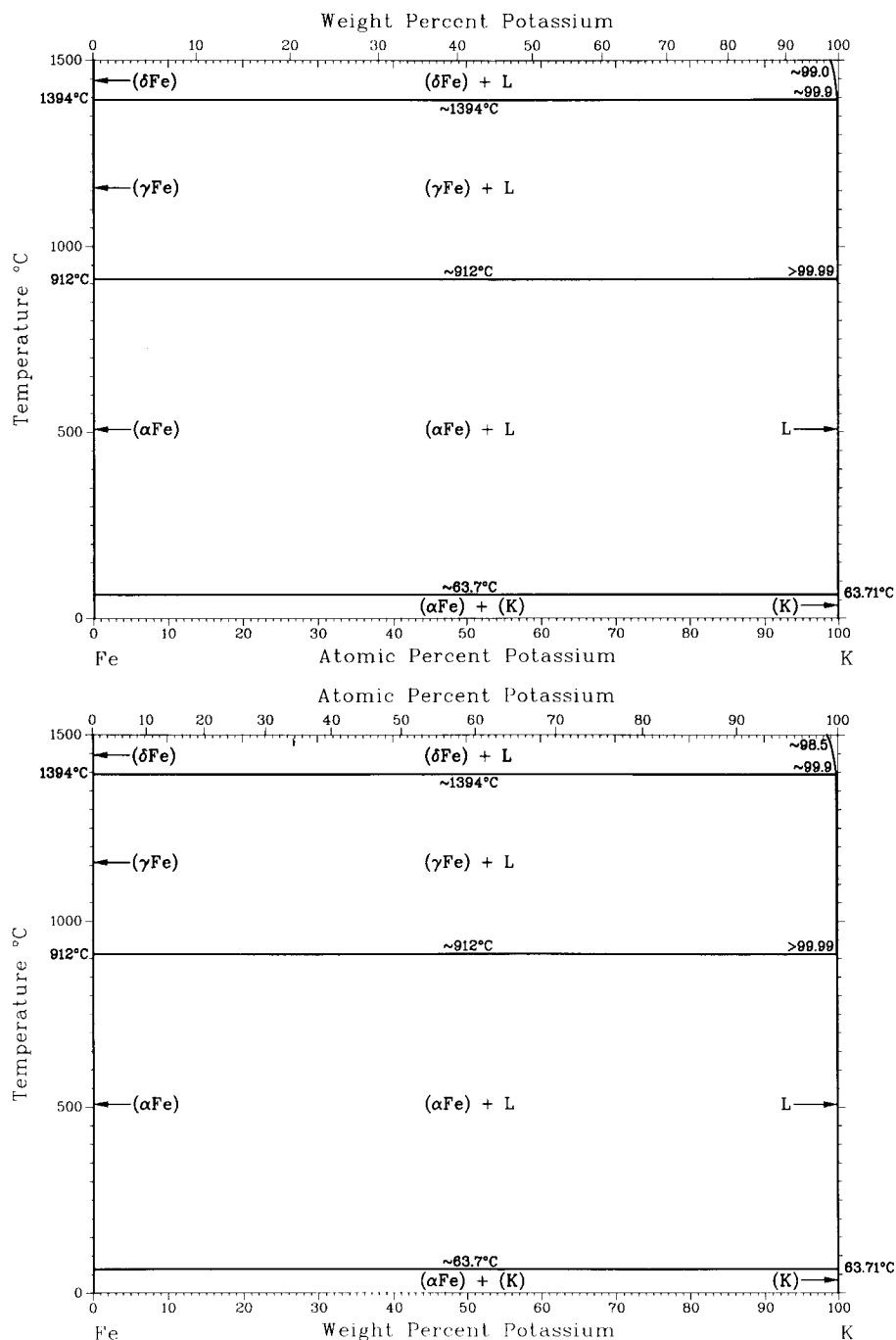


Fig. 1 Assessed Fe-K phase diagram.

Section II: Phase Diagram Evaluations

indicated less than 2 ppm H₂O. The liquid K was "purified in a zirconium-lined hot trap" containing 50-50 Zr-Ti alloy chips at 785 °C, which yielded liquid with 7 to 11 ppm O. After loading, samples were heated to 100 °C above their annealing temperatures for 1 h prior to annealing at the temperatures listed in Table 2.

[66Mck] used Fe sample cups that were brazed onto tantalum receiver cups and then fully enclosed in molybdenum capsules. Loading, heating, and unloading of capsules was done in vacuum. After annealing, the capsules were inverted and cooled. Liquid K was analyzed for Fe colorimetrically. Initial concentrations of oxygen, nitrogen, and carbon in the Fe cup were 8, 0.1, and 10 ppm respectively; in the liquid K, initial concentrations of oxygen, nitrogen, and carbon were 3.5 to 16, 4, and 10 ppm, respectively; final oxygen, nitrogen, and carbon concentrations in the annealed liquid were not reported. Regression analysis of the [66Mck] data yields:

$$\log X_{\text{Fe}} = -2.777 - 1.6820 \times 10^3 (1/T)$$

As noted above, the relationship recommended by [82Kub] was based on the results of [65Swi] with a molybdenum sampling cup, whereas [67Ant] preferred a curve that passes through the lowest observed datum (44 wt. ppm) of [65Swi] at 871 °C—the one obtained with a zirconium sampling cup.

[65Swi] observed that the solubility of Fe increases with negative standard Gibbs energies of formation of the sampling metal oxides, demonstrating the detrimental effect of oxygen on the solubility measurements. The expression of [67Ant] was used in Fig. 1, because it is assumed to be the most reliable.

Some of the measured solubility values were determined above 912 °C, the $\alpha \leftrightarrow \gamma$ transformation temperature of Fe [Melt]. A very small change in slope would be expected to occur when this temperature is passed, but the data are too sparse and ambiguous to draw any conclusions.

Table 3 Fe-K Crystal Structure and Lattice Parameter Data

Phase	Composition, at. % K	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameter, nm	Comment
δFe	0	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W	0.29315	At >1394 °C
γFe	0	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	0.36467	At >912 °C
αFe	0	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W	0.28665	At 25 °C
K	100	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W	0.5321	At 25 °C

From [Massalski].

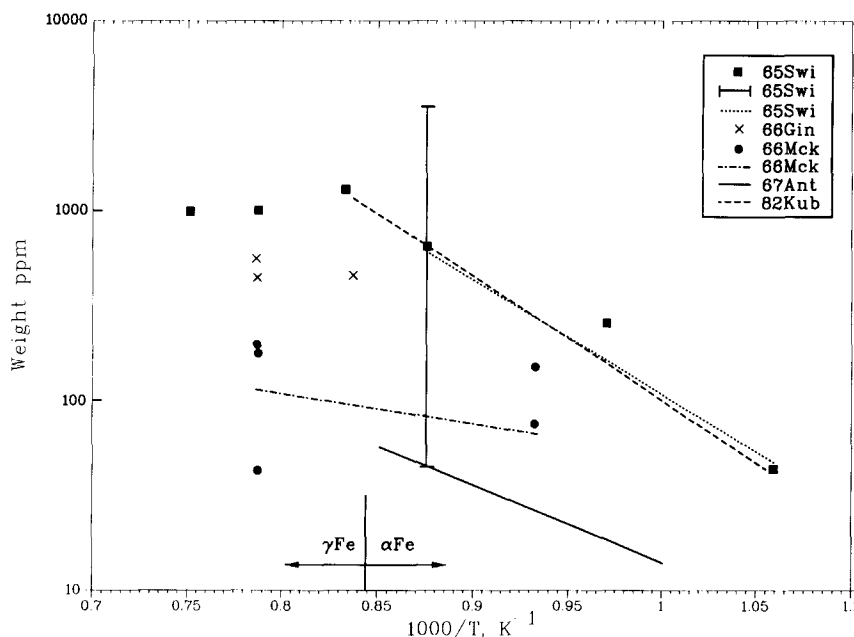


Fig. 2 Solubility of Fe in liquid K. — = Mo/sampling cup; = various sampling cups.

Crystal Structures and Lattice Parameters

Fe-K crystal structure and lattice parameter data are summarized in Table 3. No intermediate phases have been reported.

Thermodynamics

Atomic model calculations for the enthalpy of formation of solid alloys of the type $\text{Fe}_x\text{K}_{1-x}$ ($x = 0.17$ to 0.83)—the results of which are all positive [83Nie]—are consistent with the experimental findings that no Fe-K compounds are formed. The enthalpy of solution of liquid Fe in liquid K at infinite dilution was calculated from the same model [83Nie] to be 221 kJ/g-atom.

The enthalpies of solution for Fe in K derived from the parameters in Table 1 are, in kJ/g-atom: 88 [65Swi], 32 [66Mck], 63 [67Ant], and 94 [82Kub]. The value of [67Ant] was chosen as a mean between those of [65Swi] and [66Mck].

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The Ce-Zr (Cerium-Zirconium) System

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Equilibrium Diagram

No phase diagram has been established for this system, although [Moffat] drew a hypothetical phase diagram, reported in Fig. 1, assuming similarity between the Ce-Zr and Ce-Ti systems.

[59Bla] reported that the Ce-Zr system is a simple eutectic. [54Daa] and [64Har] confirmed the absence of intermediate phases. [57Dix] suggested the presence of immiscible liquids in the system with the melting point of Zr lowered to a monotectic reaction at $1490 \pm 50^\circ\text{C}$. [57Dix] also found that Ce lowers the α

Table 1 Solid Solubility of Ce in αZr

Temperature, °C	Solubility(a), at. % Ce
650.....	0.80
680.....	3.00
730.....	3.75
780.....	4.6
830.....	5.5
850.....	6.0

(a) From [64Har].