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Thermodynamics of Formation of Some Compounds with the Pseudobrookite Structure and of the $FeTi_2O_5$–Ti_3O_5 Solid Solution Series

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Abstract

The enthalpy of formation of pseudobrookite, Fe_2TiO_5, from Fe_2O_3 and TiO_2 is found by oxide melt solution calorimetry to be +1.99 ± 0.15 kcal mol^{-1} (+8.33 ± 0.63 KJ mol^{-1}). Thermochemical data for other compounds with the pseudobrookite structure are summarized. Pseudobrookites are "entropy-stabilized" high temperature phases with partially disordered cation distributions. Their decomposition at low temperatures to assemblages of binary oxides (for $A_2{}^{3+}B^{4+}O_5$ pseudobrookites) or to assemblages of phases of ilmenite and rutile structure (for $A^{2+}\ B_2{}^{4+}O_5$ pseudobrookites) reflects the balance between endothermic enthalpies of formation from these assemblages and the substantial positive entropies of formation arising from the substitutional disorder. A simple cation distribution model is applied to the distribution of iron between 4*c* (*A*) and 8*f* (*B*) sites in the $FeTi_2O_5$–Ti_3O_5 system, from which high Ti_3O_5 is predicted to have the cation distribution $(Ti^{4+}{}_{0.05}Ti^{3+}{}_{0.95})_A(Ti^{4+}{}_{0.95}Ti^{3+}{}_{1.05})_BO_5$. Interchange enthalpies (or free energies) for the reactions: $Mg^{2+}{}_A + Ti^{4+}{}_B = Mg^{2+}{}_B + Ti^{4+}{}_A$, $Fe^{2+}{}_A + Ti^{4+}{}_B = Fe^{2+}{}_B + Ti^{4+}{}_A$, and $Ti^{3+}{}_A + Ti^{4+}{}_B = Ti^{3+}{}_B + Ti^{4+}{}_A$ are +8.6, +13, and +10 kcal mol^{-1} respectively (36.0, 54, and 42 KJ mol^{-1}, respectively). $MgTi_2O_5$ exhibits somewhat disordered pseudobrookite structures derived from a "normal" structure stable at low temperature, while Ti_3O_5 and probably also Fe_2TiO_5, Al_2TiO_5, and Ga_2TiO_5 have somewhat disordered structures derived from an "inverse structure stable at low temperature. Thus Ti^{4+} appears to have a strong preference for the 8*f* (*B*) sites in all these compounds of pseudobrookite structure.

Introduction

Study of lunar basalts has resulted in considerable interest in minerals with the pseudobrookite structure. These include Fe_2TiO_5 (pseudobrookite), $FeTi_2O_5$ (ferropseudobrookite), $MgTi_2O_5$ (karrooite), $(Mg,Fe)Ti_2O_5$ (armalcolite), and solid solutions in the Fe_2TiO_5–Ti_3O_5 series. The purpose of this paper is threefold: (a) to present new high temperature solution calorimetric data for the enthalpy of formation of Fe_2TiO_5, (b) to review the existing thermochemical data for ternary oxides with the pseudobrookite structure, and (c) to correlate the thermodynamic and structural data and to apply a simple thermodynamic model to the cation distributions in $MgTi_2O_5$, $FeTi_2O_5$, and the $FeTi_2O_5$–Ti_3O_5 solid solution series.

The Pseudobrookite Structure

Early structure determinations were by Pauling (1930) and Hamelin (1958). Recently, Lind and Housley (1972) have performed structure refinements on synthetic single crystals of karrooite, $MgTi_2O_5$, and armalcolite, $Mg_{0.5}Fe_{0.5}Ti_2O_5$. In the orthorhombic pseudobrookite structure, space group *Bbmm*, with 4 AB_2O_5 formula units in the unit cell, all the cations are in octahedral coordination. There are two kinds of octahedral sites, with fourfold (4*c* or *A* sites) and eightfold (8*f* or *B* sites) multiplicity. Three octahedra share edges to form units which are then linked together into double chains as building blocks for the structure. In monoclinic pseudobrookites such as Ti_3O_5 and the titanium-rich members of the Ti_3O_5–$FeTi_2O_5$ solid solution series (Grey and Ward (1973), the 8*f* (*B*) site is further split into two non-equivalent sites. For armalcolite, Lind and Housley (1972) give the following metal oxygen distances for the 4*c* and 8*f* octahedra—8*f*, 2.061, 1.845, 1.993, 2.172, 1.938, and 1.938 Å; 4*c*, 1.960, 2.191, 1.960, 2.191, 2.030, and 2.030 Å. Thus, both octahedra are distorted. The average bond length in 8*f* is 1.992 ± 0.114 (s.d.) Å; that in 4*c* is 2.072 ± 0.096 Å. Thus the *A* site is somewhat larger and slightly less distorted than the *B* site. For the present paper, the most important feature of the pseudobrookite structure is that the two sites are sufficiently similar to allow considerable substitutional disorder of the cations occupying them. As in the spinels, we can recognize two limiting distributions, the normal, $(A)_{4c}(B_2)_{8f}O_5$ and

TABLE 1. Enthalpy of Solution of Pseudobrookite in $3Na_2O \cdot 4MoO_3$ at 692°C

Fe_2TiO_5 (in mg)	cal/obs	ΔH_{sol} (kcal mol^{-1})
46.07	-0.050	-0.26
86.06	-0.020	-0.06
114.46	±0.000	±0.00
43.60	-0.015	-0.08
49.25	-0.019	-0.09
		AV = -0.10±0.10

the inverse, $(B)_{4c}(AB)_{8f}O_5$, and we can anticipate that, especially at high temperature, intermediate distributions will be the rule rather than the exception.

Calorimetric Determination of the Enthalpy of Formation of Pseudobrookite at 692 ± 2°C

Fe_2TiO_5 was prepared by ignition of a stoichiometric mixture of dried Baker Analyzed Reagent Fe_2O_3 (hematite) and TiO_2 (rutile) for a total of 72 hours in a platinum crucible in air at 1350°C, with four intermediate grindings of the sample. At the end of each firing, the sample was cooled relatively rapidly in air. The powder X-ray diffraction pattern of the product showed it to be single phase pseudobrookite.

The high temperature Calvet-type twin microcalorimeter and the sample assembly for measuring the heat of solution of a solid oxide sample in a molten oxide solvent have been described previously (Navrotsky and Kleppa, 1968). Navrotsky and Kleppa (1967a, 1968) have shown that a sodium molybdate melt of the composition $3Na_2O$–$4MoO_3$ is a suitable solvent for the calorimetric study of anatase, rutile, Ti^{4+}-containing spinels, Fe_2O_3, and $ZnFe_2O_4$. A similar calorimeter and essentially identical conditions were used in the present work. In each solution experiment, 50–100 mg of solute was dissolved in 10–15 g of solvent at 692 ± 2°C. Two experiments each on α-Fe_2O_3 and TiO_2 (rutile) fell within experimental error of the values of the heat of solution of these oxides reported previously by Navrotsky and Kleppa (1968). Accordingly, those values, +2.38 kcal mol^{-1} and −0.49 ± 0.05 kcal mol^{-1} were used in the present work for the enthalpies of solution of rutile and hematite, respectively.[1] No difficulty was encountered in the solution of Fe_2TiO_5, although its molar enthalpy of solution was fortuitously very close to zero, so that the heat effects actually measured were always less than 0.1 calorie in magnitude. The results of five solution experiments (Table 1) give a mean of −0.10 ± 0.10 kcal mol^{-1}. One may then calculate, for the reaction:

$$Fe_2O_3 \text{ (hematite)} + TiO_2 \text{ (rutile)} = Fe_2TiO_5 \text{ (pseudobrookite)} \qquad (1)$$

$$\Delta H^\circ_{965} = +1.99 \pm 0.15 \text{ kcal mol}^{-1}$$

Discussion of the Stability of Fe_2TiO_5 and other Compounds with the Pseudobrookite Structure

Fe_2TiO_5

The calorimetric data show the enthalpy of formation of pseudobrookite from hematite plus rutile to be *positive.* This suggests that the ternary oxide is stabilized at high temperatures by a positive entropy of formation and should become unstable relative to the binary oxides at low temepratures. Such decomposition has indeed been found by Haggerty and Lindsley (1970), with an equilibrium temperature of 565 ± 15°C. We can calculate the entropy of the formation reaction since at 838 K its free energy change is zero.

$$\Delta S^\circ = \frac{+1990}{838} = +2.4 \text{ cal K}^{-1} \text{ mol}^{-1} \qquad (2)$$

The free energy of formation of Fe_2TiO_5 from Fe_2O_3 and TiO_2 is then given by the equation:

$$\Delta G^\circ = +1990 - 2.4\,T\,(T \text{ in K}) \qquad (3)$$

This equation gives ΔG° with an estimated error of ± 300 cal in the range 700–1200 K, since the difference in heat capacity between reactants and products should be small at high temperatures and one can neglect any changes in cation distribution with temperature. To our knowledge, no enthalpy or free energy of formation data have been reported for Fe_2TiO_5. Heat content and standard entropy values are tabulated by Robie and Waldbaum (1968) and by Kelley (1960). From these tabulations, the entropy of formation of pseudobrookite from hematite and rutile is given in Table 2. The agreement with our value at 858 K is excellent but, we believe, may be fortuitous. The heat capacity and heat content data are to be questioned on two counts. First, the calculated entropy of formation of pseudobrookite varies rather strongly with temperature, which is somewhat surprising. If this is a real effect, it may be related to the anomalously small thermal expansion coefficients reported for pseudobrookite-type com-

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[1] Throughout this paper, heat effects are given in calories, where 1 cal = 4.184 joule.

pounds (Bayer, 1971), or to changes in the cation distribution (see below). The data for $MgTi_2O_5$ (Table 2) show no such anomaly, though the values of $\Delta S°$ scatter somewhat. In addition, the tabulated values do not include any contribution for the configurational entropy arising from an "inverse" or partially disordered cation distribution of Fe^{3+} and Ti^{4+} over nonequivalent octahedral sites. Waldbaum (1973) has discussed this point. If the cation distribution in Fe_2TiO_5 is indeed inverse as Lind and Housley (1972) suggest, then, as Waldbaum (1973) recommends, one should add $2R\ln 2 = 2.76$ cal K^{-1} mol^{-1} to the standard entropy of pseudobrookite. This would make the entropy of formation of Fe_2TiO_5 calculated from the corrected heat capacity data more positive by about 3 cal K^{-1} mol^{-1} than the entropy we calculate at the decomposition temperature, 838 K. Assuming our calorimetric data to be correct, this discrepancy may have several causes. Fe_2TiO_5 may indeed have the normal cation distribution, since the X-ray data are not totally convincing and one does not really know the site preference of Fe^{3+} compared to Ti^{4+}. With an inverse distribution at high temperatures, the Fe^{3+} and Ti^{4+} ions may possibly order on their sublattice at lower temperatures, producing local order or even a superstructure. If this ordering occurs gradually over a range of temperature, it might not be detected as such in the heat capacity measurements, but the solid would not have much zero point entropy. The kinetics of such an ordering process probably cannot be estimated on the basis of current knowledge. Lastly, a systematic error is possible in the third law entropy of Fe_2TiO_5 (or even of Fe_2O_3 or TiO_2). The heat capacity of Fe_2TiO_5 was measured only down to 50 K (Todd and King, 1953), and the extrapolation to 0 K may produce greater uncertainty than previously thought (Waldbaum, 1974, personal communication). In addition, problems associated with the magnetic entropy of oxides containing transition metal ions with partially filled *d* shells may cause this discrepancy.

Regardless of the details of the third law entropy of Fe_2TiO_5, this work has clearly established a positive enthalpy of formation for pseudobrookite from the oxides, which is compensated by a positive entropy of formation, resulting in the stability of Fe_2TiO_5 at high temperature only.

TABLE 2. Lattice Entropies (Calorimetric Entropies) of Formation of Fe_2TiO_5 and $MgTi_2O_5$ from the Oxides

	TiO_2 [a]	MgO [a]	Fe_2O_3 [a]	Fe_2TiO_5 [a]		$MgTi_2O_5$ [b]	
T_oK	S^o_T [c]	S^o_T	S^o_T	S^o_T	ΔS^o_T	S^o_T	ΔS^o_T
298	12.04	6.44	20.89	37.40	+4.47	30.40	−0.12
800	27.85	16.98	51.64	81.75	+2.26	71.65	−1.03
1200	34.98	21.93	66.69	102.45	+0.78	91.33	−0.56
1600	40.24	25.53	76.52	117.60	+0.84	106.71	−0.70

a. Source of data, R. A. Robie and D. R. Waldbaum, U.S. Geol. Survey Bull. 1259 (1968).
b. Data for $MgTi_2O_5$ from S. S. Todd, J. Amer. Chem. Soc. 74, 4669 (1952) and R. L. Orr and J. P. Coughlin, J. Amer. Chem. Soc. 74, 3186 (1952).
c. cal K^{-1} mol^{-1}

$M^{3+}{}_2TiO_5$

The known thermodynamic data for some other compounds with the pseudobrookite structure are summarized in Table 3. Two other $M^{3+}{}_2TiO_5$ pseudobrookites, Ga_2TiO_5 and Al_2TiO_5, are even less stable than Fe_2TiO_5; their decompositions, observed by differential thermal analysis, occur at higher temperature with markedly exothermic effects. It is hard to envision that lattice effects alone could produce enough entropy to stabilize these energetically unfavorable phases, so these data argue for configurational disorder in those pseudobrookites as well. Quantitative calorimetric study of these compounds is planned.

$M^{2+}Ti_2O_5$

The $M^{2+}Ti_2O_5$ compounds present an analogous picture; thermodynamic data are summarized in Table 3. $CoTi_2O_5$, $FeTi_2O_5$, and $MgTi_2O_5$ are stable only at high temperature, the assemblage rutile plus $MTiO_3$ being stable at low temperature. The compounds $NiTi_2O_5$ and $MnTi_2O_5$ are apparently never stable with respect to $MTiO_3$ and TiO_2, but estimates of their free energies of formation have been obtained from the thermodynamics of extensive solid solutions in some ternary AO-BO-TiO_2 systems (Evans and Muan, 1971a, b). The instability of $NiTi_2O_5$ probably stems from the loss of ligand field stabilization of Ni^{2+} in the distorted octahedral sites of the pseudobrookite structure; a similar factor is probably partly responsible for the instability of $NiSiO_3$ and $NiGeO_3$ pyroxenes (Navrotsky, 1971b). The instability of $MnTi_2O_5$ suggests that Mn^{2+} may be somewhat too large for sites in the pseudobrookite structure.

The existence of $CoTi_2O_5$, $FeTi_2O_5$, and $MgTi_2O_5$ as high temperature phases only is consistent with positive entropies of formation from the oxides, coupled with enthalpies of formation close to those of the corresponding ilmenite analogs. Since both $FeTi_2O_5$ and $MgTi_2O_5$ have somewhat disordered cation distributions (Lind and Housley, 1972; also, see below), and since the equilibrium degree of disorder

TABLE 3. Thermodynamics of Formation of Compounds with Pseudobrookite Structure from the Component Oxides

	ΔG_f^o (at K) kcal mol^{-1}	ΔH_f^o (at K) kcal mol^{-1}	ΔS_f^o (at K) cal K^{-1} mol^{-1}	Decomposition
Fe_2TiO_5	0 (838 ± 15)[a]	+1.99 ± 0.15 (965)[b] very small[l]	+ 2.4[c]	$Fe_2O_3 + TiO_2$ below 838 K[a]
$FeTi_2O_5$	-4.3 ± 0.1 (1573)[d]			$FeTiO_3 + TiO_2$ below 1413 ± 10 K[a]
high Ti_3O_5	-18.0 ± 1.5 (1304)[e]			low Ti_3O_5,∿500 K[f]
$MgTi_2O_5$	-6.8 ± 1.0 (1573)[g] -7.3 ± 1.0 (1673)[j]	[-4.45 (298)][h]	[+ 1.5][i]	$MgTiO_3 + TiO_2$ below ∿823 K
$CoTi_2O_5$	-3.9 (1473)[m]			$CoTiO_3 + TiO_2$ below 1413° ± 5 K[m]
Al_2TiO_5		endothermic[l]		α-$Al_2O_3 + TiO_2$ at 1273 K[l]
Ga_2TiO_5		endothermic[l]		β-$Ga_2O_3 + TiO_2$ at 1273 K[l]
($NiTi_2O_5$)	-2.0 ± 0.4 (1673)[j]			unstable relative to $NiTiO_3 + TiO_2$ at all T[j]
($MnTi_2O_5$)	-6.3 ± 0.8 (1523)[k]			unstable relative to $MnTiO_3 + TiO_2$ at all T[k]

a. S. Haggerty and D. Lindsley, Carnegie Inst. Yearbook 68, 247 (1970). S. Kesson and D. H. Lindsley, personal communication.
b. This work.
c. Calculated from a. and b., $\Delta S_f^o = +1990/838$.
d. R. E. Johnson, E. Woermann, and A. Muan, Amer. Jour. Sci. 271, 278 (1971).
e. Calculated from data of R. R. Merritt and B. G. Hyde, Phil. Trans. Roy. Soc. London A274, 627 (1973) for reaction $TiO_2 + Ti_2O_3 = Ti_3O_5$.
f. G. Asbrink and A. Magneli, Acta Chem. Scand. 21, 1977 (1967).
g. B. Brezny and A. Muan, Thermochim. Acta 2, 107 (1971).
h. K. K. Kelley, S. S. Todd, and E. G. King, U.S. Bur. Mines Rept. Inv. 5059 (1954). Hydrofluoric acid calorimetry.
i. Estimated from g. and h., $\Delta S_f^o = [-4450-(-6800)]/1573$, see text for discussion.
j. L. G. Evans and A. Muan, Thermochim. Acta 2, 121 (1971).
k. L. G. Evans and A. Muan, Thermochim. Acta 2, 277 (1971).
l. G. Bayer, J. Less Common Metals 24, 129 (1971), decomposition temperatures do not represent reversals.
m. B. Brezny and A. Muan, J. inorg. nucl. Chem. 31, 649 (1969).

is expected to increase with increasing temperature, it seems clear that these materials are "entropy stabilized" in the same sense as are copper spinels (Navrotsky and Kleppa, 1968).

In their early calorimetric work on titanates, Kelley, Todd, and King (1954) found that the formation of $MgTi_2O_5$ from TiO_2 and $MgTiO_3$ is endothermic by 1.0 kcal at 298 K. They noted that structural disorder in this material, then of unknown structure, could cause its stabilization at high temperature.

We have several independent means for estimating the entropy change, $\Delta S°$, associated with the decomposition:

$$M\mathrm{Ti_2O_5}\ \text{(pseudobrookite structure)} \rightarrow M\mathrm{TiO_3}\ \text{(ilmenite structure)} + \mathrm{TiO_2}\ \text{(rutile)} \qquad (4)$$

The preliminary data of Kesson and Lindsley (1974, unpublished) for the decomposition of karrooite to geikelite and rutile gave a pressure-temperature slope, $\partial P/\partial T$ of about 23.4 bar/deg. Since ΔV for this transition is −5.39 cc/mol at atmospheric conditions (volume data from Robie and Waldbaum, 1968, and Lind and Housley, 1972), we can estimate from the Clausius-Clapeyron equation that $\Delta S° = 23.4 \times -5.39 \times 0.0242 = -3.0$ cal K^{-1}. Evans and Muan (1971a) have determined the standard free energies of formation from the oxides of $MgTi_2O_5$ and $MgTiO_3$ to be −7.3 ± 0.8 and −5.1 ± 0.5 kcal mol^{-1} at 1400°C, respectively. Thus for decomposition Reaction (4), $\Delta G° = 0$ at 550°C and +2.2 kcal at 1400°C. Since $(\partial \Delta G°/\partial T)_P = -\Delta S°$, we can calculate $\Delta S° = 2200/850 = -2.6$ cal K^{-1}. Lastly, the calorimetric data of Kelley, Todd, and King (1954) give an enthalpy for Reaction (4) at 823 K of $-5.85 + 4.55 = -1.30$ kcal. Then the entropy change is $-1300/823 = -1.6$ cal K^{-1}. This last calculation does not take into account any configurational entropy.

Similar calculations are possible for $CoTi_2O_5$. The decomposition temperature at one atmosphere occurs near 1135°C, and Brezny and Muan (1969) give values of free energies of formation such that for Reaction (4), $\Delta G° = -0.1$ kcal at 1100°C and +0.8 kcal at 1300°C. This gives $\Delta S° = -900/200 = -4.5$ cal K^{-1}.

Johnson, Woermann, and Muan (1971) give the free energies of formation from the oxides for $FeTiO_3$ and for Fe_2TiO_5 as −4.3 ± 1.0 kcal mol^{-1} at 1300°C. Since decomposition to ilmenite plus rutile occurs below 1140°C in this system (Haggerty and Lindsley, 1970), a value close to zero for Reaction (4) at 1300°C is reasonable. However, the data do not permit an estimate of the entropy change for this reaction.

The calculated values of $\Delta S°$ range from −1.6 to −4.5 cal K^{-1} for decomposition Reaction (4) for different metals. In view of the large uncertainties arising both from uncertainties in the equilibrium measurements and calorimetric data and from the assumptions in the calculations, this scatter is not at all surprising. Rather, the data are quite consistent and point to a probable value of $\Delta S°$ of −3 ± 1 cal K^{-1}. This value looks very reasonable in light of the probable configurational disorder in the pseudobrookite structure, although it is not altogether too large in magnitude to be caused by lattice vibrational effects alone.

Cation Distributions in AB_2O_5 Compounds and in the $FeTi_2O_5$–Ti_3O_5 Solid Solution Series

Fe_2TiO_5, Al_2TiO_5, Ga_2TiO_5

Re-evaluation of the crystallographic data favors an inverse cation distribution for Fe_2TiO_5 (Lind and Housley, 1972). The *positive* enthalpies of formation of these compounds and their instability at low temperature is consistent with substitutional disorder. Very probably these materials have intermediate cation distributions, which would be temperature dependent. The configuration of greatest entropy, the random distribution $(M_{2/3}Ti_{1/3})_{4c}(M_{4/3}Ti_{2/3})_{8f}O_5$, may be approached at high temperature. This point has been discussed in detail for spinels (Navrotsky and Kleppa, 1967b; Waldbaum, 1973), and analogous arguments hold for the pseudobrookite structure. Al_2TiO_5 may be a better candidate for crystallographic study than Fe_2TiO_5 because of the larger difference between the two cations in scattering factors for X-rays.

$MgTi_2O_5$, $CoTi_2O_5$, and $FeTi_2O_5$

X-ray diffraction study of $MgTi_2O_5$ quenched from 1500°C (Lind and Housley, 1972) has given a cation distribution $(Mg_{0.684}Ti_{0.316})_{4c}(Mg_{0.316}Ti_{1.684})_{8f}O_5$. In terms of the simple disordering model applied to spinels by Navrotsky and Kleppa (1967b), this corresponds to a degree of disorder, x, of 0.316 ($x = 0$ for a normal, 2/3 for a random, and 1 for an inverse cation distribution). The interchange enthalpy for the reaction

$$(\mathrm{Mg})_{4c} + (\mathrm{Ti})_{8f} = (\mathrm{Mg})_{8f} + (\mathrm{Ti})_{4c} \tag{5}$$

is then given by

$$-\frac{\Delta H_{\mathrm{int}}}{RT} = \ln \frac{x^2}{(1-x)(2-x)} \tag{6}$$

with $\Delta H_{\mathrm{int}} = +8.6$ kcal mol^{-1}. This value has previously been calculated by Waldbaum (1973).[2]

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[2] The model used by Navrotsky and Kleppa (1967b) for cation distributions in spinels and that discussed by Waldbaum (1973) for nonconvergent disordering in melilites, pseudobrookites, and spinels, are essentially equivalent if one assumes the "lattice entropies" of Navrotsky and Kleppa (= the "calorimetric entropies" of Waldbaum) to be independent of the degree of order. Waldbaum's order parameter, Z, is equal to $1-x$, where x is our degree of disorder. His calculation of the difference in enthalpy between normal and inverse (ordered and antiordered) distributions for $MgTi_2O_5$ from the site population of a sample quenched from 1500°C is entirely equivalent conceptually to our calculation of interchange enthalpies for some thirteen spinels from their cation distributions, each known for one temperature.

For $FeTi_2O_5$ quenched from 1400°C, Grey and Ward (1973) give a distribution, determined by Mössbauer spectroscopy, $(Fe_{0.720}Ti_{0.280})_{4c}(Fe_{0.280}Ti_{1.72})_{8f}O_5$. If $FeTi_2O_5$ has all iron present as Fe^{2+} and all titanium as Ti^{4+}, which seems reasonable, then $\Delta H_{int} = 9.2$ kcal mol^{-1}, calculated from Equation (5). However, Grey and Ward suggest that the true percent of total iron in $4c$ sites may be greater than their estimate because of difficulties in fitting the Mössbauer spectra. This would make ΔH_{int} more positive for $FeTi_2O_5$. This point is discussed further below.

Solid Solutions in the $Fe_{1-x}Ti_{2+x}O_5$ Series

The distribution of iron between $A(4c)$ and $B(8f)$ sites has been studied by Grey and Ward (1973) using Mössbauer spectroscopy. Their data can be subjected to thermodynamic analysis using the simple model applied by Navrotsky and Kleppa (1967b) to spinels and by Navrotsky (1971a) to (Mg,Fe)SiO$_3$ pyroxene solid solutions.

Consider the solid solution series $FeTi_2O_5$–Ti_3O_5. If one assumes that all iron is present as Fe^{2+}, and that the reduced titanium is present as Ti^{3+} only, then the solid solution series may be written as $Fe^{2+}{}_{1-x}Ti^{3+}{}_{2x}Ti^{4+}{}_{2-x}O_5$, where the mole fraction of Ti_3O_5 is given by x. Calling the $4c$ sites A and the $8f$ sites B, we have, nominally, six site population parameters: $Fe^{2+}{}_A$, $Ti^{3+}{}_A$, $Ti^{4+}{}_A$, $Fe^{2+}{}_B$, $Ti^{3+}{}_B$, $Ti^{4+}{}_B$, where each symbol stands for the number of moles of the given ion on the appropriate site. For the distribution of the three cations, Fe^{2+}, Ti^{4+}, and Ti^{3+} over the two sites, A and B, we can write two independent exchange reactions which lead to two independent equilibrium constants. For the first exchange reactions,

$$Fe^{2+}{}_A + Ti^{4+}{}_B = Fe^{2+}{}_B + Ti^{4+}{}_A, \tag{7}$$

with

$$K_1 = \frac{X_{Fe^{2+}{}_B} X_{Ti^{4+}{}_A}}{X_{Fe^{2+}{}_A} X_{Ti^{4+}{}_B}} \tag{8}$$

where each X is the mole fraction of a given ion on the specified site, and, in the simple model, approximates the activity. For the second exchange reaction,

$$Ti^{3+}{}_A + Ti^{4+}{}_B = Ti^{3+}{}_B + Ti^{4+}{}_A, \tag{9}$$

with

$$K_2 = \frac{X_{Ti^{3+}{}_B} X_{Ti^{4+}{}_A}}{X_{Ti^{3+}{}_A} X_{Ti^{4+}{}_B}} \tag{10}$$

However, the bulk composition, charge balance, and site balance require that

$$Fe^{2+}{}_A + Fe^{2+}{}_B = 1 - x \tag{11}$$

$$Ti^{3+}{}_A + Ti^{3+}{}_B = 2x \tag{12}$$

$$Ti^{4+}{}_A + Ti^{4+}{}_B = 2 - x \tag{13}$$

and

$$Fe^{2+}{}_A + Ti^{3+}{}_A + Ti^{4+}{}_A + 1 \tag{14}$$

$$Fe^{2+}{}_B + Ti^{3+}{}_B + Ti^{4+}{}_B = 2 \tag{15}$$

Thus, for a given composition, x, there are only two independent site population parameters,[3] which we may pick as

$$Fe^{2+}{}_A = X_{Fe^{2+}{}_A} \quad \text{and} \quad Ti^{3+}{}_A = X_{Ti^{3+}{}_A}$$

and we may re-write our equilibrium constants as

$$K_1 = \frac{(1 - x - Fe^{2+}{}_A)(1 - Fe^{2+}{}_A - Ti^{3+}{}_A)}{Fe^{2+}{}_A(1 - x + Fe^{2+}{}_A + Ti^{3+}{}_A)} \tag{16}$$

and

$$K_2 = \frac{(2x - Ti^{3+}{}_A)(1 - Fe^{2+}{}_A - Ti^{3+}{}_A)}{Ti^{3+}{}_A(1 - x + Fe^{2+}{}_A + Ti^{3+}{}_A)} \tag{17}$$

The Mössbauer data of Grey and Ward (1973) give $Fe^{2+}{}_A$ as a function of composition, x, for $FeTi_2O_5$–Ti_3O_5 solid solution samples quenched from 1400°C. For pure $FeTi_2O_5$, $Fe^{2+}{}_A = 0.72$ from the Mössbauer data and $Fe^{2+}{}_A = 0.75$ from a neutron diffraction study. This gives, from Equation (16) with $(Ti^{3+}{}_A) = 0$, and $x = 0$, $K_1 = 0.06$ and $K_1 = 0.05$, respectively. Knowing K_1, x, and $Fe^{2+}{}_A$, Equations (16) and (17) can be treated as simultaneous equations in two unknowns, $Ti^{3+}{}_A$ and K_2, and solved at each value of x for a value of $Ti^{3+}{}_A$ (which will vary with x) and of K_2 (which will remain constant if the model holds and the data are accurate). Because Grey and Ward experienced some difficulty in fitting their Mössbauer data at compositions near $FeTi_2O_5$, they suggest that their value of $Fe^{2+}{}_A$ for pure $FeTi_2O_5$ may be somewhat underestimated (leading to an overestimate of K_1). (From their data a graph of the percentage of the total iron on the $4c$ sites *vs* composition shows a maximum; but a plot of the fraction of the $4c$ sites occupied by Fe *vs* composition does not; see Fig. 1.) Thus, some uncertainty exists in the value chosen for K_1; consequently, we have calculated the values of Ti^{3+} and of K_2 for values of K_1 from 0.06 to 0.01. The results of some of these calculations are shown in Table 4. Whereas the calculated values of

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[3] Of the 5 equations 11–15, only 4 are independent.

K_2 show some scatter, they do not appear to vary systematically with composition, x. We may then take the average calculated value of K_2, and use it with the assumed value of K_1 to then calculate back values of $Fe^{2+}{}_A$ (and $Ti^{3+}{}_A$) as functions of composition, x. Using Equations (16) and (17), curves of $Fe^{2+}{}_A$ *vs* x for several values of K_1 (and K_2) are given in Figure 1, together with the experimental data points. In addition, the limits corresponding to a completely ordered distribution of iron corresponding to "normal" $FeTi_2O_5$ and of a random distribution, with one third of the iron on the 4*c* site, are shown. We can conclude the following. On the iron-poor side ($x > \sim 0.5$), the calculated distribution of iron is rather insensitive to the actual values chosen for K_1. To discriminate among values of K_1 which vary by a factor of six (from 0.01 to 0.06), one must look at the points with $x < 0.5$. For these data, and allowing that the point at $x = 0$ should lie somewhat higher than 0.72, one sees that curves for K_1 from 0.04 to 0.01 approximate the data. We do not believe that a statistical fit to the data would add much information, and would say rather that the experimental data are consistent with a value of K_1 of 0.025 ($\pm \sim 0.02$) and $K_2 = 0.055$ (± 0.04). Using these values and Equations (16) and (17), one can calculate $FeTi_2O_5$ to have the distribution $(Fe^{2+}{}_{0.81}Ti^{4+}{}_{0.19})_A(Fe^{2+}{}_{0.19}Ti^{4+}{}_{1.81})_BO_5$ and Ti_3O_5 to have the distribution $(Ti^{4+}{}_{0.05}Ti^{3+}{}_{0.95})_A(Ti^{4+}{}_{0.95}Ti^{3+}{}_{1.05})_BO_5$ at 1400°C. That is, the iron distribution data are quite well explained with the assumptions that $FeTi_2O_5$ has a slightly disordered normal pseudobrookite structure and Ti_3O_5 has a slightly disordered inverse pseudobrookite structure. For Ti_3O_5, the predicted presence of Ti^{3+} and Ti^{4+} on one sublattice raises problems analogous to those in magnetite; that is, are

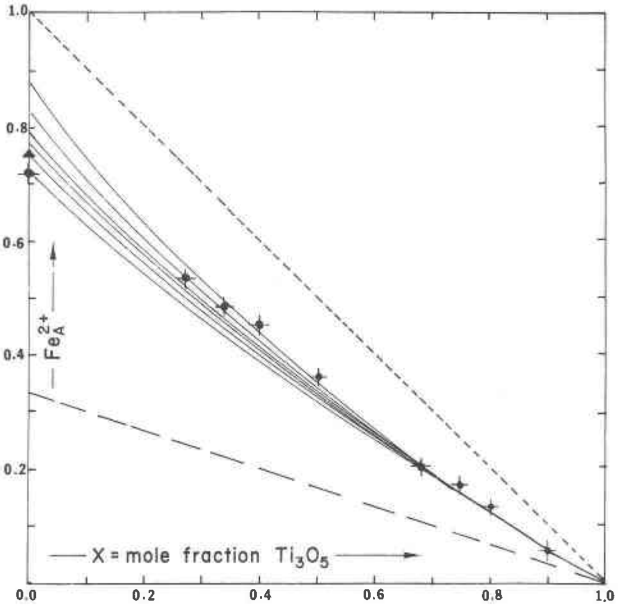

FIG. 1. Variation of fraction of 4*c* sites occupied by iron ($Fe^{2+}{}_A$) with mol fraction Ti_3O_5, x. Curves, in order of increasing $Fe^{2+}{}_A$ are for: (1) random distribution, $K_1 = 1$; (2) $K_1 = 0.060$, $K_2 = 0.187$; (3) $K_1 = 0.050$, $K_2 = 0.135$; (4) $K_1 = 0.040$, $K_2 = 0.093$; (5) $K_1 = 0.030$, $K_2 = 0.061$; (6) $K_1 = 0.020$, $K_2 = 0.035$; (7) $K_1 = 0.010$, $K_2 = 0.015$; (8) completely ordered distribution (no Fe^{2+} on 8*f* sites), $K_1 = 0$. Filled circles are cation distributions determined from Mössbauer spectra; triangle is cation distribution determined by neutron diffraction.

TABLE 4. Calculated Values of Equilibrium Constant for Exchange Reactions in $FeTi_2O_5$-Ti_3O_5 Solid Solutions

		$K_1 = 0.06$		$K_1 = 0.04$		$K_1 = 0.02$	
x	$(Fe^{2+}_A)_{exp}$	$(Ti^{3+}_A)_{calc}$	K_2	$(Ti^{3+}_A)_{calc}$	K_2	$(Ti^{3+}_A)_{calc}$	K_2
0.27	0.534	0.223	0.232	0.296	0.089	0.377	0.024
0.34	0.488	0.271	0.258	0.343	0.112	0.423	0.035
0.40	0.453	0.297	0.313	0.371	0.142	0.454	0.047
0.50	0.361	0.437	0.201	0.498	0.105	0.565	0.040
0.68	0.201	0.678	0.102	0.715	0.061	0.756	0.027
0.75	0.170	0.689	0.150	0.732	0.089	0.779	0.039
0.80	0.132	0.743	0.134	0.782	0.081	0.823	0.036
0.90	0.061	0.845	0.106	0.874	0.066	0.906	0.031
			K_2av = 0.187 ± 0.077		K_2 av = 0.093 ± 0.026		K_2 av = 0.035 ± 0.007

the Ti^{3+} and Ti^{4+} ions distinguishable, and can Ti_3O_5 have anomalously high electrical conductivity due to the hopping of electrons over sites in the $8f$ sublattice?

With $K_1 = 0.025$ and $K_2 = 0.055$, we calculate, for the exchange Reactions (1) and (2), $\Delta G_1 = +13.0$ (±5) kcal and $\Delta G_2 = +10.2$ (±5) kcal. In the simple model of Navrotsky and Kleppa (1967b) these values are just the interchange enthalpies for the above reactions.

The model used has assumed (a) that the molar interchange enthalpy is independent of composition and of degree of disorder, and (b) that the entropy of forming the solid solution is simply the change in configurational entropy, calculated from the cation distribution.[4] In particular, this neglects effects of the change from orthorhombic to monoclinic symmetry with increasing Ti_3O_5 content in the solid solution series. Since this structural change causes changes in the metal-oxygen bond lengths and angles (Grey and Ward, 1973), its neglect in the thermodynamic model is clearly an oversimplification. However, the present data do not seem to warrant equations using a larger number of parameters, and the model used appears adequate as a first approximation.

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[4] This model is again essentially identical to that used by Waldbaum (1973) for the melilite solid solution series, when the assumption that the $\Delta S = 0$ is used. Waldbaum wrote his equations for the free energy of a phase relative to the elements or the oxides; we write ours for the free energy of mixing between end members.