

Experimental Study of Equilibria in the Ta₂O₅-Fe-Fe₂O₃ System at 1200°C

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Phase equilibria in the system Ta₂O₅-Fe-Fe₂O₃ were established at 1200°C by changing the oxygen partial pressure from 0 to 16.60 in $-\log(P_{O_2}/\text{atm})$. In this system FeTaO₄, FeTa₂O₆, and Fe₄Ta₂O₉ are stable in addition to the well known two compounds in the Fe-Fe₂O₃ system. These compounds have nonstoichiometric compositions. In particular, FeTaO₄, FeTa₂O₆, and a spinel solid solution, which have an end member Fe₃O₄, have a considerable wide range of nonstoichiometry. Lattice constants of the compounds and the solid solutions which appeared in the system were also determined and discussed with respect to their dependence on the atmosphere in which the samples were made. By calculating the activities of each component in the above solid solutions, the standard Gibbs energies of reactions, (1) $\text{Fe} + \text{Ta}_2\text{O}_5 + \frac{1}{2}\text{O}_2 = \text{FeTa}_2\text{O}_6$, (2) $2\text{FeTa}_2\text{O}_6 + \frac{1}{2}\text{O}_2 = 2\text{FeTaO}_4 + \text{Ta}_2\text{O}_5$, (3) $\text{FeTa}_2\text{O}_6 + 3\text{Fe} + \frac{3}{2}\text{O}_2 = \text{Fe}_4\text{Ta}_2\text{O}_9$, and (4) $\text{Fe}_4\text{Ta}_2\text{O}_9 + \frac{1}{2}\text{O}_2 = \text{FeTa}_2\text{O}_6 + \text{Fe}_3\text{O}_4$, were calculated as -221.4, -6.8, -522.4, and -133.7 kJ, respectively. © 1986 Academic Press, Inc.

There are several previous publications on the double oxides involving the Ta oxides (1-3). These works principally treated natural tantalate minerals (1) and were performed from the viewpoint of the structure of compounds formed by solid reactions (2-4) and of the physical properties (5, 6). In these studies (2, 3), the double oxides, Fe-TaO₄ and FeTa₂O₆, were found to be stable.

Subsolidus phase relations of the oxides in the system Fe-Ta-O were experimentally determined at 1200°C under conditions of the variable oxygen partial pressure by Turnock (7). In that report the following ternary compounds were synthesized: Fe₄Ta₂O₉ and Fe₃Ta₂O_{8.1} in addition to FeTaO₄ and FeTa₂O₆, a solid solution between these two compounds, and tantalum magnetites. However, these results are in-

sufficient for a complete understanding of the phase equilibria. For example, since the quench method was adopted, the isothermal projection of the Fe-Ta-O system (Fig. 1 in (7)) would be uncertain and the oxygen partial pressure in equilibrium with three-solid phases would be in much error (Table II in (7)). Therefore, thermochemical data for the reactions found in the system were not calculated successfully. In view of the uncertainty in the system arising from the results in the literature, further investigation seemed desirable to understand the phase relations more completely.

Experimental

Guaranteed reagent grade Fe₂O₃ (99.9%) and Ta₂O₅ (99.9%), which were previously

dried, were used for starting materials. Ta₂O₅ is a very stable oxide with a melting point of $1877 \pm 5^\circ\text{C}$ and exists in two distinctly different crystalline forms with a quenchable phase transition at $\sim 1350^\circ\text{C}$ (8). It was confirmed on preliminary experiments that Ta₂O₅ was stoichiometric in the present experimental conditions.

Desired ratios of Ta₂O₅/Fe₂O₃ were obtained by mixing thoroughly in an agate mortar under ethyl alcohol. The mixtures thus obtained were treated by the same procedures as in the previous paper (9). The apparatus and procedures for controlling the oxygen partial pressure and keeping a constant temperature, the method of the thermogravimetry, and the criterion for establishing equilibrium were the same as those described in the previous papers (9-11).

Results and Discussions

Phase Equilibria

The Fe-Fe₂O₃ system, which is the partial system of the present one, was reinvestigated to confirm the calibration of the apparatus used. The results obtained were in good agreement with those of Darken and Gurry (12, 13).

Ten samples with Ta₂O₅/Fe₂O₃ mole ratios of 8/2, 7/3, 5/3, 1, 4/6, 3/7, 2/8, 15/85, 1/9, and 5/95 were prepared to be used in the thermogravimetry.

In Fig. 1 the relationships between the oxygen partial pressure, $-\log(P_{\text{O}_2}/\text{atm})$, on the ordinate and the weight change, $W_{\text{O}_2}/W_{\text{T}}$, on the abscissa are shown with four representative samples, 7/3 (a), 4/6 (b), 2/8 (c), and 1/9 (d). Here, W_{O_2} is the weight decrease of the samples from the reference weight in 1 atm O₂, and W_{T} is the total weight decrease of the sample which might be expected if all the Fe₂O₃ in the sample changes to Fe-metal in H₂ atmosphere, for each sample. The $W_{\text{O}_2}/W_{\text{T}}$ ratio in the present experiment usually had values in

the range from 0.998 to 1.000 in the atmosphere of H₂. Therefore, the procedures might be reasonable in the present experiment. From Fig. 1 and referring to previous data (12, 13), the oxygen partial pressures in equilibrium with three-condensed phases or two-condensed phases are found as 2.94, 3.80, 6.70, 9.14, 9.72, 11.94, 12.00, 12.35, and 15.60 in $-\log P_{\text{O}_2}$.

The identification of the phases was done with quenched samples using a powder X-ray diffractometer with FeK α radiation. The following phases occur under the present experimental conditions: Ta₂O₅(B), FeTaO₄(R), FeTa₂O₆(T), Fe₄Ta₂O₉(S), Fe₃O₄(M), Fe₂O₃(H), "FeO"(W), and Fe. The results of the phase identification are shown in Table I in the form of the two-phase combinations except for a few samples.

Based upon the above experimental results of the thermogravimetry and the identification of phases, a phase diagram can be drawn and is shown in Fig. 2. The present diagram is more simple than that of Turnock (7) which can be seen in Fig. 3. This figure was redrafted from the original one by the author in the same form as that of Fig. 2 to facilitate comparison of both diagrams.

Figure 2 is considerably different from that of Turnock: (1) The phase N, Fe₃Ta₂O_{8.1}, is not stable and (2) the tantalian magnetite solid solution is stable but the width of its homogeneity range is not as wide as he had presented. It must be more narrow, considering the other present results, for example, the composition of M₆, Table II, and the constancy of the $W_{\text{O}_2}/W_{\text{T}}$ of the sample 1/9 in the oxygen partial pressure range from 8.75 to 9.70 in $-\log P_{\text{O}_2}$, Fig. 1d.

From (1) above, no three-condensed phase area exists which contains phase N.

The three-solid phase area, $S_p + \text{FeTa}_2\text{O}_6 + \text{FeTaO}_4$, corresponding to the No. 3 area of Turnock, was difficult to find be-

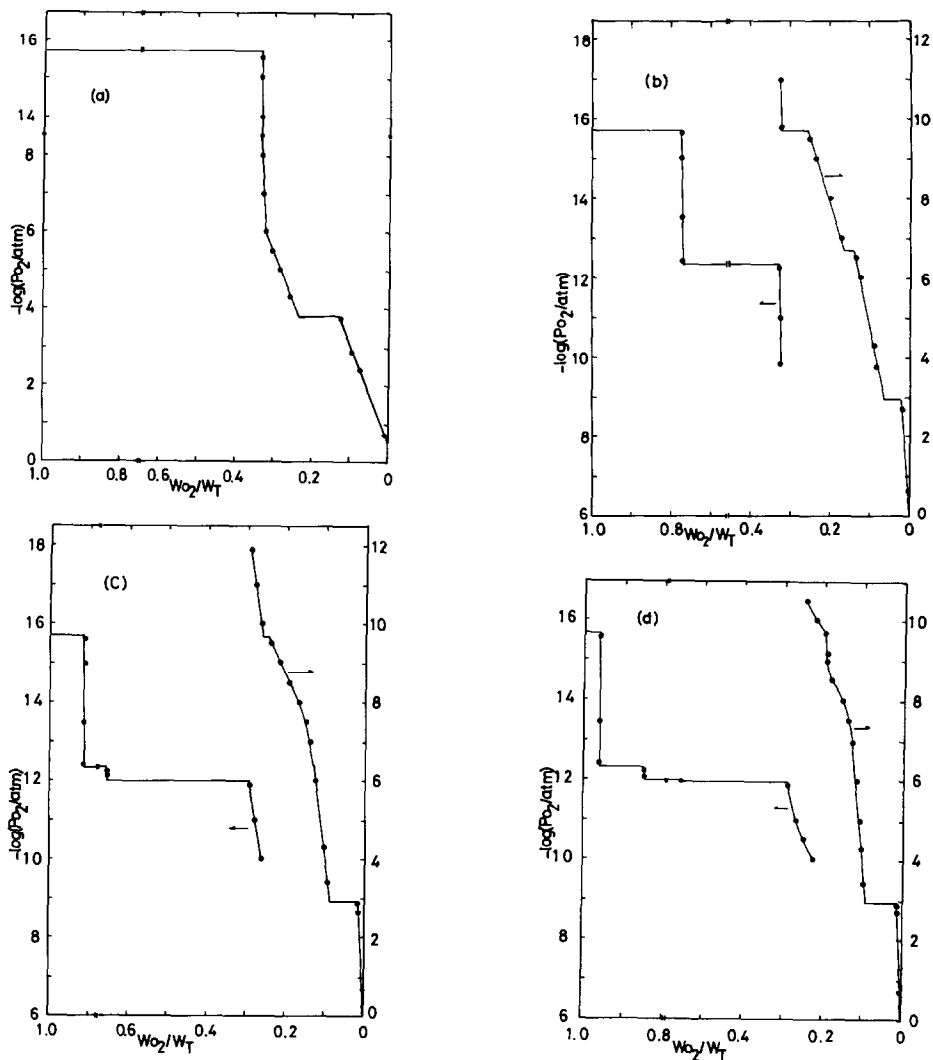


FIG. 1. The relationship between the oxygen partial pressure, $-\log(P_{O_2}/\text{atm})$, and the weight change of the samples, W_{O_2}/W_T . (a) $Ta_2O_5/Fe_2O_3 = 7/3$, (b) $Ta_2O_5/Fe_2O_3 = 4/6$, (c) $Ta_2O_5/Fe_2O_3 = 2/8$, (d) $Ta_2O_5/Fe_2O_3 = 1/9$.

cause of the sluggish reaction in the range of high P_{O_2} and in the short range of the abrupt weight change. The existence of the area was confirmed by the results shown in Fig. 1b and by the identification of the phases. It can be seen by a small gap in the weight change between 7.00 and 6.50 in $-\log P_{O_2}$ in Fig. 1b although the gap is not clear in Figs. 1c and d. Also the change in

the two-phase combinations can be found from $FeTa_2O_6 + Sp$ at $-\log P_{O_2} = 7.00$ to $FeTaO_4 + Sp$ at $-\log P_{O_2} = 6.50$ in the samples 1/9 and 2/8.

It is very difficult to determine the two-phase line, from Fe to M_6 , on account of the small difference in the adjacent equilibrium oxygen partial pressure, 12.00 and 11.94 in $-\log P_{O_2}$.

TABLE I
 THE IDENTIFICATION OF PHASES

Ta ₂ O ₅ /Fe ₂ O ₃ (mole ratio)	-log P _{O₂} (atm)	Time (hr)	Phase
8/2	16.60	8	Fe + Ta ₂ O ₅ ^a
	13.50	7	Ta ₂ O ₅ + FeTa ₂ O ₆
	5.00	46	Ta ₂ O ₅ + FeTa ₂ O ₆
1	3.60	39	Ta ₂ O ₅ + FeTaO ₄
	16.60	8	Fe + Ta ₂ O ₅
	13.50	7	Fe + FeTa ₂ O ₆
	12.20	7	FeTa ₂ O ₆ + Fe ₄ Ta ₂ O ₉
	10.00	16	FeTa ₂ O ₆ + Fe ₄ Ta ₂ O ₉
3/7	9.50	16	Sp + FeTa ₂ O ₆
	11.90	14	Sp + Fe ₄ Ta ₂ O ₉
	10.00	22	Sp + Fe ₄ Ta ₂ O ₉
	9.00	22	Sp + FeTa ₂ O ₆
	6.50	19	Sp + FeTaO ₄
	5.00	46	Sp + FeTaO ₄
	2.40	41	Fe ₂ O ₃ + FeTaO ₄
2/8	13.50	7	Fe + FeTa ₂ O ₆
	12.20	7	Fe + Fe ₄ Ta ₂ O ₉
	11.90	14	Sp + Fe ₄ Ta ₂ O ₉
	10.50	13	Sp + Fe ₄ Ta ₂ O ₉
	9.00	14	Sp + FeTa ₂ O ₆
	7.00	17	Sp + FeTa ₂ O ₆
	6.50	19	Sp + FeTaO ₄
1/9	11.97 ^b	6	Sp + Fe + (FeO) ^c
	9.00	22	Sp
	7.00	17	Sp + FeTa ₂ O ₆
	6.50	19	Sp + FeTaO ₄
5/95	11.97 ^b	6	Sp + Fe + (FeO) ^c
	11.90	14	Sp + FeO
	9.20	31	Sp
	9.00	22	Sp
	8.00	24	Sp + FeTa ₂ O ₆

^a Low-temperature form (β).

^b The mixture of Fe + Fe₄Ta₂O₉ was used as the starting material.

^c Trace "FeO" was found sometimes.

The end and intermediate compositions of the solid solutions were graphically determined after finishing the thermogravimetric experiments. The compositions of the end members of the solid solutions, *T*₄ and *R*₃, are in considerable doubt because of the reasons described above. These results are shown in Table II together with the symbol, the activity, and the oxygen partial pressure in which these compounds are stable.

Turnock (7) had shown three two-phase areas resulting from a six-angled spinel solid solution area, but these two-phase areas could not be found in the present diagram.

Lattice constants of the compounds are tabulated in Table III. These values are not affected by the coexisting compounds, which are shown in the fourth column, judging from values of FeTa₂O₆ at log *P*_{O₂} = -12.20, of FeTaO₄ at log *P*_{O₂} = 0, of Fe₄Ta₂O₉ at log *P*_{O₂} = -11.90, and of *Sp* at log *P*_{O₂} = -11.90. This fact might suggest that nonstoichiometry of the respective compounds toward the coexisting compounds does not exist or is very small. However, these lattice constants depend upon the atmosphere in which the compounds were prepared. This is very reasonable because the oxygen partial pressure changes the composition in this case. The lattice constants decrease with the increase of the oxygen partial pressure, for example, in the case of FeTa₂O₆ and the spinel solid solution, and increase with the increase of the oxygen partial pressure, for example, in the case of FeTaO₄. The variation of the lattice constant of the spinel solid solution with the oxygen partial pressure in equilibrium is shown in Table III and is illustrated in Fig.

 TABLE II
 COMPOSITIONS OF COMPOUNDS, SYMBOLS,
 ACTIVITIES AND RELATED OXYGEN
 PARTIAL PRESSURES

Component (<i>i</i>)	Composition	Symbol	-log P _{O₂} (atm)	log <i>a_i</i>
FeTa ₂ O ₆	FeTa ₂ O _{6,00}	<i>T</i>	15.70-8.00	0
	FeTa ₂ O _{6,00} ^a	<i>T</i> ₁	12.35	~0
	FeTa ₂ O _{6,00} ^a	<i>T</i> ₂	9.72	~0
	FeTa _{1,69} O _{5,37}	<i>T</i> ₃	3.80	0.83
	FeTa _{1,61} O _{5,20}	<i>T</i> ₄	6.70	1.26
FeTaO ₄	FeTaO _{4,00}	<i>R</i>	0-0.50	—
	FeTa _{1,08} O _{4,17}	<i>R</i> ₁	2.94	—
	FeTa _{1,41} O _{4,82}	<i>R</i> ₂	3.80	0
	FeTa _{1,47} O _{4,95}	<i>R</i> ₃	6.70	-0.29
Fe ₄ Ta ₂ O ₉	Fe ₄ Ta ₂ O _{9,00}	<i>S</i>	12.35	0
	Fe ₄ Ta ₂ O _{9,08}	<i>S</i> ₁	9.72	-0.052
Fe ₃ O ₄	Fe ₃ O _{4,04}	<i>M</i> ₁	2.94	-0.062
	Fe ₃ O _{4,01}	<i>M</i> ₂	6.70	-0.010
	Fe ₃ O _{4,00}	<i>M</i>	9.14	0
	Fe _{2,88} Ta _{0,15} O _{4,00}	<i>M</i> ₃	9.14	0
	Fe _{2,64} Ta _{0,39} O _{4,00}	<i>M</i> ₄	9.72	-0.17
	Fe _{2,54} Ta _{0,51} O _{4,00}	<i>M</i> ₅	11.94	-0.93
Fe _{2,54} Ta _{0,51} O _{4,00} ^a	<i>M</i> ₆	12.00	-1.09	

^a The composition does not change with the oxygen partial pressure.

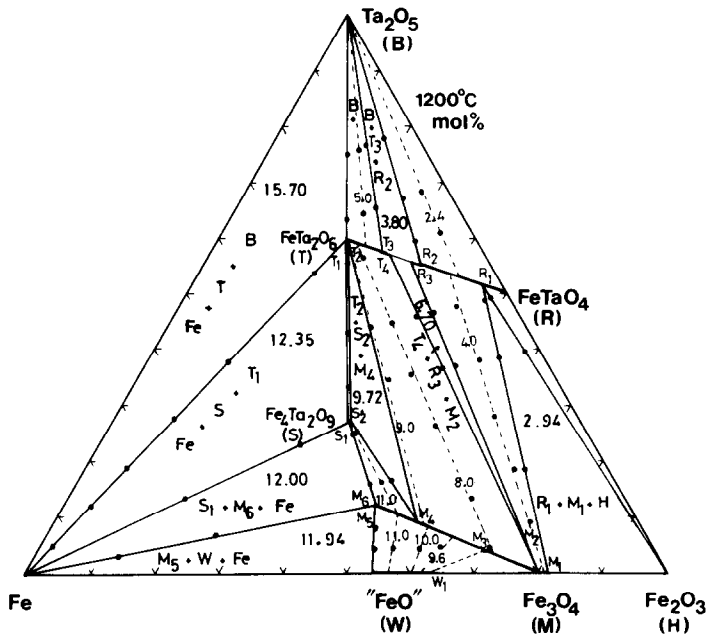


FIG. 2. Phase equilibria in the Ta_2O_5 -Fe- Fe_2O_3 system at $1200^\circ C$. Numerical values in the three-solid phase regions are the oxygen partial pressures in $-\log(P_{O_2}/atm)$ in equilibrium. Symbols are the same as those in Table II. The dotted lines in the two-solid phase areas are the iso-oxygen partial pressure lines shown by numerical values on the lines.

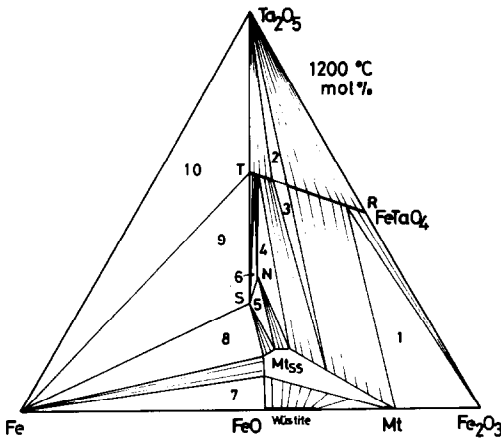


FIG. 3. Phase equilibria in the Ta_2O_5 -Fe- Fe_2O_3 system at $1200^\circ C$ by Turnock. The diagram was redrafted in the same form as that of Fig. 2. Numbers in the three-solid phase areas and symbols of compounds correspond to those in the original diagram.

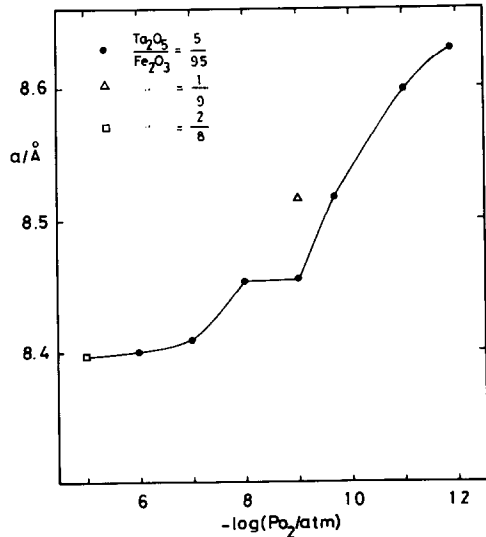


FIG. 4. The relationship between the lattice constant of the spinel solid solution and the oxygen partial pressure.

TABLE III
 LATTICE CONSTANTS OF COMPOUNDS

Compound	Ta ₂ O ₅ /Fe ₂ O ₃ (mole ratio)	-log P _{O₂} (atm)	Other phase	a (Å)	c (Å)	V (Å ³)	Ref.
FeTa ₂ O ₆	2/1	12.20	—	4.775 ± 0.001	9.199 ± 0.004	208.0 ± 0.1	Present
	7/3	12.20	Ta ₂ O ₅	4.756 ± 0.001	9.199 ± 0.003	208.1 ± 0.1	Present
	5/3	12.20	Fe ₄ Ta ₂ O ₉	4.756 ± 0.001	9.203 ± 0.003	208.1 ± 0.1	Present
	8/2	5.00	Ta ₂ O ₅	4.744 ± 0.001	9.192 ± 0.002	206.9 ± 0.1	Present
				4.7451 ± 0.0004	9.179 ± 0.001		(5)
			4.750	9.205		(2)	
FeTaO ₄	3/7	6.00	Sp	4.716 ± 0.001	3.063 ± 0.001	68.10 ± 0.02	Present
	3/7	5.00	Sp	4.697 ± 0.001	3.055 ± 0.001	67.41 ± 0.02	Present
	8/2	3.70	Ta ₂ O ₅	4.717 ± 0.001	3.062 ± 0.001	68.13 ± 0.01	Present
	8/2	2.40	Ta ₂ O ₅	4.703 ± 0.002	3.044 ± 0.005	67.3 ± 0.1	Present
	9/11	0	Fe ₂ O ₃	4.679 ± 0.001	3.048 ± 0.001	66.73 ± 0.03	Present
	1	0	—	4.684 ± 0.001	3.046 ± 0.002	66.83 ± 0.05	Present
				4.708	3.075		(2)
			4.678 ± 0.002	3.048 ± 0.004		(7)	
Fe ₄ Ta ₂ O ₉	1/2	11.90	—	5.230 ± 0.001	14.226 ± 0.002	336.9 ± 0.1	Present
	3/7	11.90	Sp	5.230 ± 0.002	14.220 ± 0.005	336.8 ± 0.2	Present
	4/6	11.90	FeTa ₂ O ₆	5.228 ± 0.002	14.239 ± 0.006	337.1 ± 0.3	Present
				5.224	14.202		(7)
Spinel	5/95	11.90	FeO	8.629 ± 0.002		642.4 ± 0.4	Present
	2/8	11.90	Fe ₄ Ta ₂ O ₉	8.633 ± 0.002		643.5 ± 0.2	Present
	5/95	11.00	FeO	8.599 ± 0.002		635.5 ± 0.4	Present
	5/95	9.70	FeO	8.515 ± 0.001		617.3 ± 0.2	Present
	1/9	9.00	FeTa ₂ O ₆	8.518 ± 0.001		618.0 ± 0.1	Present
	5/95	9.00	—	8.456 ± 0.001		604.4 ± 0.1	Present
	5/95	8.00	FeTa ₂ O ₆	8.453 ± 0.001		604.1 ± 0.1	Present
	5/95	7.00	FeTa ₂ O ₆	8.409 ± 0.001		594.6 ± 0.2	Present
	3/7	6.00	FeTaO ₄	8.400 ± 0.001		592.7 ± 0.2	Present
	2/8	5.00	FeTaO ₄	8.396 ± 0.002		591.9 ± 0.3	Present
				8.3963			(16)

4. An increase of the lattice constant with a decrease in the oxygen partial pressure was found, which corresponds to an increase in the content of Ta₂O₅.

The Standard Gibbs Energy of Reactions

On the basis of the established phase diagram, the standard Gibbs energies of the reactions which appear in the phase diagram can be calculated by the equation, $\Delta G^\circ = -RT \ln K$, where the R is the gas constant, the T the absolute temperature, and K the equilibrium constant of a reaction. Reactions and ΔG° values calculated are shown in Table IV together with the

oxygen partial pressures in equilibrium. The activities of each component in the solid solutions, which are necessary in the calculations of ΔG° , are tabulated in the last column in Table II. The standard state was

 TABLE IV
 THE STANDARD GIBBS ENERGY OF REACTIONS

Reaction	-log P _{O₂} (atm)	-ΔG° (kJ)
(1) Fe + Ta ₂ O ₅ + ½O ₂ = FeTa ₂ O ₆	15.70 ± 0.04	221.4
(2) 2FeTa ₂ O ₆ + ½O ₂ = 2FeTaO ₄ + Ta ₂ O ₅	3.80 ± 0.05	6.8
(3) FeTa ₂ O ₆ + 3Fe + ½O ₂ = Fe ₄ Ta ₂ O ₉	12.35 ± 0.03	522.4
(4) Fe ₄ Ta ₂ O ₉ + ½O ₂ = FeTa ₂ O ₆ + Fe ₃ O ₄	9.72 ± 0.04	133.7

arbitrarily chosen in each solid solution, as shown in Table II. Some of the details of the calculation were reported in Kimizuka and Katsura (14). The rest will be briefly described in the Appendix.

Appendix

A phase diagram being established, activities of all components of the compounds and solid solutions have to be the same if two or three phases are stable in equilibrium. For the case of solid solutions with compositions that change with the equilibrium oxygen partial pressure, the calculation was made using the Gibbs-Duhem equation by Kimizuka and Katsura (14) and many applications were reported for the system Ln_2O_3 - V_2O_3 - V_2O_5 by Kitayama *et al.* (17).

The method of the calculation of the activity of the Fe_3O_4 component in the spinel solid solution will be shown as an example. Activities of iron in the wüstite solid solution were previously calculated by Darken and Gurry (12) on the basis of the Fe-O system with the Gibbs-Duhem equation. According to their results, the activity of iron at the composition (W_1), $a_{Fe}(W_1)$, is $10^{-1.545}$, and is in equilibrium with iron in $Fe_3O_4(M)$ at $\log P_{O_2} = -9.14$. Here, the activity of iron at the composition (W) in equilibrium with pure solid Fe at $\log P_{O_2} = -11.94$ is set at unity. The same standard was adopted in this case.

Let us consider a reaction, $3Fe + 2O_2 = Fe_3O_4$. Fe_3O_4 is not in equilibrium with pure solid Fe at $\log P_{O_2} = -9.14$, but is in equilibrium with the Fe component at the composition (W_1). The equilibrium constant $K = a_{Fe}^3(W_1) \times P_{O_2}^2 / a_{Fe_3O_4}(M) = (10^{-1.545})^3 (10^{-9.14})^2$ setting $a_{Fe_3O_4}(M)$ as unity. The same reaction is found for the end member of the spinel solid solution M_6 at $\log P_{O_2} = -12.00$. As the same reaction occurs, the constant K has to be the same in this case

providing that the activity of iron is unity; that is $K = a_{Fe}^3 \times P_{O_2}^2 / a_{Fe_3O_4}(M_6)$. Therefore, $a_{Fe_3O_4}(M_6) = 10^{-1.09}$.

$a_{Fe_3O_4}(M_4)$ was also determined using $\log P_{O_2} = -9.72$ and $a_{Fe} = 10^{-1.22}$, which is the activity of iron in the wüstite solid solution at the same P_{O_2} and is calculated from Darken and Gurry (12).

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