The Fe-O (Iron-Oxygen) System

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Equilibrium Diagram

The stable solid phases in the Fe-O system at 0.1 MPa are (1) the terminal bcc solid solution with a narrow range of compositions denoted ferrite, (αFe), or (δFe), with the latter designations used below 912 and above 1392 °C, respectively; (2) the terminal fcc solid solution denoted austenite or (γFe), with a narrow range of compositions extending approximately from 912 to 1394 °C, the stable temperature range of γFe; (3) the fcc oxide denoted FeO, $Fe_{1-x}O$, Fe_xO, FeO_{1+x}, FeO_x (sometimes with specific *x* values), wustite, wuestite, wüstite, or iozite, with a broad range of compositions, which may possibly be subdivided into regions with differing types or degrees of order; (4) the oxide denoted Fe_3O_4 or magnetite, which is monoclinic and almost stoichiometric below –149 °C and is fcc above, with a range of compositions considerably broadened at high temperatures; and (5) the rhombohedral oxide denoted Fe_2O_3 or hematite, which is almost stoichiometric at low temperatures, but has an appreciably broadened range of compositions at high temperatures.

The assessed Fe-O phase diagram (Fig. 1) essentially follows the form published by [46Dar]. As in other assessments [Hansen, 82Kub] that retained all the main features of that diagram, details of univariant and invariant positions were modified because of perceived improvements in measurements. The special points of the system are listed in Table 1.

In addition to the above-mentioned stable phases, two phases stabilized by elevated hydrostatic pressure—(εFe) and Fe_3O_4(P)—and seven metastable phases—four wustite and three Fe_2O_3 forms—are described in the "Crystal Structures and Lattice Parameters" section, below.

Terminal Solid Solutions, (αFe), (δFe), and (γFe)

The temperatures of the allotropic transformations, Curie point, and melting point of Fe listed in Table 1 are from [82Swa].

The experimental investigations of the (Fe) boundaries in the Fe-O system prior to 1955 were listed and summarized by [Hansen] and [62Vol]. Most of these results are discredited from application to the high-purity Fe-O system, because they were made before the advent of zone-refined Fe. [58Sif] and [59Sey] showed that apparent O solubility values measured in impure Fe specimens exhibited gross errors that were not due simply to precipitates of known oxides of reactive impurities. The results in Table 2 were obtained with zone-refined Fe.

The 881 °C point on the (αFe) boundary (Table 2) was considered by the investigators themselves [67Swi] to be inaccurate. Their

Table 1 Special Points of the Assessed Fe-O Phase Diagram (Condensed System, 0.1 MPa)

Reaction(a)	Composition of the respective phases, at.% O			Temperature, °C	Reaction type
Stable					
$L_1 \leftrightarrow \delta Fe$		0		1538	Melting point
$\delta Fe \leftrightarrow \gamma Fe$		0		1394	Allotropic
$\gamma Fe \leftrightarrow \alpha Fe$		0		912	Allotropic
αFe (para) $\leftrightarrow$ αFe (ferro)		0		770	Curie point
$(\gamma Fe) + W \leftrightarrow (\alpha Fe)$	0.0007	51.2	0.0008	~912	Peritectoid
$(\delta Fe) \leftrightarrow (\gamma Fe) + L_2$	0.019	0.0098	50.9	1392	Catatectic
$L_1 \leftrightarrow (\delta Fe) + L_2$	0.58	0.029	50.5	1528	Monotectic
$L \leftrightarrow L_1 + L_2$		~47(b)		~2830(b)	Critical point
$L_2 \leftrightarrow (\gamma Fe) + W$	50.9	0.0094	51.3	1371	Eutectic
$W \leftrightarrow (\alpha Fe) + Fe_3O_4$	51.4	...	57.1	570	Eutectoid
$L_2 + Fe_3O_4 \leftrightarrow W$	54.2	57.1	54.6	1424	Peritectic
$L_2 \leftrightarrow Fe_3O_4$		57.1		1596	Congruent melting
Fe_3O_4 (para) $\leftrightarrow$ Fe_3O_4 (ferri)		57.1		580	Néel (or Curie) point
$Fe_3O_4 \leftrightarrow Fe_3O_4$ (LT)		57.1		–149	Polymorphic
$L_2 \leftrightarrow Fe_3O_4 + O_2(g)$(0.1013 MPa)	57.9	57.7	100	1582	Eutectic type
$Fe_3O_4 + O_2(g)$(0.1013 MPa) $\leftrightarrow \alpha Fe_2O_3$	58.0	100	59.8	1457	Peritectic type
αFe_2O_3 (para) $\leftrightarrow$ αFe_2O_3 (antiferro + ferro)		60.0		688	Curie + Néel point
αFe_2O_3 (antiferro + ferro) $\leftrightarrow$ αFe_2O_3 (antiferro)		60.0		–10.5	Magnetic
Other					
$L_2 \leftrightarrow Fe_3O_4 + \alpha Fe_2O_3$(c)	58.9	58.2	59.7	1539	Eutectic
$L_2 \leftrightarrow \alpha Fe_2O_3$(d)		60.0		~1572	Congruent(?) melting

Note: W = wustite. (a) Magnetic transitions are indicated in Fig. 1 but associated three-phase equilibria are omitted from Table 1. (b) Roughly estimated [84Oht1], P_{O_2} unknown. (c) P_{O_2}~0.78 MPa . (d) P_{O_2}~5.3 MPa).

recommended value was 0.0006 at.% O at 881 °C; their phase diagram depicts the composition of (αFe) coexisting with (γFe) and wustite at 912 °C as 0.0008 at.% O. The magnitude of these values is about one third that of the [58Sif] values, but it is concordant with the theoretical estimate of 0.00007 to 0.0013 at.% O at 906 °C by [67Fra]. The [67Swi] values are, however, below the 0.0007 to 0.0042 at.% O range at 727 °C estimated by [69Fuj], with which the [58Sif] values are consistent. Because the theoretical estimates are not decisive, whereas the trend with use of purer Fe is towards lower values, the [67Swi] recommendation is preferred.

The result of [70Kus] obtained with electrolytic Fe for (δFe) coexisting with L_1 and L_2 at 1528 °C is 0.042 at.% O, somewhat higher than that (0.031 at.% O) indicated by extrapolation of the [66Hep] data, but far below that (0.110 at.% O) indicated by

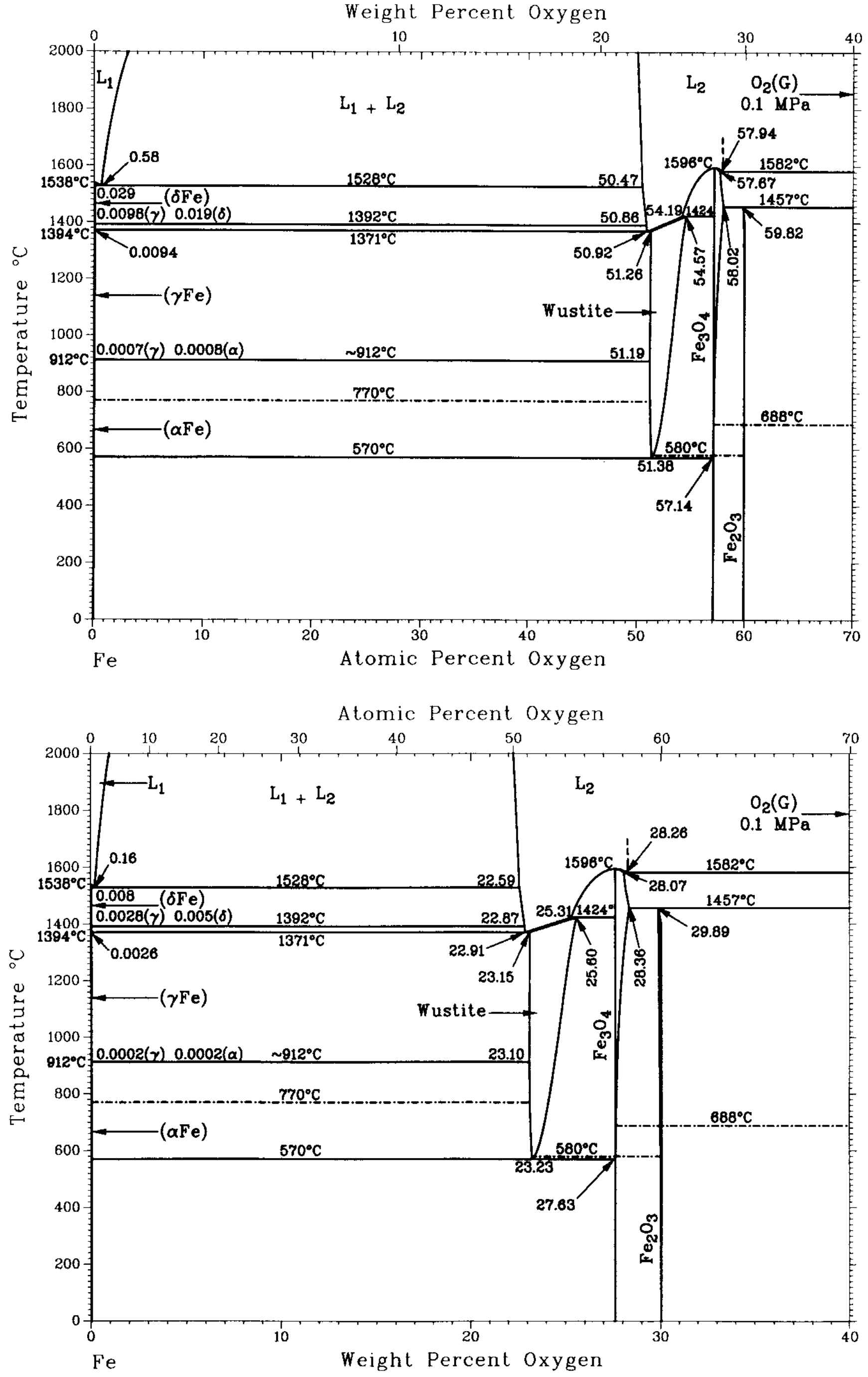

Fig. 1 Assessed Fe-O phase diagram (condensed system, 0.1 MPa).

[61Tan]. This [70Kus] datum is for the monotectic terminus of the (δFe) solidus, which was observed to be linear between the points (1537.5 °C, 0 at.% O) and (1529 °C, 0.0375 at.% O). The *k* ratio, at.% O(δFe)/at.% O(L_1), was evaluated by [70Kus] from their experimental (δFe) solidus and liquidus (also linear) as 0.076. This value agrees poorly with the *k* value 0.119 reported by [78Fuj]. The latter value, when combined with the fairly well established monotectic composition of L_1, 0.58 at.% O, yields the value 0.069 at.% O for monotectic (δFe). The preponderance of evidence suggests that the [61Tan] values in Table 2 are too high. The compositions of (δFe) coexisting with L_2 that were reported by [66Hep] are adopted, but may be lower than the actual values. The revised value 0.029 at.% O [67Swi] for monotectic (δFe) at 1528 °C is adopted; a linear solidus is depicted in Fig. 1. The [67Swi] composition, 0.019 at.% O, for (δFe) coexisting with (γFe) and L_2 is also adopted.

Table 2 (αFe), (δFe), and (γFe) Boundaries: Experimental O Contents of (Fe) in Equilibrium with Wustite or with Liquid Oxide (L_2)

Terminal solid solution	Coexisting phase	Reference	Temperature, °C	O content, at.% × 10^4
(αFe)	Wustite	[58Sif]	700	24
			850	21
			880	24
		[59Sey]	875	≤70
		[67Swi]	881	13
(δFe)	L_2	[61Tan]	1420	394(a)
			1450	582(a)
			1475	638(a)
			1510	837(a)
		[66Hep]	1450	230
			1510	290
(γFe)	Wustite	[67Swi]	951	9
			1049	19
			1250	59
			1350	86

(a) Values read by present author from original graphical data.

Because there are apparently no other reported data, the experimental [67Swi] values for the compositions of (γFe) coexisting with wustite are adopted. The assessed compositions of (γFe) coexisting with (αFe) and wustite at 912 °C, with L_2 and wustite at 1371 °C, and with (δFe) and L_2 at 1392 °C are those proposed by [67Swi]: 0.0007, ~0.0094, and ~0.0098 at.% O, respectively.

Wustite

The compositions stable at 0.1 MPa hydrostatic pressure range from 51.2 at.% O at about 912 °C to 54.6 at.% O at 1424 °C (Fig. 2). (The stoichiometric composition "FeO" is outside the range.) At its Fe-rich boundary compositions, wustite coexists with (αFe) from 570 to 912 °C, with (γFe) from 912 to 1371 °C, and with liquid from 1371 to 1424 °C. At its O-rich boundary compositions, wustite coexists with Fe_3O_4 between 570 and 1424 °C, which are the temperature limits of its stable range. Except at its eutectic and peritectic termini, the solidus apparently was investigated directly only by [31Pfe]. The curve shown in Fig. 1 and 2 is that derived by [46Dar] by combining their experimental solidus temperatures and gas compositions with their thermodynamic data relating gas and solid compositions. Data from investigations of the other boundaries of the wustite field at 0.1 MPa are listed in Table 3.

Wustite (W) participates in four invariant equilibria of the condensed Fe-O system at 0.1 MPa (Table 1). In its stable range, wus-

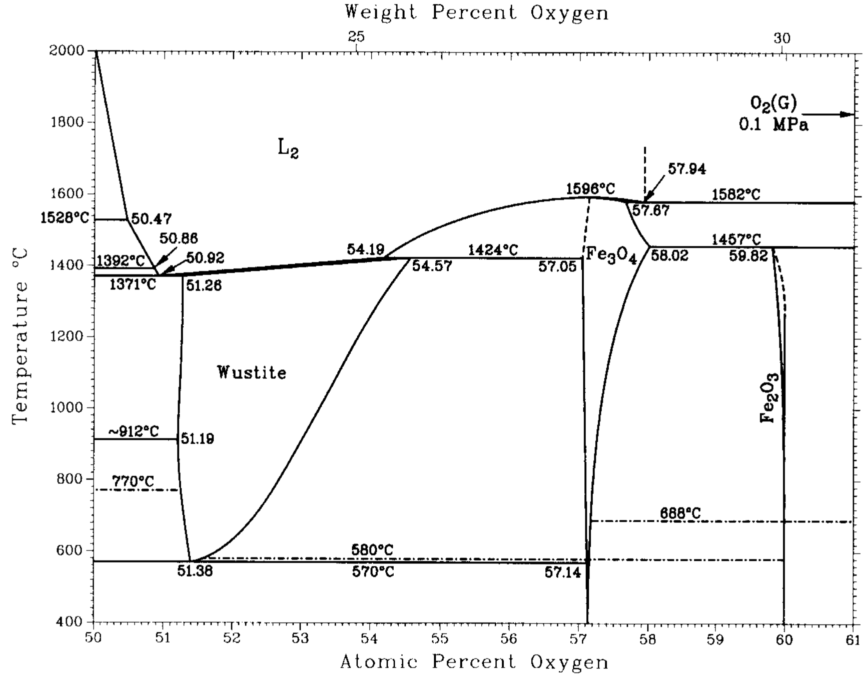

Fig. 2 Assessed Fe-O phase diagram from 50 to 60 at.% O (condensed system, 0.1 MPa).

tite exhibits no first-order transformations, but metastable wustite cooled below about –80 °C undergoes antiferromagnetic ordering (see "Metastable Phases"). Controversy surrounds claims that stable wustite exhibits second-order transformations, with boundaries separating several discrete fields in *X*-*T* space [89Val]. These transformations are assumed to be associated with changes in defect ordering. This issue is discussed briefly below.

Of the four invariants involving wustite (Table 1), that of (γFe) + W ↔ (αFe) may be placed quite accurately at 912 °C because of the very small O solubility in Fe. The assessed composition of wustite, 51.2 at.% O, is that reported by [45Dar] and confirmed by others. (See discussion of the Fe-rich wustite boundary below.) Values for the temperature of the eutectoid equilibrium W ↔ (αFe) + Fe_3O_4 were reported from 518 to 620 °C [21Cha1, 29Sch, 31Pfe, 33Jet2, 46Dar, 64Bar1, 64Bar2, 64Val, 65Val2, 66Ack, 66Bir, 69Fen, 69Luc, 69Riz, 70Asa, 86Mal, 86Val], but most values are between 560 and 580 °C. The most direct measurements, involving little or no extrapolation, appear to be 569 [64Bar2] and 565 °C [66Bir]. The chosen value is 570 °C at 51.4 at.% O, in agreement with the [83Kna] nonexperimental assessment.

The third invariant, the eutectic equilibrium L_2 ↔ (γFe) + W, is located at 1370 [24Tri, 31Pfe], 1380 [32Bow], or 1371 °C [46Dar]. There is excellent agreement in the eutectic wustite compositions 51.2 and 51.3 at.% O reported by [31Pfe] and [46Dar], respectively. The [46Dar] values are adopted. ([83Kna] preferred 1372 °C at 51.2 at.% O; the [80Goe] assessment was 1369 °C at 51.2 at.% O.) The fourth invariant, the peritectic equilibrium L_2 + Fe_3O_4 ↔ W, was located at 1430 °C by [31Pfe] and at 1424 °C by [46Dar]. Disagreement between [31Pfe] and [46Dar] on the indicated compositions of peritectic wustite (53.8 and 54.6 at.% O, respectively) is appreciable. The [46Dar] values are adopted. ([83Kna] preferred 1424 °C at 54.8 at.% O; the [80Goe] assessment was 1420 °C at 54.5 at.% O.)

The existence of a fifth invariant point at a presumably peritectoid equilibrium, (αFe) + W + Fe_3O_4, is implicit in the claim of [84Liu1] that stoichiometric FeO is stable relative to (αFe) and Fe_3O_4 below 465 °C. This claim was rejected in the preparation of Fig. 1.

In assessing the Fe-rich and O-rich boundaries of the wustite phase field, compositions in equilibrium with (αFe), (γFe), or Fe_3O_4, only the data of Table 3 were considered. Several sets of data (all graphical presentations, except for [56Fos]) were

Table 3 Experimental Compositions of Wustite in Equilibrium with (αFe) at $T \leq 912$ °C, (γFe) at $T \geq 912$ °C, or Fe_3O_4 at 0.1 MPa Hydrostatic Pressure

Reference	Temperature(a), °C	Boundary composition, at.% O		Temperature(a), °C	Boundary composition, at.% O	
		(αFe) or (γFe)	Fe_3O_4		(αFe) or (γFe)	Fe_3O_4
[29Sch]	600	51.20	52.76	900	50.82	53.12
	650	51.28	52.83	1000	50.75	53.27
	700	51.13	52.91	1100	50.58	53.49
	800	50.97	52.91			
[31Pfe](b)	575	51.16	51.16	1200	...	53.35
	600	...	51.54	1370	51.18	...
	800	...	52.35	1400	...	53.74
	1000	...	52.89	1430	...	53.78
	1070	...	53.14			
[33Jet2]	582	...	52.03	950	51.44	...
	610	51.69	51.99	1018	...	52.69
	627	51.69	...	1031	51.41	...
	686	51.58	...	1047	...	52.66
	690	...	51.21	1176	...	52.81
	793	51.40	52.56	1290	...	52.51
	794	51.34	...	1340	...	52.62
	888	...	52.66	1420	51.41	52.27
	912	51.40	...	1440	...	52.34
[45Dar]	600	51.35(c)	51.70(c)	1100	51.17	53.55
	700	51.25(c)	52.27(c)	1200	51.20	53.82
	800	51.20(c)	52.65(c)	1300	51.23	54.12
	900	51.18(c)	52.98(c)	1350	51.25	...
	1000	51.17(c)	53.27(c)	1400	...	54.48
[49Ben]	595	50.90	...	800	...	52.43
	610	...	51.88	805	...	52.43
	620	50.69	...	860	50.12	...
	660	50.48	52.16,52.23	910	49.90	...
	700	50.19	...	925	...	52.71
	720	...	52.36	980	50.04	...
	750	50.12	...	1040	49.97	...

(continued)

(a) Temperatures as published, uncorrected to IPTS-68. (b) Read by present author from partly or completely graphical presentation in original; all other data sets numerical in original. (c) By original authors' extrapolation. (d) Average of two or more reported values. (e) As quoted by [69Riz], related to [68Fuj] data. (f) Related to the [64Ger1, 64Ger3, 65Ger2] data set. (g) Probably same experiment as [51Cir]. (h) Nonexperimental paper summarizing experimental data of authors' group.

Table 3 Experimental Compositions of Wustite in Equilibrium with (αFe) at $T \leq 912$ °C, (γFe) at $T \geq 912$ °C, or Fe_3O_4 at 0.1 MPa Hydrostatic Pressure (continued)

Reference	Temperature(a), °C	Boundary composition, at.% O		Temperature(a), °C	Boundary composition, at.% O	
		(αFe) or (γFe)	Fe_3O_4		(αFe) or (γFe)	Fe_3O_4
[49San]	700	...	52.41	1000	...	53.22
	800	...	52.78	1100	...	53.38
	900	...	53.03	1200	...	53.50
[51Cir](b)	700	51.60	52.36	1000	51.22	52.49
	900	51.43	52.54			
[54Ari]	831	51.06	52.32	909	50.96	52.55
[55Mar]	630	...	52.34	970	51.44(d)	53.41(d)
	692	51.69	52.53	1040	51.44	53.38
	711	51.63(d)	...	1095	51.47	53.41
	813	51.48	52.81	1100	51.41	...
	840	51.54(d)	...	1140	51.46	53.46
	870	51.54(d)	...	1150	...	53.43
	895	51.46(d)	...	1180	...	53.27
	900	51.44(d)	...	1210	...	53.31
	916	51.44	53.10	1230	51.44	53.35
[56Hov](b)	689	51.86	...	980	...	53.33
	771	51.59	...	1106	...	53.77
	795	...	52.96	1150	51.18	53.93
	871	51.31	...	1251	...	54.31
[63Off1]	1100	...	52.97	1380	51.36	...
	1200	...	52.93(d)	1400	...	52.91(d)
	1300	...	52.99			
[64Bar2](b)	570	...	51.60	800	51.25	52.43
	600	51.43	51.84	850	51.22	52.53
	650	51.36	52.03	900	51.18	52.67
	700	51.34	52.14	950	51.15	52.79
	750	51.28	52.32	1000	51.13	52.89
[64Ger1,64Ger3,65Ger2]	800	51.22	52.72			
[65Meu](e)	700	51.41	52.45	1000	51.17	53.25
	850	51.20	52.87			
[66Ack]	699	51.31	52.29	909	51.31	53.10
	750	51.36	52.67	1004	51.27	53.21
	802	51.27	52.83			
[67Swa2]	950	51.26	...	1150	51.21	...
	1000	51.23	...	1200	51.22	...
	1050	51.21	...	1250	51.22	...
	1100	51.21	...			
[68Fuj]	1000	51.15	53.23			
[68Riz1](b)	765	51.23	52.58	965	51.21	53.24
	865	51.21	52.91			
[69Cam,70Cam](f)	700	51.44	...	1075	51.10	53.37
	800	51.22(d)	52.72(d)	1076	...	53.35
	900	51.11	52.99	1171	...	53.62
	1000	51.12	53.24(d)	1172	...	53.63
	1074	...	53.35	1306	...	53.85(d)
[69Lyk](b)	700	51.27	52.50	1000	51.18(d)	53.33(d)
	750	51.24	52.68	1050	51.18(d)	53.42(d)
	800	51.20(d)	52.79(d)	1100	51.18	53.55
	850	51.20(d)	52.95(d)	1150	51.18	53.67
	900	51.19(d)	53.07(d)	1200	51.17	53.79
	950	51.19(d)	53.20(d)	1300	51.18	54.12
[69Riz]	800	...	52.08	1000	...	53.29
	894	...	52.61	1100	51.22	53.49(d)
[70Asa](b)	577	51.60	51.60	761	...	52.63
	589	...	51.64	800	51.53	...
	646	...	51.99	900	51.52	53.21
	690	...	52.24	1000	51.53	...
	700	51.56	...			

(continued)

(a) Temperatures as published, uncorrected to IPTS-68. (b) Read by present author from partly or completely graphical presentation in original; all other data sets numerical in original. (c) By original authors' extrapolation. (d) Average of two or more reported values. (e) As quoted by [69Riz], related to [68Fuj] data. (f) Related to the [64Ger1, 64Ger3, 65Ger2] data set. (g) Probably same experiment as [51Cir]. (h) Nonexperimental paper summarizing experimental data of authors' group.

Table 3 Experimental Compositions of Wustite in Equilibrium with (αFe) at $T \leq 912$ °C, (γFe) at $T \geq 912$ °C, or Fe_3O_4 at 0.1 MPa Hydrostatic Pressure (continued)

Reference	Temperature(a), °C	Boundary composition, at.% O		Temperature(a), °C	Boundary composition, at.% O	
		(αFe) or (γFe)	Fe_3O_4		(αFe) or (γFe)	Fe_3O_4
[70Cir](g)	700	51.57	52.38	1000	51.31	52.55
	900	51.41	52.55			
[70Mar2]	1075	51.10	53.38			
[74Gid]	980	...	53.32	1055	...	53.39
	1015	...	53.33	1075	...	53.46
	1023	...	53.35	1112	...	53.65(d)
[80Tak](b)	1100	51.18	53.53	1250	51.24	53.95
	1150	51.20	53.66	1300	51.22	54.12
	1200	51.21	53.83			
[81Bar]	600	51.36	51.85	850	51.15	52.72
	650	51.29	52.11	900	51.12	52.83
	700	51.27	52.31	950	51.10	52.92
	750	51.20	52.47	1000	51.08	53.03
	800	51.17	52.61	1050	51.05	53.10
[89Val](h)	592	51.69	51.69	950	51.44	53.24
	600	51.68	51.75	1000	51.39	53.31
	650	51.61	52.05	1050	51.34	53.39
	700	51.52	52.37	1100	51.29	53.49
	750	51.47	52.58	1150	51.24	53.58
	800	51.42	52.75	1200	51.19	53.75
	850	51.35	52.86	1250	51.15	53.97
	900	51.24	52.97	1300	51.12	54.19
	911	51.21(W'_1)	53.00(W'_3)	1350	51.11	54.41
	911	51.47(W_1)	53.17(W_3)	1371	51.10	54.51

(a) Temperatures as published, uncorrected to IPTS-68. (b) Read by present author from partly or completely graphical presentation in original; all other data sets numerical in original. (c) By original authors' extrapolation. (d) Average of two or more reported values. (e) As quoted by [69Riz], related to [68Fuj] data. (f) Related to the [64Ger1, 64Ger3, 65Ger2] data set. (g) Probably same experiment as [51Cir]. (h) Nonexperimental paper summarizing experimental data of authors' group.

omitted from the table: [56Fos] and [74Tou] subordinated their own data to those of [33Jet1] and of [70Cam] and [70Mar2], respectively; [57Eng] presented data in two figures inconsistently; [69Fen], [71Ono], and [78Now] presented their data in figures that were too small for precise reading. Moreover, [69Fen] was criticized for faulty experimental technique [74Gid, 80Tak].

The tabulated data for the Fe-rich side fall into three main groups. The first group are far removed from each other and from the great majority of the data or follow curves crossing the latter at relatively high angles [29Sch, 49Ben, 54Ari, 56Hov, 89Val]. These investigations were disregarded in this assessment. The second group [33Jet2, 51Cir, 55Mar, 70Asa, 70Cir] scatter about a curve that is roughly parallel to the curve through the third group and displaced from the latter by about +0.3 at.% O. The data points of most investigators of the third group [45Dar, 60Off1, 64Ger1*, 64Ger3*, 65Ger2*, 65Meu**, 67Swa2, 68Fuj**, 68Riz1, 69Cam*, 69Lyk, 69Riz, 70Cam*, 70Mar2*, 80Tak] lie within ±0.1 at.% O of the curve proposed by [45Dar] through their experimental and calculated points. In a few other studies, all but one or two data points of each set lie within the ±0.1 at.% O limits of the main third-group band [31Pfe, 64Bar2, 66Ack, 81Bar]. Several experimental techniques were employed in the second and third groups: gas-solid or solid-solid equilibration plus weighing, chemical analysis, microscopy, X-ray diffraction (XRD), or electrical conductivity to determine compositions [31Pfe, 33Jet2, 45Dar, 51Cir, 55Mar, 56Hov, 63Off1, 70Cir]; emf measurements with solid electrolytes [64Bar2, 68Riz1, 69Lyk, 69Riz, 70Asa, 81Bar]; and thermogravimetry [64Ger1, 64Ger3, 65Ger2, 66Ack, 67Swa2, 69Cam, 70Cam, 80Tak]. The preponderance of evidence favors the third group. Because the [45Dar] results are near the center of this group, they are adopted here. The [78Spe] and [83Kna] analyses of the available data are essentially in agreement with this conclusion.

Most data in Table 3 for the O-rich boundary of the wustite field are in fair agreement up to about 1100 °C, with several exceptions [29Sch, 31Pfe, 33Jet2, 49Ben, 51Cir, 54Ari, 55Mar, 63Off1, 64Bar2, 69Riz, 70Cir, 81Bar]. The data of this latter group either are removed appreciably from the majority or lie on divergent curves intersecting its band at substantial angles. Among the data lying on these divergent curves, however, most points of [55Mar] and [81Bar] lie within the ±0.25 at.% O band of data from the major group of investigations that are considered herein to be concordant [45Dar, 49San, 56Hov, 64Ger1, 64Ger3, 65Ger2, 65Meu, 66Ack, 68Fuj, 68Riz1, 69Cam, 69Lyk, 70Asa, 70Cam, 70Mar2, 74Gid, 80Tak, 89Val]. Although there is good agreement within a subgroup [31Pfe, 49Ben, 64Bar2, 81Bar] of the "exceptions," which otherwise are scattered, the data sets that include that of [45Dar] are adopted as the most reliable. Included in the adopted data are results from thermogravimetry, from emf measurements with solid electrolytes (including [74Gid]), and from solid-solid or gas-solid equilibration (including [49San]). (See the preceding paragraph on the Fe-rich wustite boundary for the classification of other references in each category).

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*[64Ger1], [64Ger3], [65Ger2], [69Cam], [70Cam], and [70Mar2] are related data.
**[65Meu] and [68Fuj] are related data.

The data for the Fe_3O_4-saturated boundary above 1100 °C are sparser and more divergent than those for lower temperatures. Because of their scatter and large displacement from other data, the results of [33Jet2] and [63Off1] are rejected. Of the others, there is excellent agreement (about ±0.1 at.% O) of [45Dar], [69Lyk], [71Ono] (not in Table 3), [74Gid], [80Tak], and [89Val], with only moderate deviations by [56Hov] (about +0.4 at.% O at 1250 °C) and by [49San] and [69Cam] (about −0.3 at.% O at 1200 and 1306 °C, respectively.) The [31Pfe] and [55Mar] sets continue their trends from below 1100 °C to considerably lower O concentrations than those of the foregoing sets. Adoption of the [45Dar] curve representing the O-rich wustite boundary above (as well as below) 1100 °C therefore appears reasonable. The analysis of available data by [83Kna] trends from a slightly lower O content (by −0.1 at.% O) at 570 °C to a slightly higher O content (by +0.2 at.% O) at 1424 °C. The other fairly recent reviews of [78Spe] and [82Kub] also adopted the [45Dar] boundary.

The existence of subboundaries in the wustite field corresponding to second-order transformations, was proposed about 30 years ago [62Rac2, 64Car, 64Val]. This proposition, developed in numerous papers by Vallet and his associates, including Raccah and Carel, is considered herein to have been presented in its current state by [89Val]. In this presentation, ten domains of the wustite phase field, associated with six varieties of wustite (W′1, W′2, W′3, W1, W2, and W3) are depicted, with some like domains separated by unlike domains. Explicit, distinguishing characteristics of the six varieties have not been described, but essentially all commentaries have related them qualitatively to differences in defect ordering.

The evidence for the wustite subboundaries, which Vallet and his associates adduced mainly from thermodynamic (thermogravimetric), lattice parameter, and dilatometric studies, depends on their interpretation of these data as showing discontinuities in the derivatives of properties with respect to composition or temperature. Because of the consensus that defect structures may vary in complex ways with those variables, there is a question in individual data sets whether the precision of the data justifies recognition of a second-order discontinuity rather than

Table 4 Experimental Compositions of Fe_3O_4 in Equilibrium with Other Iron Oxides or Liquid ($P_{O_2} \neq 0.1013$ MPa) or with O_2 Gas ($P_{O_2} = 0.1013$ MPa)

Reference	Temperature, °C	Conjugate condensed phase	O_2 pressure, MPa	Composition, at.% O
Lower boundaries (Fe-rich)				
[46Dar]	<560	(αFe)	<0.1013	~57.143(a)
[46Dar]	560 to 1424	Wustite	<0.1013	~57.143(a)
[82Die](b)	900	Wustite	<0.1013	57.085
	1000	Wustite	<0.1013	57.094
	1100	Wustite	<0.1013	57.100
	1200	Wustite	<0.1013	57.107
	1300	Wustite	<0.1013	57.096
	1400	Wustite	<0.1013	57.058
[46Dar]	1424 to 1596	L(c)	<0.1013	~57.143(a)
Upper boundaries (O-rich)				
[35Gre]	1076	αFe_2O_3	<0.1013	57.38
	1452	αFe_2O_3	<0.1013	58.02
[35Whi](d)	1314	αFe_2O_3	<0.1013	57.74
	1346	αFe_2O_3	<0.1013	57.82
	1366	αFe_2O_3	<0.1013	57.72
	1415	αFe_2O_3	<0.1013	58.08
[38Whi]	1368	αFe_2O_3	<0.1013	58.11
	1425	αFe_2O_3	<0.1013	58.33
	1450	αFe_2O_3	<0.1013	58.27
[41Sch]	1311	αFe_2O_3	<0.1013	57.76,57.67
	1331	αFe_2O_3	<0.1013	(57.84),57.70
	1351	αFe_2O_3	<0.1013	57.82,57.74
	1370	αFe_2O_3	<0.1013	57.87,57.80
	1390	αFe_2O_3	<0.1013	57.91,57.86
	1410	αFe_2O_3	<0.1013	57.93,57.90
[46Dar](b)	1102	αFe_2O_3	<0.1013	57.408
	1202	αFe_2O_3	<0.1013	57.502
	1263	αFe_2O_3	<0.1013	57.576
	1302	αFe_2O_3	<0.1013	57.633
	1393	αFe_2O_3	<0.1013	57.813
	1402	αFe_2O_3	<0.1013	57.836

(continued)

Note: Original temperature values corrected to IPTS-68 values. (a) Deviations from stoichiometric Fe_3O_4 not measured. (b) Read from smooth curve. (c) O/Fe ≤ 1.33. (d) Read from plotted points. (e) O/Fe ≥ 1.33. (f) Extrapolation of [46Dar] data by [60Phi], read at [71Cro] temperature and O_2 pressure. (g) Correction by [41Sch] to original values. (h) Congruent melting point.

Table 4 Experimental Compositions of Fe_3O_4 in Equilibrium with Other Iron Oxides or Liquid ($P_{O_2} \neq 0.1013$ MPa) or with O_2 Gas ($P_{O_2} = 0.1013$ MPa) (continued)

Reference	Temperature, °C	Conjugate condensed phase	O_2 pressure, MPa	Composition, at.% O
[46Dar](b)(cont.)	1459	αFe_2O_3	0.1013	58.015
	1539	αFe_2O_3,L(e)	0.78	58.24(f)
[57Smi]	1181	αFe_2O_3	<0.1013	57.481
[69Sch](d)	1269	αFe_2O_3	<0.1013	57.548
	1309	αFe_2O_3	<0.1013	57.675
	1332	αFe_2O_3	<0.1013	57.776
	1352	αFe_2O_3	<0.1013	57.640
	1353	αFe_2O_3	<0.1013	57.886
	1372	αFe_2O_3	<0.1013	57.715
	1392	αFe_2O_3	<0.1013	57.826
	1403	αFe_2O_3	<0.1013	57.958
	1407	αFe_2O_3	<0.1013	57.959
	1412	αFe_2O_3	<0.1013	57.955
	1420	αFe_2O_3	<0.1013	58.127
	1425	αFe_2O_3	<0.1013	58.112
	1432	αFe_2O_3	<0.1013	58.170
[70Roe]	1284	αFe_2O_3	<0.1013	57.61
	1400	αFe_2O_3	<0.1013	57.84
[82Die](b)	900	αFe_2O_3	<0.1013	57.310
	1000	αFe_2O_3	<0.1013	57.291
	1100	αFe_2O_3	<0.1013	57.418
	1200	αFe_2O_3	<0.1013	57.566
	1300	αFe_2O_3	<0.1013	57.710
	1400	αFe_2O_3	<0.1013	57.833
[35Gre]	1573	L(e)	>0.1013(?)	57.681
	1584	L(e)	<0.1013	57.426
[38Whi](g)	1564	L(e)	>0.1013(?)	58.005
	1572	L(e)	>0.1013(?)	57.806
	1589	L(e)	<0.1013	57.627
[46Dar]	1582	L(e)	0.1013	57.666
	1593(b)	L(e)	<0.1013	57.382
	1596	L(e)	<0.1013	57.143(h)
	1500	...	0.1013	57.861
	1517	...	0.1013	57.813

Note: Original temperature values corrected to IPTS-68 values. (a) Deviations from stoichiometric Fe_3O_4 not measured. (b) Read from smooth curve. (c) O/Fe ≤ 1.33. (d) Read from plotted points. (e) O/Fe ≥ 1.33. (f) Extrapolation of [46Dar] data by [60Phi], read at [71Cro] temperature and O_2 pressure. (g) Correction by [41Sch] to original values. (h) Congruent melting point.

continuity of a curve. Partial experimental support for the interpretation that discontinuities occur was given by [66Gei] (electrical conductivity), by [69Fen]* and [80Tak] (both with thermodynamic properties), and by [85Sor] (analysis of [68Bra] thermodynamic data). However, in these instances, the subboundaries reported do not conform to those of [89Val]. Most other measurements of wustite properties have failed to detect the existence of subboundaries.

At least two aspects of the [89Val] diagram are extraordinary: (1) the depiction of four condensed phases—(αFe), (γFe), W'1, and W1—coexisting at 911 °C; and (2) the continuous, isothermal (911 °C) nature of the W'1/W1, W'1/W2, W'2/W2, W'3/W2, and W'3/W3 subboundaries and their relationship, if any, to the (αFe)/(γFe) transformation at 912 °C. The offset depicted in the Fe-rich boundary of wustite at 911 °C (W'1 to W1) is contrary to all determinations independent of the Vallet group. Because of lingering uncertainty regarding their existence and possible locations, the wustite subboundaries, which are undefined physically, are omitted from the assessed diagram (Fig. 1).

According to [58Ark1] and [58Ark2], elevation of the hydrostatic pressure lowers the eutectoid temperature of wustite, displaces the eutectoid composition to higher O concentrations, and shifts its Fe-rich and O-rich boundaries to higher Fe and O concentrations, respectively. At ≥3.6 GPa, the Fe-rich boundary at 770 °C is about at the composition of stoichiometric "FeO" [67Kat]. According to thermodynamic calculations of [75Kur] for 700, 1000, and 1300 °C, which contradict part of the [58Ark2] conclusions, both the Fe-rich and O-rich boundaries are shifted by increasing pressure until they reach a limit at the "FeO" composition (50.0 at.% O). Higher pressures (different for each boundary) are required to reach this limiting composition as temperature increases; above about 30 GPa, stable wustite is essentially a line compound with 50.0 at.% O at all temperatures. It was indicated that at pressures above about 18 GPa, Fe_3O_4 is unstable at all temperatures** and O-saturated wustite coexists stably with Fe_2O_3. The eutectoid temperature was reported to decrease by 64 [75Kur], 13.5 [83She], or 45.5 °C/GPa [84Liu1]. According to [83She] and [84Mcc], Fe-saturated wustite approaches stoichi-

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*Experimental technique criticized by [74Gid] and [80Tak].

**For contradictory data on Fe_3O_4 stability at high pressure, see the [74Mao] findings in the section on Fe_3O_4.

Table 5 Compositions of αFe_2O_3 in Equilibrium with Fe_3O_4

Reference	Temperature, °C	Composition, at.% O	Reference	Temperature, °C	Composition, at.% O
[35Gre]	1075	>59.986	[61Sal](a)	950	59.990
	1452	>59.972		1000	59.988
[35Whi](a)	1200	59.697		1100	59.981
	1239	59.659		1200	59.969
	1272	59.609,59.672		1300	59.956
	1283	59.664		1400	59.940
	1333	59.557		1500	59.919
	1345	59.554	[67Kom]	900	59.981
	1353	59.571		1000	59.966
	1415	59.470,59.500		1253	59.925
	1426	59.495		1294	59.909
	1433	59.462		1338	59.881
	1446	59.481		1384	59.831
	1461	59.473	[69Sch]	1300	59.92
[38Whi]	1368	59.517		1400	59.88
	1425	59.411	[70Roe]	1284	59.84
	1450	59.411		1400	59.73
[41Sch]	1310	59.821	[80Gul2](b)	1450	59.796
	1330	59.798		1500	59.766
	1350	59.786		1539(c)	59.743
	1370	59.706			
	1390	59.637			
	1410	59.510			

(a) Data points or line values read by present author from original drawings. (b) Extrapolation of [67Kom] data. (c) Eutectic temperature.

ometric "FeO" in composition as pressure increases up to about 10 GPa (depending on temperature), then retreats to higher O concentrations at still greater pressures. Very high pressure (>70 GPa) induces a transformation, possibly to the $B2$ (CsCl) structure [80Jea].

Fe_3O_4

Stoichiometric Fe_3O_4 exhibits a transformation and a transition that have been documented voluminously at –149 °C (T_V, the Verwey transformation temperature, with polymorphic change) and +580 °C (variously T_C or T_N, the ferrimagnetic-paramagnetic transition temperature, also called the Curie or Néel point, without polymorphic change). The ferrimagnetic-paramagnetic transition is discussed in the "Magnetism" section. The existence of a transition at –262 °C that was reported [77Tod] on the basis of heat capacity (C_p) measurements was denied by subsequent investigators [79Iid, 80Iid, 83Gme, 83Rig, 84She], using XRD, nuclear magnetic resonance, and C_p measurements. A transition observed at about –160 °C [72Eva, 83Rig], which was "probably independent of the Verwey" ordering [83Rig], was absent from specimens subsequently searched specifically for confirmation of the magnetization and heat capacity anomalies involved [83Gme, 84Gme]. Shifting of T_V in inhomogeneous specimens due to stress or nonstoichiometry may have produced the –160 °C effect.

An anomaly in properties at –73 °C was mentioned in the [82Hon] review without attribution. An anomaly found only in the magnetic permeability was reported [85Ara1] at about –23 °C (but with "pronounced thermal hysteresis") in cation-deficient Fe_3O_4. On the basis of a thermodynamic analysis of Fe_3O_4 solidus wustite equilibria, [81Car] contended that a first-order transformation, which had not been observed in conventional enthalpy measurements [51Cou], occurs at 1160 °C. Until independent support of an 1160 °C effect is forthcoming, the [51Cou] data are accepted.

The Verwey transformation apparently was discovered by [26Par] from its enthalpy effect, but received its name from the investigator who elucidated the main features of the transformation [39Ver, 41Ver, 47Ver]. The transformation was identified with long-range ordering of electrons among the cations in octahedral sites [39Ver], but detailed analysis has remained a subject of investigation to recent times, for example [88Ara]. Although [41Ver] showed that T_V is sensitive to composition and declines with Fe deficit at O/Fe > 1.333, values of T_V often have been published without exact O/Fe values. (Evidence of [72Miy] suggests that T_V also declines with Fe excess at O/Fe < 1.333.)

Several fairly recent measurements with stoichiometric Fe_3O_4 specimens yielded T_V values from –150 to –148 °C [83Gme, 83Rig, 84Gme, 85She2]. The adopted value is –149 °C. At small Fe deficits relative to the stoichiometric composition, the temperature of the first-order transformation is depressed with a slope of -1.4×10^2 °C/ at.% O [85She2, 88Ara]. ([83Gme] also measured the effect of cation vacancies on T_V.) Beyond an Fe deficit corresponding to the composition 57.24 at.% O, the transformation is second order [85Ara1, 85Ara2, 85She2, 88Ara], and T_V is depressed with increasing cation vacancy concentration at a lesser slope of about -1.0×10^2 °C/at.% O [88Ara]. The [88Ara] data indicated that a discontinuous decrease (–8.5 °C) occurs in T_V at 57.24 at.% O in the change from first-order to second-order behavior. At a sufficiently large cation vacancy concentration, the Verwey transformation is suppressed [41Ver]; the extreme of T_V was located recently at 57.44 at.% O and –192 °C [88Ara].

The effects of pressure and the O isotopic mass on T_V were reviewed [83Sri1, 83Sri2]. Elevation of hydrostatic pressure depresses the value of T_V, but there is disagreement in the experimental values of dT_V/dP: –4.4 to –4.8 [68Sam] and –2.7 °C/GPa [79Kak]. Substitution of 43% ^{18}O for ^{16}O in Fe_3O_4 saturated with O at 800 to 1000 °C raised T_V by 6.1 °C (dT_V/dC = +0.15 °C/ at.% ^{18}O) [79Ter, 81Wol].

The possibility of incommensurate features to the Verwey transformation were considered by [79Iiz], who regarded the change as commensurate-to-commensurate "bypassing a possible intermediate phase of incommensurately modulated structure." [84Bel] concluded from thermal expansion data near T_V, with and without a magnetic field, that a magnetic field "induces an incommensurate crystal structure."

Application of hydrostatic pressure to Fe_3O_4 induces a transformation at room temperature [70Mao]. The equilibrium pressure for coexistence of the low-pressure (cubic) phase (LPM) and the high-pressure phase (HPM) has not been evaluated accurately because of hysteresis. Transformation to HPM at room temperature requires 22 to 27 GPa [70Mao, 74Mao, 75Syo, 86Hua], but reversion to LPM does not occur above 5 [70Mao] or 3.4 GPa [86Hua]. Severe hysteresis persisted to 600 °C; from consideration of the experimental transition pressures (increasing and decreasing), a value –68 °C/GPa for the temperature dependence of the actual boundary pressures and a value near 21 GPa at 25 °C were estimated [86Hua].

On its Fe-rich side, Fe_3O_4 coexists with (αFe) below 570 °C, with wustite from 570 to 1424 °C, and with L_2 from 1424 °C to its congruent melting point at 1596 °C (Fig. 2). Experimental data from the boundary compositions on this side and on the O-rich side of the Fe_3O_4 phase field are listed in Table 4.

Although lower O concentrations have been reported in metastable Fe_3O_4, for instance 56.657 at.% O at 245 °C [67Col], the stable lower boundary for coexistence with (αFe) is quite precisely at the stoichiometric composition 57.143 at.% O [46Dar]. No data showing deviations therefrom are available.

For wustite coexistence (and, indeed, for the solidus to the melting point of Fe_3O_4), most publications show the Fe_3O_4 boundary at 57.143 at.% O, as depicted by [46Dar]. However, [82Die] reported experimental data corresponding to O concentrations slightly below the stoichiometric from 900 to 1400 °C. A minimum deviation was depicted at about 1200 °C. The indicated increase in deviation (larger Fe excess) with temperature decreasing from 1200 to 900 °C is unexpected. The [82Die] data indicate that Fe_3O_4 contains about 57.05 at.% O at its 1424 °C peritectic equilibrium with wustite and L_2. The solidus, which is unmeasured, runs from this point to the congruent melting point at 1596 °C and 57.14 at.% O.

On its O-rich side, Fe_3O_4 is in equilibrium with αFe_2O_3 at lower temperatures. In the condensed system without O_2 pressure restriction, this boundary terminates at 1539 °C [71Cro] in a eutectic equilibrium, where Fe_3O_4, αFe_2O_3, and L_2 coexist. From 1539 to 1596 °C, the upper boundary of the Fe_3O_4 phase field is its solidus. In instances where the system is restricted to O_2 pressures of 1 atm (0.1013 MPa), the upper boundary between 1457 and 1582 °C corresponds to this O_2 isobar, intersecting the curve for coexistence with αFe_2O_3 and the solidus at these respective temperatures.

Among the several measurements of Fe_3O_4 compositions conjugate to αFe_2O_3, it is useful to compare other data sets against those of [46Dar]. Below 1100 °C, the [35Gre] and [82Die] sets fit quite well with an extrapolation of the [46Dar] data as originally presented or as slightly modified by [57Smi]. Above 1100 °C, the [35Whi] and [38Whi] data scatter too widely to be considered, those of [69Sch] scatter widely on either side of [46Dar] below 1400 °C, and others [35Gre, 57Smi, 70Roe] and the lower-oxygen set of [41Sch] fit quite well with the [46Dar] points. Although closely in agreement with [46Dar] at 1100 and 1400 °C, [82Die] indicated somewhat higher O contents (difference not greater than 0.1 at.% O) on the boundary between those temperatures. Because of the small difference and substantial support from other investigators, the [46Dar] line is adopted here. Extrapolation of the [46Dar] curve through the region lacking data to 1539 °C (rather than the value 1568 °C suggested by [60Phi]) indicates that eutectic Fe_3O_4 contains about 58.2 at.% O.

The points along the Fe_3O_4 solidus (O/Fe > 1.333) reported by [35Gre], [38Whi] (as corrected by [41Sch]), and [46Dar], whether at O_2 pressures above or below 0.1013 MPa, are quite compatible with each other and with the 1539 °C eutectic temperature. The only data available for the boundary of the Fe_3O_4 phase field along the 0.1013 MPa isobar are those of [46Dar].

αFe_2O_3

There are no stable polymorphic transformations. Magnetic transitions at –10.5 and 688 °C, the latter also involving an electrical transition, are discussed in the "Magnetism" section.* This oxide decomposes to Fe_3O_4 without melting at 1457 °C (see discussion below) under 0.1013 MPa O_2 pressure [46Dar]. Stoichiometric αFe_2O_3 melts at ~1572 °C under ~5.3 MPa O_2 pressure [71Cro].

On its Fe-rich side, αFe_2O_3 is in equilibrium with Fe_3O_4. Boundary compositions of αFe_2O_3 coexisting with Fe_3O_4 were reported several times (Table 5). All results lie between 59 and 60 at.% O, but the reported deviations from 60 at.% O vary by more than a factor of 10, with no two unrelated sets agreeing, except [41Sch] and [70Roe] partially. The more recent sets of measurements, with a range of >200 °C [61Sal, 67Kom] differ by a factor of 2 to 3, although the quality of experimentation appears comparable. The tentative adoption of the [67Kom] data (and their extrapolation [80Gul2]) in the assessed diagram (Fig. 1 and 2) is arbitrary. According to [78Spe], the composition of αFe_2O_3 coexisting with Fe_3O_4 at 1457 °C and 0.1013 MPa O_2 is 59.82 at.% O, in good agreement with the [80Gul2] value, 59.79 at.% O.

On the O-rich side of αFe_2O_3, no higher oxide has been observed in stable coexistence, even at O_2 pressures far exceeding 0.1 MPa. Up to 1447 °C, αFe_2O_3 equilibrated with O_2 at 0.1 MPa exhibits no detectable deviation from the stoichiometric composition (60.0 at.% O) [78Spe]. Moreover, [71Dra] observed no excess O in αFe_2O_3 equilibrated with O_2 at 0.1 GPa and 500 to 700 °C. Above 1447 °C, αFe_2O_3 at 0.1 MPa O_2 is substoichiometric [78Spe], reaching the composition 59.8 at.% O and saturation with respect to Fe_3O_4 at 1457 [46Dar] or 1455 °C [69Sch] (see

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*No evidence was found supporting the report [70Izy], based on neutron-diffraction data, that rhombohedral Fe_2O_3 transforms to a monoclinic form (space group *B2/b* or *B2'/b'*) at T_M, the lower of these magnetic transition points.

preceding paragraph). The [46Dar] value is adopted, consistent with the [78Spe] and [82Kub] assessments.

Liquidus

The compositions of the liquid in equilibrium with another condensed phase at O_2 pressures of ≤0.1 MPa lie on six curve segments separated by discontinuities of slope: (1) the (δFe) liquidus corresponding to L_1; (2) the boundary of the miscibility gap, with Fe-rich liquids termed L_1 coexisting with O-rich liquids termed L_2 on either side of a maximum at the experimentally unobserved critical (consolute) point; (3) the (δFe) liquidus corresponding to L_2, which is theoretically but unobservably continuous with curve 1 above; (4) the (γFe) liquidus; (5) the wustite liquidus; and (6) the Fe_3O_4 liquidus, continuous on either side of the maximum at 57.1 at.% O. At O_2 pressures somewhat above 0.1 MPa, an Fe_2O_3 liquidus exists. Published phase diagrams often depict a curve of liquid compositions at 0.1 MPa or 1 atm O_2 pressure intersecting the Fe_3O_4 liquidus.

The O concentrations of L_1 in equilibrium with (δFe) between 1538 °C, the melting point of pure δFe, and the monotectic point were shown experimentally to be linear with temperature [68Kus, 70Kus]. The monotectic temperature was reported experimentally at 9 or 11 °C below the melting point value used for δFe [46Dar, 70Kus, 83Ndu]. Based on 1538 °C for this value, we adopt the value 1528 °C [70Kus, 83Ndu] for the monotectic temperature. The monotectic L_1 composition is calculated from the adopted curve for L_1 compositions on the miscibility gap boundary (see next paragraph) as 0.58 at.% O. This adopted value is slightly different from other assessed values—0.56 [46Dar, 70Kus], 0.57 [78Spe, 82Kub], and 0.59 at.% O [83Ndu].

The L_1 compositions on the miscibility gap boundary were investigated repeatedly, and the results have been compiled several times [Hansen, Elliott, Shunk, 56Gok, 67Bel, 83Ndu]. Not included in those compilations were the experimental results of [71Dis], [78Fis], and [83Oht1]. Of the last three, the [84Oht1] data are scattered and not clearly for equilibrium. There is excellent agreement among three sets of data [43Tay, 71Dis, 83Ndu] over the range 1380 (undercooled L_1) to 1960 °C with the [71Dis] equation:

$$\log C_O = -6380/T + 3.303$$

where C_O and T are in at.% O and K, respectively. Other slightly discordant equations (except for those of [78Fis]) described measurements over much smaller temperature ranges. The [78Fis] equations (1508 to 1850 and 1850 to 2046 °C), which indicate a kink in the boundary at 1850 °C, yield considerably higher values of O concentration on the L_1 boundary. Adoption here of the [71Dis] equation is in agreement with the choice in the [78Spe] and [82Kub] reviews. The critical point of the miscibility gap has not been observed; [84Oht1] roughly estimated its location from the [78Fis] data at about 2830 °C and 47 at.% O.

Compositions of L_2 on the O-rich side of the miscibility gap apparently were measured only by [71Dis]. They reported three points at 1785, 1880, and 1960 °C close to a line that can be described by:

$$C_O = 52.087 - 0.00103\,T$$

where C_O and T are in at.% O and °C, respectively. This equation yields the composition 50.51 at.% O at 1528 °C, in excellent agreement, despite the long extrapolation, with the monotectic L_2 composition, 50.48 at.% O, reported by [46Dar] for 1524 °C. The data points of [46Dar] are nearer to the invariant point, so their line is adopted, but it is extrapolated herein to 1528 °C. The invariant composition 50.47 at.% O is therefore adopted.

The curves representing L_2 compositions on the (δFe) liquidus and the (γFe) liquidus were determined experimentally only by [46Dar]. (By extrapolation of wustite liquidus data, [31Pfe] established the L_2 composition at 1370 °C at the $L_2 \leftrightarrow$ (γFe) + W eutectic equilibrium as 50.72 at.% O, in fair agreement with but probably less accurately than [46Dar].) [46Dar] located two points on the (δFe) liquidus (1528 to 1392 °C) and one point on the (γFe) liquidus (1392 to 1371 °C). Because of the sparse data and brevity of these liquidus segments, no appreciable deviation from linearity is known to occur. The [46Dar] data and assessed invariant L_2 loci (Table 1) yield the following equation that describes both the (δFe) and (γFe) liquidi adequately, even though a slight discontinuity in slope occurs at 1392 °C:

$$C_O = 54.90 - 0.0029\,T$$

where C_O and T are in at.% O and °C, respectively. The adoption of 1392 °C for coexistence of (δFe) + (γFe) + L_2 is based on the [67Swi] calculation that O depresses the δFe ↔ γFe transformation by 2 °C. L_2 at this invariant contains 50.86 at.% O. The experimental composition 50.92 at.% O of eutectic L_2 [46Dar] is adopted, in preference to the calculated value 50.85 at.% O suggested by [80Goe] or the [31Pfe] value.

Elevation of hydrostatic pressure increases the monotectic temperature by about 20.5 °C/GPa between 0 and 4 GPa [84Oht2]. An increase of pressure from 0 to 3 GPa displaces the L_1 monotectic composition from 0.6 to 1.7 at.% O [84Oht2]. In calculations of the phase equilibria involving liquid between 0 and 50 at.% O at pressures from 0.1 MPa to 30 GPa, the same authors indicated that the monotectic is suppressed at about 20 GPa and that a eutectic reaction $L_1 \leftrightarrow$ (Fe) + W occurs.

The only experimental values for compositions of L_2 on the wustite liquidus at 0.1 MPa are apparently those of [31Pfe] and [46Dar]. The former obtained two rough points on this liquidus segment. He extrapolated a fitted curve to its $L_2 \leftrightarrow$ (γFe) + W (1370 °C at 50.72 at.% O) terminus and to intersect his experimental Fe_3O_4 liquidus at 1430 °C and 53.78 at.% O. His convex upwards curve lies higher than the shallowly inflected (almost straight) curve that [46Dar] drew through their six experimental points between 1371 °C at 50.92 at.% O and 1424 °C at 54.19 at.% O. The upper terminus of the curve that [80Goe] calculated is at 1420 °C and 54.26 at.% O and, thus, in good agreement with the [46Dar] curve adopted herein.

The Fe_3O_4 liquidus was studied experimentally by [31Pfe], [38Whi], and [46Dar]. Only [46Dar] observed the curve on both sides of the maximum at the congruent melting point of Fe_3O_4 (57.14 at.% O); the [31Pfe] and [38Whi] data are for only lower or higher O concentrations, respectively. Agreement of [38Whi] and [46Dar] is excellent; that between [31Pfe] and [46Dar] is fair (<0.5 at.% O difference) above 1450 °C, but the older data are imprecise, somewhat scattered, and crossing those of [46Dar] at an appreciable angle. Moreover, [31Pfe] indicated that Fe_3O_4 melts incongruently, in contradiction of most others [38Whi, 46Dar, 60Phi]. From the foregoing considerations, the [46Dar] data are adopted.

For the restriction that O_2 pressure may not exceed 0.1013 MPa, the Fe_3O_4 liquidus terminates at 1582 °C and 57.94 at.% O [46Dar]. The compositions of L_2 on the 0.1013 MPa O_2 isobar above 1582 °C were determined also by [46Dar], who showed that O concentration was nearly constant at 57.9 at.% O (or declined very slightly) with increasing temperature to 1635 °C. In the condensed system at O_2 pressures above 0.1 MPa, the Fe_3O_4 liquidus terminates at 58.9 at.% O [80Gul1] (or slightly lower), the eutectic composition for the coexistence of $L_2 + Fe_3O_4 + Fe_2O_3$ at 1539 °C [71Cro]. There are apparently no reliable data for the Fe_2O_3 liquidus compositions.

Gas

The equilibrium gases over solids or liquids of the Fe-O system, according to the composition of the condensed phase, may contain significant fractions of the following molecular species: Fe, O_2, O, FeO, and FeO_2. Claims that Fe_3O_4 and $(FeO)_3$ molecules occur in the gas phase [63Gle] were disputed by [63Was]; moreover, these particular species apparently were not observed in subsequent studies. The existence of $FeO_2(g)$ first was reported by [75Hil] in gas over Fe_2O_3; [84Smo] recognized its presence in their analysis of gas thermodynamics. Molecular FeO_2 is not known to be the dominant gaseous species in any condition, but Fe, FeO, O_2, or O may be dominant.

According to [78Shc], the congruently vaporizing composition of the condensed phase is displaced to lower O concentrations as temperature increases. Below about 1360 °C, the congruently vaporizing solid is Fe_3O_4; for a short interval above 1360 °C, it is wustite. At still higher temperatures, the congruently vaporizing condensed phase is liquid. It was recently shown [84Smo] that the widely quoted value for O concentration, 52.74 at.% O, in congruently evaporating liquid at 1600 °C [46Dar] is greater than the actual value.

Metastable Phases

Wustite

When quenched below about 200 °C, wustite can be retained without transformation to (αFe) and Fe_3O_4 or other metastable phases for indefinite periods. As discussed in the section on crystal structures, below, the quenched wustite may not have retained exactly the defect structure of the original at higher temperature. Three types of metastable wustite—P′, P″, and P‴—were distinguished [68Man]. Their natures and rather uncertain ranges of occurrence are discussed in the section on crystal structures. [66Her] reported a possible miscibility gap in supercooled wustite from electron microscopy and XRD studies with boundaries at 300 °C of 50.5 and 52.1 at.% O. Metastable wustite with the composition of stoichiometric "FeO" was reported to occur as a decomposition product of annealing at 225 °C wustite quenched from the stable region [70Hen]. In another study of decomposing quenched wustite, various transient wustite compositions were reported [59Hof].

With low-temperature heat-capacity measurements, [29Mil] detected a transition in metastable wustite at about –90 °C. Subsequent studies, including magnetic susceptibility measurements, showed that the anomaly was due to a change from paramagnetic to antiferromagnetic [70Mic]. A change in crystal structure from cubic to rhombohedral (wustite (LT)) at this Néel point, T_{N}, was discovered by [50Tom]. The deviation from cubic is almost undetectable at O-rich compositions; the deviation of α from 60 increases with Fe content. There is considerable variation among measured values of T_{N}, which depends on composition (O/Fe) and apparently is sensitive also to other often ill-defined factors, such as thermal history and impurity content. Different

Table 6 Fe-O Crystal Structure Data

Phase	Composition, at.% O	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
Stable						
(αFe)	~0	*cI*2	$Im\bar{3}m$	*A*2	W	[Pearson2]
(δFe)	~0	*cI*2	$Im\bar{3}m$	*A*2	W	[Pearson2]
(γFe)	~0	*cF*4	$Fm\bar{3}m$	*A*1	Cu	[Pearson2]
Wustite	51.2 to 54.6	*cF*8	$Fm\bar{3}m$	*B*1	NaCl	[Pearson2]
Fe_3O_4(LT)	~57.1	*mC*224	*Cc*	...	Fe_3O_4(LT)	[77Yos]
Fe_3O_4	57.1 to 58.0	*cF*56	$Fd\bar{3}m$	$H1_1$	Al_2MgO_4	[Pearson2]
αFe_2O_3	59.8 to 60.0	*hR*10	$R\bar{3}c$	$D5_1$	αAl_2O_3	[Pearson2]
Other						
(εFe)(a)	0 to ?	*hP*2	$P6_3/mmc$	*A*3	Mg	[Pearson2]
P′(wustite)	~51.3 to ~53.5	*c***(?)(b)	...	...	...	[80Bau2]
P″(wustite)	~52 to ~54	*mP*500(?)	$P2_1/m$	...	...	[85Ish]
P‴(wustite)	...	...	...	...	...	[68Man]
Wustite(LT)	51.3 to 53.2	*hR*2(c)	$R\bar{3}$	...	NiO(LT)	[70Mic]
Fe_3O_4(P)(d)	~57.1	*m**14	...	...	...	[74Mao]
βFe_2O_3	~60.0	*cI*80	$Ia\bar{3}$	$D5_3$	Mn_2O_3	[58Sve]
γFe_2O_3	~60.0	*tP*160	$P4_32_12$	...	...	[83Gre]
εFe_2O_3	~60.0	*m**100	...	...	...	[63Sch2]

(a) Stable at pressures >13 GPa. (b) Incommensurate ([83Leb] dissenting); [77And] claimed orthorhombic. (c) Magnetic reflections may indicate linear cell dimensions are doubled, corresponding to *hR*16 [79Bat]. (d) Stable at pressures >25 GPa.

methods of measurement also yielded slightly different values [67Koc]. Measurements of the composition effect on T_N [67Koc, 68Fin, 68Mai, 70Mic, 84Sri] are not concordant, but most indicate that T_N increases about 8 to 12 °C/at.% O and that T_N is near −80 °C in Fe-rich (metastable) wustite. According to [67Oka], increasing pressure up to 0.6 GPa raises T_N by 6.5 °C/GPa.

Different opinions were published on whether metastable wustite with 51.5 at.% O undergoes a change of crystal structure when subjected to shock compression over 70 GPa [82Liu, 84Jac, 84Liu2].

Fe_2O

The possible existence of Fe_2O in subsurface layers of the Earth was hypothesized by [71Sor]. There is no evidence that the phase has been observed.

$FeO_x (1.33 > x > 1.15)$

The occurrence of several phases intermediate in composition between O-rich wustite and Fe_3O_4 was claimed by [69Riz] in emf oxidation/reduction studies at 1100 to 1200 °C. This finding does not appear to have been confirmed independently.

βFe_2O_3, γFe_2O_3, and εFe_2O_3

These metastable forms are described in Tables 6 and 7 and discussed in the "Crystal Structures and Lattice Parameters" section below.

Crystal Structures and Lattice Parameters

Fe-O crystal structure and lattice parameter data are listed in Tables 6 and 7, respectively.

(Fe)

The effects of dissolved O on the lattice parameters of (αFe), (γFe), and (δFe) apparently have not been measured because of the very low solubility.

Wustite

The structure is a highly defective form of an ideal fcc (NaCl-type) lattice composed of Fe^{++} and $O^{=}$ ions. This was established originally in quenched (metastable) specimens by [25Wyc] using XRD. All specimens equilibrated at atmospheric pressure are Fe-deficient relative to "ideal" ferrous oxide with O/Fe = 1. This deficiency is associated with a predominance of vacancies in the Fe sublattice [33Jet1]. For charge balance, Fe^{+++} ions occur together with the Fe^{++} ions. ([84Haz] drew attention to the lack of exact knowledge of vacancies in the O sublattice, which are, however, in low concentration compared to those of the Fe sublattice and certainly fewer than 2% of the available O sites.) Detailed reviews of the voluminous literature on wustite structures [76Gav, 80Bau1, 84Haz, 87Mro] are available. Only a brief description is included here.

The view that the defects associated with the Fe deficit were always Fe-site (octahedral) vacancies and Fe^{+++} ions was contradicted by the [60Rot] finding with neutron diffraction on quenched (metastable) specimens that some Fe ions occur interstitially in tetrahedral sites normally vacant in NaCl-type struc-

Table 7 Fe-O Lattice Parameter Data

Phase	Composition, at.% O	Lattice parameters, nm a	b	c	Comment	Reference
Stable						
αFe	0	0.28665	...	...	At 25 °C	[King1]
		0.2904	...	...	At 912 °C	[83Neu]
δFe	0	0.2932	...	...	At 1394 °C	[83Neu]
		0.2941	...	...	At 1538 °C	[83Neu]
γFe	0	0.3647	...	...	At 912 °C	[83Neu]
		0.3688	...	...	At 1394 °C	[83Neu]
Wustite	52.1	0.43536	...	...	At 1000 °C	[74Tou]
Fe_3O_4(LT)	57.1	1.1868	1.1851	1.6752	$\beta = 90°12'$, at −263 °C	[82Iiz]
Fe_3O_4	57.23	0.8396	...	...	Room temperature	[69Bha]
αFe_2O_3	60.0	0.54277	...	...	$\alpha = 55°15'$, at 20 °C(a)	[68Kas]
Other						
εFe	0	0.2485	...	0.3990	Room temperature	[King3]
P′	~52.3	~1.16	...	...	Supercell	[77And]
P″	52.6	~1.54	1.54	~2.18	Room temperature, $\gamma = 90°$	[85Ish]
P‴	...	...	...	...	...	...
Wustite(LT)	51.3	0.3050	...	...	$\alpha = 59°30'$, at −183 °C(b)	[70Mic]
Fe_3O_4(P)	~57.1	0.422	0.543	0.560	$\beta = 106°$, at 25 °C and 25 GPa	[74Mao]
βFe_2O_3	~60	0.9393	...	...	Room temperature	[76Ben]
γFe_2O_3	~60	0.83396	...	2.4966	At −269 °C	[83Gre]
εFe_2O_3	~60	1.297	1.021	0.844	Room temperature, $\beta = 95°20'$	[63Sch2]

(a) Converted from original parameters for hexagonal indexing ($a = 0.50340$ and $c = 1.3752$ nm). (b) Magnetic reflections may indicate linear cell dimensions are doubled [79Bat].

tures. The original [60Rot] concept was modified by [69Koc], who described the vacancies and tetrahedral ions as occurring in 13/4 clusters of 13 vacancies and 4 tetrahedral ions.

The concept of a basic defect complex from which larger defects were formed by aggregation was developed by [71Che]. With neutron diffraction at 800 to 1200 °C, they discovered that the basic complex comprises a tetrahedral Fe ion surrounded by four octahedral vacancies of the Fe sublattice positioned relative to one another at the corners of a tetrahedron. This complex is called a "4/1" defect. Experimental data showing that for most equilibration conditions, the vacancy/interstitial ratios were less than 4 were explained in terms of clusters of 4/1 defects, in which vacancies were shared among the conjoined defects. Experiment and theory have focused attention on certain clusters, distinguished by the number and the joining configuration of the constituent 4/1 defects, as being more probably than others [69Koc, 75Cat, 79Gav, 85Sor, 85Tom, 86Gar1, 86Gar2, 86Gri, 87Gar]. The formation of clusters sometimes is characterized as a short-range ordering process. Uncertainty remains regarding the dominant type of cluster in any particular set of conditions; a mixture of cluster types is probably present in equilibrium wustite under most conditions of composition, temperature, and pressure.

Description of the defect structures is further complicated by the incompletely understood long-range ordering of the defect clusters. Room-temperature data from quenched specimens have been used frequently for discussion of structures in the temperature range of wustite stability, but the assumption of their applicability is questionable. Observations in the stable *T-P-X* range of wustite, however, sometimes have indicated that long-range ordering of the clusters occurs up to 1000 °C [67Man, 70Ben, 73Hay]. In other studies it was not detected [69Koc].

In the many papers of Vallet and his associates, summarized by [70Val], [76Car], and [89Val], dilatometric, XRD, and thermodynamic evidence was presented for the subdivision of the wustite field into ten regions separated by transformations of second (or higher) order. The differences among the six structures of the ten regions were not described, but speculations often have associated the subboundaries with changes in ordering. The Vallet concept was supported at least partly by independent thermodynamic data and analysis [69Fen, 85Sor], but in spite of directed effort, other investigators, working with stable wustite at elevated temperatures, have not found evidence of the transformations claimed [72Hay, 74Hay, 74Tou]. The absence of two-phase fields and first-order discontinuities is undisputed; the existence and location of second- (or higher-) order features interrupting a continuous structural change in wustite remain controversial propositions.

The data are insufficient for quantitative exposition, but a qualitative picture of structural variation within the stable wustite field emerges from many experiments and calculations [83Leb, 84And, 84Rae]. At temperatures approaching the solidus, isolated octahedral Fe vacancies and ferric ions may be present and are perhaps dominant. At lower temperatures within the stable field, the octahedral vacancies tend to occur with tetrahedral ferric ions in 4/1 defects that conjoin to form various kinds of clusters. The dominant type in a mixture of cluster types probably varies with temperature and O/Fe ratio. The clusters tend towards long-range order at lower temperatures and higher O/Fe ratios.

Lattice parameter values and structural analyses of metastable wustite quenched from the stable range are often unreliable indications of the equilibrated high-temperature state, not only because of thermal expansion and quenching strains, but also because of unsuppressed ordering or other changes in defects. Unit cell dimensions of equilibrated wustite at high temperature may be expected to be affected by changes in defect clustering and ordering with temperature and composition changes. Measurements at temperatures and compositions in the stable range were reported. The lattice parameter of the basic cell (4Fe + 4O ion sites, NaCl type) varies linearly with composition (800 to 1075 °C) [72Hay, 74Tou] and with temperature (600 to 1075 °C) [65Gor, 74Tou]. No trace of the subboundaries was detected in any of these works, although argument was presented [73Car, 74Car] that the [72Hay] data were, nevertheless, compatible with the existence of subboundaries.

The data for lattice expansion with temperature yield the following values for (10^6 *da*/*dT*)nm/°C at 42.1 at.% O (1.087 O/Fe): 6.1 [65Gor], 8.6 [72Hay], 6.9* [74Tou]. The averaged effects of composition changes measured by [72Hay] (950 and 1050 °C) and [74Tou] (800 to 1075 °C) are 0.0357 and 0.0349* nm/(O/Fe), respectively. Because the stable range of wustite is extensive, the choice of location for the lattice parameter value quoted in Table 7 at 1000 °C and 52.1 at.% O (0.920 Fe/O or 1.087 O/Fe) appears to be rather arbitrary. However, it is a point within the experimental ranges of [65Gor], [72Hay], and [74Tou], whose data are quite concordant there, with the [74Tou] value located at their average.

Long-range ordering of defects produces superstructures with unit cell dimensions larger than the *a* value (denoted *a'* here) of the basic NaCl-type unit cell. Cells with the periodicity 2.6a' at 840 °C with O/Fe = 1.11 or 1.05 [73Hay] and about 2.5a' at 900 °C with O/Fe = 1.08 [87Gar] were reported. Resemblance of the ordering of clusters in stable wustite to that in the metastable phases P' and P'' at lower temperature was reported by [68Man] (also [70Ben]) and by [86Gar1], respectively.

Effects of elevated hydrostatic pressure on wustite in its stable range apparently have not been reported.

Fe_3O_4

The cubic structure and space group at ambient temperature and pressure were correctly identified by [15Bra]. The identification of the space group as $Fd\bar{3}m$ was reconfirmed by [74Sam] after it has been questioned. The structure is that of an inverse spinel at ambient temperature, but [81Wu] showed that the distribution of Fe^{++} and Fe^{+++} ions between tetrahedral and octahedral sites gradually becomes random with increasing temperature. Prior published lattice parameter values were listed by [67Swa1] without exactly specified compositions. Table 7 lists the adopted value for stoichiometric Fe_3O_4 [69Bha]. The initial measurement of the effect of composition on *a* [41Ver] indicated a much larger effect than that of [69Bha], whose data exhibit a contraction in *a* with increasing O content, corresponding to about -1.2×10^{-3} nm/at.% O. Somewhat larger, concordant values, -1.9×10^{-3} and -2.1×10^{-3} nm/at.% O were reported by [67Col] and [75Vol], respectively. The [81Tou] data indicate the values -2.5×10^{-3} and -3.3×10^{-3} nm/at.% O for 900 and 1200 °C, respectively. The

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*Recommended.

nonlinear effect of temperature on *a* from –152 to +22 °C was measured [79Iid, 79Yos, 83Rig] with $d \ln a/dT \sim 7 \times 10^{-6}/°C$ [79Iid]. Lattice parameter values also were reported from room temperature to 1000 °C [65Gor] and to 1200 °C [81Tou]. An anomaly occurs in the nonlinear relationship near the Curie temperature. The coefficient of lattice parameter change with pressure at zero pressure, $d \ln a/dP$, was reported to be 1.82×10^{-3}/GPa [74Mao] and 1.84×10^{-3}/GPa [86Nak]. The response is not linear.

Two other modifications of Fe_3O_4, both monoclinic, exist (Tables 6 and 7): (1) Fe_3O_4(P) at elevated pressures (>25 GPa at room temperature); and (2) Fe_3O_4(LT) at low temperatures (below –149 °C at ambient pressure). There is apparently only one determination of Fe_3O_4(P) symmetry (Table 6). The effects of changes in composition, temperature, and pressure on its unit cell dimensions (Table 7) are apparently unknown. The tentative identification by [74Mao] of the Fe_3O_4(P) structure—monoclinic with two molecules of Fe_3O_4 per unit cell—was regarded as being quite dubious by [86Hua]; however, no alternative was suggested.

The crystal symmetry of Fe_3O_4(LT) was described as probably tetragonal [47Ver], rhombohedral [51Tom], orthorhombic [53Abr], "possibly" triclinic [71Chi2], and monoclinic [77Yos]. Uncertainty remains; the structure is probably monoclinic, but possibly triclinic [80Goo]. The space group *Cc* [77Yos] was adopted in later papers [79Iid, 82Chi, 82Iiz], but Iida, who coauthored [77Yos], adopted *Pc* at "finite" temperatures [80Iid]. For Fe_3O_4(LT), the effect of variation in temperature (but not of composition or pressure) on the lattice parameters was measured. The variations in *a*, *b*, *c* and β were observed from –193 to –153 °C [79Iid, 79Yos]. Sets of values at –189 [77Yos] and –263 °C [82Iiz] (Table 7) also were reported.

αFe_2O_3

The rhombohedral structure, unit cell, and $R\bar{3}c$ space group as identified by [25Pau] were confirmed with refinements by [66Bla] and generally are accepted. The lattice parameter values adopted in Table 7 [68Kas] were determined with XRD on a very pure polycrystalline specimen. The lattice parameters reported by [70Bla], which agree with those of [68Kas] within experimental error, were measured precisely with a single crystal of lower purity.

The effect of temperature on the lattice parameters was measured by [65Gor] (25 to 1000 °C), [65Sai] (20 to 1100 °C), and [67Str] (20 to 750 °C). No anomalies were observed by [65Gor], possibly because of the wide temperature intervals between measurements or because of impurities in the mineral specimen. Natural hematite from a different source and a synthetic specimen were used by [65Sai], who observed in each anomalous behavior near 300 °C, in addition to that probably identifiable with the Néel point near 700 °C. Contradicting [65Gor] and [65Sai], [67Str] observed the parameter *c* (hexagonal indexing) to decrease with increasing temperature to 640 °C, above which it increased. No set of results depicts a discontinuity in *a* or *c* (hexagonal). The [65Gor] results are adopted tentatively.

The effect of hydrostatic pressure on the unit cell dimensions was observed by [66Lew] (to 23 GPa), [79Sat] (to 11 GPa), [80Fin] to 5 GPa) and [85Suz] (to 55 GPa). An anomaly at 3 GPa [79Sat], attributed tentatively to a Morin transformation, was not reported by the other investigators and specifically denied by [80Fin], who suspected that an impurity effect had been involved. Anisotropy of linear dimensional changes of the unit cell during compression was noted by [79Sat] and [80Fin], but not by [66Lew]. A phase transformation at about 55 GPa was detected by [85Suz], but an attempt to identify the high-pressure structure with XRD and Mössbauer tests as a perovskite-type orthorhombic lattice was unsatisfactory.

Wustite (Metastable)

The three metastable forms, P′, P″, and P‴, observed at and above room temperature (but below 570 °C), and one low-temperature rhombohedral form with antiferromagnetic ordering (below a –80 °C Néel point) are discussed in this section.

Early observations of "wustite" were performed with metastable products of quenching from the stable state [25Wyc, 33Jet1]. These investigations revealed an "ideal" NaCl-type fcc structure with eight (octahedral) ion sites (half Fe, half O) per unit cell and also that many such sites, predominantly those of Fe, were vacant. This description was accepted until [60Rot] with neutron diffraction and [66Smu] with XRD showed on specimens quenched to room temperature that some cations (mostly Fe^{+++}) were in tetrahedral interstices. The investigations of [63Man] and [68Man] showed that the defects present exhibited long-range order, which according to composition and thermal history, exhibited three forms, designated P′, P″, P‴. [69Koc] first showed that the cation vacancies and cation interstitials occur in clusters involving more than one or two vacancies per defect. The voluminous literature dealing with the predominant types of clusters and their ordering is summarized in the reviews that are listed in the section on the crystal structure of stable wustite.

Numerous measurements of the lattice parameter, *a*′, of the basic cubic unit cell were reported, many over a range of composition. Several summaries and comparisons of data are available [55Mar, 63Off1, 66Lev, 68Fuj, 73Dob, 74Tou, 84Mcc]. Linear equations were adopted to describe the decrease of *a*′ with increasing O concentration [66Lev, 68Fuj, 80Bau2]. Based on specimens quenched from 1000 °C, the [66Lev] equation (with the original units for *a*′ and C_O, the O concentration, transformed herein to nm and at.% O, respectively) is $a' = 0.53528 - 0.0020316\, C_O$.

Values of *a*′ from this equation agree quite well with other measured values [33Jet1, 51Cir, 56Fos, 68Fuj, 74Tou, 79Bat, 80Bau2], but the [68Fuj] and [80Bau2] equations indicate a lower sensitivity of *a*′ to composition, that is, approximately -1.59×10^{-3} nm/at.% O. Quenched specimens of wustite with 50.04 at.% O (almost stoichiometric "FeO") prepared under 5.2 GPa hydrostatic pressure at 770 °C exhibited an *a*′ value of 0.4323 nm at room temperature and pressure [67Kat]. This is slightly lower than the value of 0.4336 nm from the [66Lev] equation extrapolated. With stoichiometric "FeO" produced as a metastable decomposition product of wustite, [70Hen] obtained the value 0.4333 nm. A value, $1.227 \times 10^{-5}/°C$, for the thermal expansion coefficient, $d \ln a'/dT$, was measured with XRD between 25 and 450 °C [66Ark]. The nonlinear dependence on hydrostatic pressure of a'/a'_0, where the subscript denotes the zero pressure condition, was measured to 29 GPa [66Cle, 66Dri].

The P′ phase is obtained in rapid quenching of wustite from the stable range, particularly at those compositions with moderate Fe deficits from stoichiometric. Its extra XRD reflections over those of the "ideal" *B*1 structure manifest the presence of order, but are of a less developed superstructure than those of P″ and P‴ [68Man, 70Ben]. The ordered P′ structure was considered to be cubic or pseudocubic with $a \approx 2.6a'$ [68Man], $2.74a'$ [77And], 2.6 to $2.7a'$ [83Leb], or $3a'$ [69Koc]. However, tetragonal or orthorhombic symmetry was suggested [77And]. Reinvestigation by [80Bau2] produced XRD and electron microscopy results that were regarded as explicable only if the structure is incommensurate, with a superperiod that varies with composition. The range agreed well with that reported by [77And]. [82Yam] regarded P′ as incommensurate with the six-dimensional space group P^{Fm3m}_{Pm3m}. A discussion of the space group of tri-incommensurate P′ was also given by [87Wei]. However, the contradictory conclusion, that P′ is indeed commensurately ordered, was reached by [83Leb] (see their "Note added in proof"). Small domain size was said to be responsible for misleading diffraction results. Thus, the structure of P′ remains controversial.

The P″ modification of metastable wustite tends to form in quenching to room temperature of stable wustites with larger Fe deficits (especially with slower quenching rates than those producing P′) or in annealing of P′ at slightly elevated temperatures, for example, 225 °C [68Man, 70Ben, 77And]. In P″, the superstructure is better developed than in P′. The structure was described by [68Man] as being cubic with $a = 5a'$, but [77And] regarded it as "orthorhombic" (space group *Abm*2) with $a = b = c = 5a'$ (sic). The superstructure is commensurate with the *B*1 parent lattice according to [83Leb], who, however, also found agreement with their data with a monoclinic (space group *C*2) supercell with linear dimensions $5a' \times 5a' \times 10a'$. [83Nag] reported two orthogonal supercell dimensions as $5a'$ and $2.5a'$ while stating their agreement with [77And]. Like [83Leb], [85Ish] identified the structure as monoclinic, but with the space group $P2_1/m$ and the lattice parameters $a = b = 2.5\sqrt{2}a'$, $c = 5a'$, and $\gamma = 90°$. The clusters were reported to be composed of two edge-conjoined vacancy tetrahedra, but, unlike the usual 4/1 clusters, most lack the tetrahedral Fe ion.

The P‴ modification of metastable wustite forms when quenched wustite (P″) is annealed at 500 °C [68Man, 70Ben]. The structure apparently has not been analyzed.

The antiferromagnetic ordering of metastable wustite below about −80 °C causes a rhombohedral distortion of the cubic disordered structure [50Tom, 53Wil]. The deviation from cubic symmetry in wustite (LT) increases with decreasing temperature [65Suz] and with decreasing O concentration [70Mic, 79Bat]. With increasing proximity to the Néel point and at high O concentrations, the deviation approaches zero.

βFe_2O_3

The bcc structure reported by [58Sve] (Table 6) was confirmed by [76Ben], who reported the lattice parameter more precisely (Table 7). The effect of composition and temperature on the lattice parameter have not been reported.

γFe_2O_3

Despite research for more than 50 years, complete agreement on the structure and unit cell apparently does not exist [86Ho]. The significant developments in determination of the structure prior to 1960 were reviewed by [63Sch1]; more recently [80Mor], [83Bou], and [86Ho] summarized investigators' results. Initially, the structure was viewed as a modification of cubic Fe_3O_4. According to [35Hag], [35Kor], and [35Ver], the proposal of a cubic face-centered cell (space group $Fd\bar{3}m$), nearly equal in size to that of Fe_3O_4 ($a = 0.8396$ nm, Table 7), was rendered untenable when the ordering of the Fe site vacancies was established with the discovery of XRD lines incompatible with the spinel structure. Since the work of [58Oos], identification of the structure as primitive is undisputed.

The ordered unit cell is tetragonal, with $a = 0.833$ nm and $c/a = 3$ according to [58Oos] and [63Sch1]. These results were confirmed by [83Gre] using neutron diffraction (Tables 6 and 7). However, [83Gre] identified the space group as $P4_32_12$ rather than $P4_1$ (or $P4_3$) [58Oos]. Other fairly recent investigations [83Bou, 86Ho] reported that the unit cell is cubic with a lattice parameter of about 2.5 nm. The space group was reported by [86Ho] as being $Pm\bar{3}m$, $Pm\bar{3}n$, $Pn\bar{3}m$, or $Pn\bar{3}n$. The disagreement among investigators in attributable mainly to difficulty in obtaining individual crystals sufficiently large in all three dimensions for definitive measurements. Variations in the degree of ordering of Fe ion vacancies and inclusion of hydrogen impurity many have been responsible for different findings in some instances.

εFe_2O_3

A complete description of the monoclinic structure (Table 6) apparently has not been published. The effects of composition and temperature on the lattice parameters (Table 7) are also unknown.

"δFe_2O_3"

This compound is not binary, because it yields water during decomposition [59Oka].

Thermodynamics

(αFe) and (δFe)

The standard Gibbs energy change for the reaction:

$1/2O_2(g) \leftrightarrow O$ (dissolved in αFe or γFe)

was reported by [67Swi]. It was based mainly on the (δFe) data of [66Hep] and was approximate for (αFe). Conversion of the original equation for use with standard states of O_2 gas at 0.1 MPa and of dissolved O (a_O value unity, with $a_O/C_O \to 1$ as C_O (in at.% O) → zero) yields

$$\Delta G^0 = -155\,600 + 32.34\,T$$

where ΔG^0 and T are in J/0.5 mol of O_2 and K, respectively.

(γFe)

The corresponding standard Gibbs energy change for dissolution of gaseous O_2 in (γFe), obtained by conversion of the original standard states used by [67Swi] to O_2 gas at 0.1 MPa and O dissolved in (γFe) so that $a_O/C_O \to 1$ as C_O (in at.% O) → zero, is

$\Delta G^0 = -175\,100 + 50.16\,T$

where ΔG^0 and T are in J/0.5 mol of O_2 and K, respectively.

Wustite

Measurements of low-temperature heat capacities were made on wustites quenched from the stable range by [29Mil] (−203 to +7 °C, with a relatively poor specimen) and [51Tod] (−221 to +25 °C, 1.056 O/Fe*). A revised analysis [52Hum] of the latters' data rejected their allowance for zero-point entropy and yielded the $S^0(Fe_{0.947}O, s, 25\ °C)$ value 57.49 J/K · mol of $Fe_{0.947}O$. This value was adopted in several compilations [82Wag, 82Pan, 84Pan]; the 1965 JANAF value, 57.59 J/K · mol of $Fe_{0.947}O$ [85Cha] is only slightly larger. The value assessed by [78Spe] from high-temperature equilibrium data, 59.79 J/K · mol of $Fe_{0.945}O$, is significantly higher and concordant within experimental error with the original [51Tod] value (59.41) J/K·mol. However, [62Chi] had used equilibrium data to support the [52Hum] procedure.

Both [29Mil] and [51Tod] observed λ-type peaks in the heat capacity of metastable wustite at the Néel point near −80 °C. Relative values of the heat capacity near this low-temperature transformation were compared for several compositions [68Mai].

High-temperature enthalpies and entropy increments determined by [51Cou] from 25 to 1511 °C (above the melting point) with 1.056 O/Fe* agree with earlier enthalpy points of [33Whi] at 700 and 900 °C. The enthalpy of fusion in incongruent melting at about 1377 °C is 31.39 kJ/mol of $Fe_{0.947}O$ [51Cou].

Experimental investigations of the thermodynamics of the equilibrium:

$x\mathrm{Fe}(s) + 1/2\mathrm{O}_2(g) \leftrightarrow \mathrm{Fe}_x\mathrm{O}(s)$

by equilibration of the solids with $H_2O + H_2$ or $CO_2 + CO$ mixtures (some thermogravimetric) or by emf (solid electrolyte) techniques were very numerous—35 studies prior to 1976 were listed in the [78Spe] review. Other reports of experimental investigations since 1920** [21Cha1, 21Cha2, 22Mat, 24Eas, 29Kri, 29Sch, 30Kri, 31Jom, 33Emm, 34Bri, 54Ari, 59Pet, 62Hoc, 64Mat, 64Tay, 64Vor, 65Mci, 65Val1, 65Val2, 66Bul, 66Got, 66Mat, 70Asa, 70Mar2, 71Ono, 72Sai, 75Hue, 75Now] may also be mentioned; in addition, several more recent investigations were reported [80Sug, 81Bar, 81Jac, 81Sch, 82Li, 82Sik, 84Fre, 86Mal, 86Sjo]. The measurements of all these instances were of O_2 fugacity, f_{O_2}, but often values of $RT \ln f_{O_2}$, that is, of the relative partial molal Gibbs energy of O_2 in wustite, $2G(O) - G^0(O_2)$, were reported as values of $2 \cdot \Delta_f G^0(Fe_xO, s, T)$.

Equating these quantities defines the standard states of Fe and Fe_xO as O-saturated Fe and Fe-saturated wustite, respectively, each of which varies continuously with temperature. Ignoring the solubility of O in Fe (<0.1 at.% at 1371 °C) is insignificant, but some investigators and reviewers, particularly recent ones, such as [86Sjo] and [87Lyk], preferred to describe the data with separate functions above and below 912 °C, the αFe ↔ γFe transformation temperature. The small but not negligible variation in the composition of Fe-saturated wustite, especially below 800 °C, usually was not specifically noted, so that $\Delta_f G^0(Fe_xO, s, T)$ values reported are then per 0.5 mol of O_2 rather than for a fixed composition. However, values from measurements at $T \geq 800$ °C apply to Fe-saturated wustite with an almost fixed composition (~51.2 at.% O). In some tabulations, such as those of [82Pan] and [84Pan], the values were given for wustite of a fixed composition (51.36 at.% O, 1.056 O/Fe) near that of eutectoid wustite (and for unstable stoichiometric "FeO"), rather than for the Fe-saturated compositions. For the standard Gibbs energy of formation of Fe-saturated wustite from (αFe) or (γFe) and $O_2(g)$, $\Delta_f G^0(Fe_xO, s, T)$, equivalent to values of $0.5\,RT \ln f_{O_2}$, the equations of [86Sjo] are adopted:

$\Delta_f G^0 = -251\,480 - 18.100\,T + 23.456\,T \log T$ at 593 to 911 °C

and

$\Delta_f G^0 = -286\,248 + 181.419\,T - 31.909\,T \log T$ at 911 to 1067 °C

in which $\Delta_f G^0$ and T are in J/0.5 mol of O_2 and K, respectively. The standard state of O is O_2 gas at 1 atm (0.1013 MPa) and f_{O_2} is in atm. These results were described by [86Sjo] as being in agreement with the values assessed from selected earlier data by [78Spe] and [83Esd]. (The O_2 fugacity data for the Fe_xO/Fe_3O_4 equilibrium are discussed with thermodynamic data for the latter phase.)

Measurements of O_2 fugacity across the wustite phase field were also numerous. [78Spe] listed 18 studies, to which others may be added [49San, 54Ari, 56Hov, 62Rac1, 62Rac2, 63Val, 63Yak, 64Bar2, 64Kat, 65Val1, 66Bul, 66Lev, 68Fuj, 68Hem, 68Riz2, 70Asa, 70Mar2, 71Ono, 73Cho, 73Jan, 73Mak, 74Ben, 74Gid, 74Jan, 79Tak, 80Tak, 81Bar]. The thermodynamic models based on structural considerations are outside the present scope. Of many reviews and/or analyses of the foregoing experimental results, a few deserve special mention [73Gid, 78Spe, 82Lyk, 89Val***]. Relative partial molal Gibbs energies of Fe were derived by the Gibbs-Duhem procedure from those measured directly for O, with Fe-saturated wustite as the fiducial compositions. Values for other partial and integral properties (and component activities) usually were derived from the O_2 fugacity measurements. However, relative partial molal enthalpies of O_2 in wustite were measured directly at short composition intervals with microcalorimetry at 800, 1050, and 1075 °C [64Ger2, 65Ger1, 70Mar1, 87Tet]. The tabulated values of $H(O) - 0.5\,H^0(O_2)$ at 1075 °C exhibited a minimum, −279.5 kJ/0.5 mol of O_2, at the composition 52.04 at.% O, with values −251.5 and 273.4 kJ/0.5 mol of O_2 at 51.17 and 53.27 at.% O, near the Fe- and O-saturated limits, respectively [70Mar1]. In the combination of composition dependence (curve shape) and magnitude, these results are closer to those of [45Dar] than to those of others [63Val, 66Ack, 69Fen]. Combination of these $H(O) - 0.5\,H^0(O_2)$ values with their measured $G(O) - 0.5\,G^0(O_2)$ values at 1075 °C enabled [70Mar2] to evaluate $S(O) - 0.5\,S^0(O_2)$ at 0.005 O/Fe in-

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*Slightly lower ratio than that in eutectoid wustite (1.057 O/Fe, 51.4 at.% O).

**Unrecognized thermal separation effects in gases used for equilibration affected some investigations [32Emm, 33Emm].

***[89Val] presented a particular analysis predicated on the existence of several subvarieties of wustite—a view not universally accepted.

tervals from 1.05 to 1.14 O/Fe (51.22 to 53.27 at.% O). These values differ somewhat from the assessed values of [78Spe] (see below).

From their analysis of the available data, [78Spe] calculated and tabulated at 0.01 O/Fe intervals from 1.06 to 1.16 O/Fe (51.46 to 53.70 at.% O) a self-consistent set of values for the following thermodynamic properties of wustite in its stable range of temperature: relative partial enthalpies and entropies of O and Fe, integral enthalpies, and entropies of formation. These quantities were approximated as being temperature independent. In developing these tabulated values, [78Spe] had found that use of the [70Mar1] partial enthalpies for O at 1075 °C yielded partial Gibbs energies for O inconsistent with other reliable data at temperatures removed by only 200 to 300 °C from 1075 °C. [78Spe] therefore developed their values from analysis of variations with temperature and composition of selected equilibrium measurements of O_2 fugacities. Although there were several analyses of individual sets of data that yielded values for partial and integral properties within the wustite field, including some more recent than [78Spe] (for instance [80Tak], [81Bar], and [82Lyk]), the [78Spe] assessment for wustite (Table II of that paper) is adopted because of its breadth of sources and critical approach.

Because of instability of the compounds below 570 °C and the lack of C_p data, partial and integral enthalpies for wustite at 25 °C as a function of composition are unavailable. Values for the enthalpy of formation derived from equilibrium data (−263.0 kJ/mol of $Fe_{0.945}O$ [78Spe] or −266.3 kJ/mol of $Fe_{0.947}O$ [82Wag, 82Pan, 84Pan, 85Cha] are preferred to the older calorimetric data for "FeO" [29Rot, 30Rot, 34Rot].

Fe_3O_4

Broad-range, low-temperature relative enthalpy and heat capacity measurements [26Par, 29Mil, 69Wes, 73Ala, 76Bar, 84She, 85She1] were complemented by several narrower-range measurements [73Bar, 75Kam, 75Wol, 77Mat, 77Tod, 83Gme, 83Rig, 84Gme, 85Ara2, 85She2]. A reported anomaly in C_p near −263 °C [77Tod] was not found subsequently [83Gme, 83Rig, 85She1]. Most limited-range experiments were concerned with the vicinity of the Verwey transition, where evidence of more than one C_p peak was reported [69Wes, 73Bar, 75Wol, 76Bar, 83Rig]. [76Bar] proposed that the occurrence of single C_p peaks in other investigations, for example [29Mil], was due to impurities, but [77Mat] found that stress induced a single peak to split, and others [83Gme, 84Gme, 85She1] found only a single, sharp peak in high-purity, homogeneous, stress-free specimens. The importance of homogeneity was shown by studies [73Ala, 85Ara2, 85She2] of the variation in C_p at low temperatures and in T_V and ΔS_V with slight changes in Fe_3O_4 composition. The effect of magnetic field strength on C_p near the T_V was measured by [75Kam].

The reported values for T_V and the entropy change ΔS_V in the Verwey transition were summarized by [85She1]. Agreement among tabulated values for the purer, more nearly stoichiometric specimens is only moderate. The magnitude of the entropy change at T_V (5.88 J/K · mol of Fe_3O_4 at −149 °C for stoichiometric Fe_3O_4 [85She2]) declines sharply with increasing Fe deficit [85Ara2].

The standard entropy $S^0(Fe_3O_4, s, 25\ °C)$ was evaluated from their low-temperature heat capacities by [26Par], [29Mil], and [69Wes]. [85She1] refrained from evaluating S^0 from their data, possibly because of uncertainties in the ΔS_V contribution. The [69Wes] value, 146.1 J/K · mol of Fe_3O_4, was adopted in the [78Spe] review and the [82Pan] and [84Pan] compilations. ([69Wes] recognized that this value was actually for $S^0(Fe_3O_4, cr, 25\ °C) - S^0(Fe_3O_4, cr, -273.15\ °C)$, because theoretical grounds suggest that the latter term may be >0.) A slightly higher value (146.4 J/K · mol was adopted in the [82Wag] compilation. From studies of equilibrium among Fe oxides, [72Rau] obtained the $S^0(Fe_3O_4, s, 25\ °C)$ value 146.6 J/K · mol of Fe_3O_4. They interpreted their results as being consistent with the assumption that $S^0(Fe_3O_4, s, -273{,}15\ °C)$ is 0 J/K · mol of Fe_3O_4, but [74Gro] showed that the results are consistent with a zero-point entropy value of 4.13 J/K · mol. This value is fairly near the calculated value of 3.41 J/K · mol [74Gro] for the latter quantity. An analysis of Gibbs energy data by [78Spe] found a better fit when a zero-point entropy value 3.35 J/K · mol of Fe_3O_4 was included. More recently, [87One] concluded from his measurements that there is no zero-point entropy. It would be premature to consider the controversy settled.

Since the early (pre-1934) investigations, high-temperature heat capacities and relative enthalpies were measured only by [51Cou], [74Gro], and [75Bar]. The most extensive of these [51Cou] detected no transformation at 1160 °C, where [81Car] reported a first-order change with an enthalpy change of 9.99 kJ/mol of Fe_3O_4. The existence of an 1160 °C transformation is unconfirmed. Only a short range (30 to 275 °C) was covered by [75Bar]. The [51Cou] and [74Gro] sets diverge somewhat above the Curie temperature, where a λ-type peak occurs in C_p. Those of [51Cou] were preferred by [87One]. The [82Pan] and [84Pan] compilations used a combination of the two sets; these tabulations are adopted. They include the [46Dar] value for the enthalpy of fusion, 138 kJ/mol of Fe_3O_4, which apparently has not been superseded.

The standard enthalpy of formation of Fe_3O_4, $\Delta_f H^0(Fe_3O_4, s, 25\ °C)$, was evaluated by bomb calorimetry [29Rot, 75Tur], acid solution [34Rot], and from combinations of the investigators' own experimental data for the Fe/Fe_3O_4, wustite/Fe_3O_4, or other equilibria [46Dar, 72Rau, 87One]. Values also were obtained by correction or analysis of other investigators' data [74Gro*, 75Tur, 78Spe]. Except for one pre-1935 result and that derived by [78Spe], the values all fall between −1115.4 and −1118.2 kJ/mol of Fe_3O_4. The tabulated $\Delta_f H(Fe_3O_4, s, T\ °C)$ values of [82Pan] and [84Pan] are based on the [82Wag] (selected) value, −1118.4 kJ/mol of Fe_3O_4 at 25 °C. The values are thus slightly more negative than the average of the concordant group $\Delta_f H^0(Fe_3O_4, s, 25\ °C)$ values would indicate. However, the [82Pan] and [84Pan] tabulations for $\Delta_f H^0(Fe_3O_4, s, T)$ and those for $\Delta_f G^0(Fe_3O_4, s, T)$ are considered satisfactory. Equations describing $\Delta_f G^0(Fe_3O_4, s, T)$ in various limited ranges of temperature considerably above 25 °C were derived from emf experiments [72Vik, 80Sug]. From their analysis of available data, [78Spe] tabulated relative partial molal Gibbs energies of O and Fe in Fe_3O_4 and relative integral Gibbs energies of Fe_3O_4 at 100 °C intervals from 600 to 1300 °C.

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*The [74Gro] value for −273.15 °C was corrected to 25 °C with the [82Wag] enthalpy difference for the present discussion.

The foregoing values were evaluated for Fe_3O_4 at coexistence with wustite, where the composition differs only very slightly from the stoichiometric (see [82Die] and Table 4).

Numerous measurements of O_2 pressures at the coexistence of Fe_3O_4 and wustite or (αFe) were reported. The earlier data were reviewed by [45Dar] and [65Val1] and compared with their own; later measurements include [65Kle], [68Cha], [69Chi], [69Riz], [71Car], [71Chi1], [72Rau], [81Sch], [82Sik], [83Mye], and [85Jac]. The equation of [85Jac], based on data from 687 to 1327 °C for the Fe_3O_4/wustite equilibrium, is

$$\log P_{O_2} = -12.973 - 28\,365/T + 8.8730 \log T$$

where P_{O_2} and T are in Pa and K, respectively. According to a comparison by [85Jac], the P_{O_2} values calculated with this equation agree within a factor of 1.8 with those of [45Dar], [68Cha], [81Sch], and [83Mye]; they deviate by less than the 1.8 factor from values that [83Elr] calculated with an equation fitted to the data of [45Dar], [65Val1], and [69Riz]. Other equations for various ranges were included in the review of [89Val]. The [85Jac] equation is adopted. Data related to O_2 pressures at coexistence of Fe_3O_4 and (αFe) below 570 °C were presented in tabular and graphical form [33Emm, 72Rau]. [86Mal] described their own measurements with the following equation (P_{O_2} in Pa, T in K):

$$\log P_{O_2} = 29.80 - 41\,720/T$$

(Measurements of the O_2 pressures at coexistence of Fe_3O_4 and αFe_2O_3 are discussed below.)

Thermodynamic properties at compositions displaced from those at the boundaries for coexistence with wustite or Fe_2O_3 could be derived from measurements of O_2 fugacities using gas equilibration with chemical analysis [35Gre, 46Dar] or with thermogravimetry [57Smi, 82Die] or by using a solid-electrolyte emf technique [68Soc]. Mathematical relationships between O_2 fugacity and composition were presented by [57Flo] using the [46Dar] data and by [82Die] using his own data. The [82Die] data and mathematical expressions are adopted. Relative partial and integral molal Gibbs energies at 1200, 1400, and 1575 °C for compositions across single-phase Fe_3O_4 were calculated from available data and tabulated by [78Spe]. For 1200 and 1300 °C, using data of [46Dar] and [57Smi], [75Kur] calculated and tabulated O_2 fugacities and activities of various other components at several compositions of the phase. A theoretical solution model for Fe_3O_4 was recently published [88Hil].

αFe_2O_3

Based on the low-temperature heat capacity data of [26Par] and [59Gro], values for the standard entropy $S^0(\alpha Fe_2O_3, 25\,°C)$ were reported in reviews and compilations: 87.45 [78Spe] and 87.40 [82Wag, 82Pan, 84Pan] J/K · mol of αFe_2O_3, in agreement within the uncertainties. The enthalpy effect at the Morin temperature (−12 °C) was measured as 2.8 J/mol of αFe_2O_3 [76Man]. High-temperature heat capacities were measured by [51Cou] and [72Rez]; those of the former were used for the tables of [82Pan] and [84Pan], which are adopted here. A λ-type peak occurs in C_p at the Néel temperature.

The values for $\Delta_f H^0(\alpha Fe_2O_3, 25\,°C)$ assessed by [78Spe] (−823.4 kJ/mol of αFe_2O_3) and [82Wag] (−824.2 kJ/mol of αFe_2O_3) differ by only 0.1%— for consistency and the convenience of using the [82Pan] and [84Pan] tables for $\Delta_f H^0$, $\Delta_f G^0$, and S^0 up to 1527 °C, the [82Wag] value is adopted.

Concordant pre-1969 experimental data from seven investigations (not including [67Kom]) on the variation of O_2 fugacity with temperature at coexistence of Fe_3O_4 and αFe_2O_3 were described in an equation by [69Bry]. Values calculated with this equation from 627 to 1527 °C and the post-1967 experimental data from five investigations agree everywhere within a factor of 2.1 with the equation developed by [85Jac] from her emf measurements with solid electrolyte at 817 and 1317 °C:

$$\log P_{O_2} = -9.484 - 21\,154/T + 8.2561 \log T$$

where P_{O_2} and T are in Pa and K, respectively. The data of [78Cho] show greater deviation toward 627 °C, where they differ from [85Jac] by a factor of 8.1. The [85Jac] equation is adopted. It indicates an O_2 pressure of 0.1013 MPa at 1455 °C, in close agreement with [46Dar].

With emf measurements at 800 to 1000 °C and direct static measurements at 1253 to 1384 °C, [67Kom] determined O_2 fugacities in stoichiometric and in O-deficient αFe_2O_3 as far as the boundary for $Fe_3O_4/\alpha Fe_2O_3$ coexistence. They tabulated these fugacities, relative partial molal enthalpies of O_2, $H(O) - 0.5H^0(O_2)$ (approximately temperature independent), and activities of αFe_2O_3 (temperature dependent, 1000 to 1384 °C) across the phase field. From these results, [80Gul2] derived an equation describing the activity of αFe_2O_3 at $Fe_3O_4/\alpha Fe_2O_3$ coexistence as a function of temperature.

Liquid

Studies of L_1 ("liquid iron") were numerous; those of L_2 ("liquid oxide") were relatively few. Summaries of the data on the relative dilute solutions of O, L_1, were published by [74Sig], [76Chi], and [78Spe]. With slightly different descriptive equations, the [74Sig] and [76Chi] analyses accepted the [58Flo] results as the main basis for their analyses. According to [74Sig], but with corrections to different standard states, the standard Gibbs energy change ΔG^0 for the reaction:

$$\tfrac{1}{2}O_2(g) = O\ (\text{dissolved in } L_1)$$

where the O_2 gas is at 0.1 MPa and dissolved O is in the hypothetical standard state so that $a_O/C_O \rightarrow 1$ as $C_O \rightarrow 0$, is

$$\Delta G^0 = -117\,000 - 13.23\,T$$

where a_O represents the activity of dissolved O and ΔG^0, C_O, and T are in J/0.5 mol of O_2, at.% O, and K, respectively. According to [74Sig], deviations from Henry's law cannot always be ignored; thus, k_O, the activity coefficient defined by $a_O = k_O \times C_O$, may be evaluated from

$$\log k_O = C_O(0.210 - 500/T)$$

Combination of the foregoing equations yields

$$\log P_{O_2} = 2 \log C_O + C_O(-1000/T + 0.42) - 12\,240/T + 3.62$$

where P_{O_2}, C_O, and T are in Pa, at.% O, and K, respectively. Calculated values of the relative partial molal enthalpy and entropy of O and the relative integral molal enthalpy and entropy of L_1 compositions from 0.05 to 0.8 at.% O were tabulated by [78Spe], who assumed Henrian behavior.

Values of the relative partial molal Gibbs energy of O in L_1 and L_2 on the miscibility gap boundaries from 1550 to 1750 °C and in L_2 coexisting with (δFe) from 1400 to 1500 °C were tabulated by [78Spe]. Experimental data [40Chi, 46Dar, 66Got, 70Fis] on the Gibbs energy of formation of L_2 coexisting with (γFe) or (δFe) were compared by [70Fis] and [78Spe]; the data, except for those of [70Fis], are in good agreement. Of the three later investigations, only [70Fis] included an analytical expression for the Gibbs energy of formation of L_2 along its Fe-rich boundary from 1365 to 1528 °C. O_2 pressures at the coexistence of L_1 and L_2, determined by [56Gok] are concordant with [46Dar] values. The thermodynamic properties of L_2 at O concentrations greater than those at the Fe-rich boundary were investigated by [38Whi], [46Dar], and [63Off2].

In the present assessment, the preferred method of evaluating the Gibbs energy of formation of L_2, per gram-atom of Fe + O, at any selected temperature and composition, is by combination of the [78Spe] values for the enthalpy and entropy of formation, which were tabulated at compositions from 51.46 to 53.70 at.% O. Activities or partial pressures of Fe or O_2 in L_2 may be calculated from the relative partial enthalpies and entropies of each element that [78Spe] also tabulated. Reasonable extrapolation or interpolation of the tabulated values may be used for compositions not specifically listed, either on the Fe-rich boundaries or at higher O concentrations. The reader is referred to Table V of [78Spe], which is not reproduced here. Other thermodynamic descriptions of L_2 were published by [69Kul] and [88Bur].

Magnetism

(αFe)

The effect of dissolved O on the Curie point of (αFe) is unknown, but because of the very small O solubility, the displacement from 770 °C is probably not detectable.

Wustite

No magnetic changes occur in the stable range of wustite. The Néel point in metastable wustite at about −80 °C is discussed in the "Metastable Phases" section.

Fe_3O_4

The ferrimagnetic ↔ paramagnetic transition was observed at 576 [84Has] and 580.3 °C [87Hau1, 87Hau2]. Data on the effect of O concentration are unavailable, but the breadth of the composition range is very slight at 580 °C, which is the adopted value. Increasing pressure raises this transition temperature [69Sam, 79Leb, 82Gov] by about 20 °C/GPa.

αFe_2O_3

Pure, annealed, coarse-grained oxide at 0.1 MPa pressure and zero external magnetic field exhibits magnetic transitions at −10.5 ± 1.5 °C (first order) [63Mor, 64Ise, 65Fla1, 71Jac, 81Gie, 87Ami] and at 688 ± 7 °C (second order) [62Fre, 63Gil, 64Ise, 65Hil, 65Lie, 67Sch1, 75Gro, 75Hon, 87Nov]. Values of the lower transformation temperature are denoted by T_M, with M referring to Morin, who rediscovered this transition [50Mor, 71Jac]. Below T_M, αFe_2O_3 is antiferromagnetic, with the spins parallel (and antiparallel) to the hexagonal *c* axis; above T_M, the spins are in the hexagonal basal plane, but their slight deviations from perfectly balanced antiparallelism confer weak ("parasitic") ferromagnetism with the basic antiferromagnetism. Values of the higher transformation temperature are coincidentally Néel temperatures, Curie temperatures, and temperatures of the insulator-to-metallic conductor transition ($T_N = T_C = T_{MIT}$) [87Nov].

The Morin temperature, T_M, is shifted by variation in stoichiometry [74Gal], by impurities and lattice defects [75Pov, 82Mue], by hydrostatic pressure or other stress [66Kaw, 66Ume, 67Sea, 67Way, 67Wor, 68Kaw, 79Sat, 86Tam], by externally applied magnetic fields (with effects dependent on their magnitude and crystallographic orientation) [65Fla2, 67Cin, 71Jac, 79Hon, 82Mue, 86Pan], and by variation in particle size [67Sch2, 82Mue, 87Ami].

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*Indicates key paper.

#Indicates presence of a phase diagram.

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The Fe-Pb (Iron-Lead) System

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Equilibrium Diagram

A possible Fe-Pb compound ($FePb_2$) as suggested by [32Dan], but neither [46Now] nor [47Sch] found any evidence for such a phase. There is very limited mutual solubility in either the solid or liquid phases. Data on the solubility of Pb in liquid Fe (Fig. 1) were reported by [60Lor], [60Mil], [63Ara], and [71Mor]. Of these, the [60Mil] data appear to constitute the most internally consistent set. Data on the solubility of Fe in liquid Pb (Fig. 2) were reported by [60Mil], [61Ste], and [82Ali]. The data of [61Ste] are preferred, because they form an internally consistent set and because the equilibrium phase boundary was bracketed by collecting data with both heating and cooling runs.

Solubility of Pb in Liquid Fe

Data from [60Lor] are listed in Table 1 and plotted in Fig. 1 (open and closed squares). Each value represents an average of three to ten analyses. They used 99.9% pure Fe and Pb of unspecified purity. Two types of experiments were done: (1) "equilibration" of liquid Fe with Pb vapor (closed squares in Fig. 1); and (2) direct "liquid/liquid equilibration" (open squares in Fig. 1). In the liquid/vapor experiments (Table 1) about 9 g Fe were contained in a small alumina crucible placed in a larger alumina crucible that also contained about 20 g Pb. A 10 to 1 argon-to-hydrogen gas mixture was passed through the furnace at 1100 cm^3/min during the runs, which lasted 2 h (1 h heating plus 1 h annealing); [60Lor] claimed that separate kinetic studies indicated 1/2 h heating is sufficient to reach saturation. After annealing, the furnace was shut off and entire ingots were analyzed by the Sulfide-Molybdate

Table 1 Solubility of Pb in Liquid Fe

Reference	Temperature, °C	Solubility, at.% Pb	Comment
[60Lor]..........	1550	0.081(23)	Liquid Fe and liquid Pb
		0.059(13)	(a)
	1600	0.084(20)	Liquid Fe and liquid Pb
		0.068(20)	(a)
	1650	0.086(11)	Liquid Fe and liquid Pb
	1700	0.100(09)	Liquid Fe and liquid Pb
[60Mil]..........	1550	0.14 to 0.16	Liquid Fe and liquid Pb
[71Mor]..........	1550	0.081(03)	In contact with quartz
		0.082(02)	Under synthetic slag
	1600	0.122(19)	Under synthetic slag
	1650	0.162(11)	Under synthetic slag
	1700	0.244(15)	Under synthetic slag

Note: Numbers in parentheses are standard deviations for the last two digits.
(a) "Equilibration" of liquid Fe with Pb vapor; other [60Lor] values are for direct "liquid-liquid equilibration" experiments.