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ACTIVITY-COMPOSITION RELATIONS OF SOLID SOLUTIONS AND STABILITIES OF END-MEMBER COMPOUNDS IN THE SYSTEM MgO–NiO–TiO_2 IN CONTACT WITH METALLIC NICKEL AT 1400°C*

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ABSTRACT

Equilibria between metallic nickel, a gas phase of known oxygen pressures, and pairs of solid-solution phases in the system MgO–NiO–TiO_2 are used to derive activity–composition relations for the solid solutions Mg_2TiO_4–Ni_2TiO_4 (spinel), $MgTiO_3$–$NiTiO_3$ (geikielite) and $MgTi_2O_5$–$NiTi_2O_5$ (pseudobrookite), and free energies of formation of the end-member compounds at 1400°C.

The activity–composition curves for the spinel and pseudobrookite solutions are practically linear, whereas the curves for the geikielite solid solution display a slight positive deviation from linearity at 1400°C. The only stable compound in the system NiO–TiO_2 at 1400°C is $NiTiO_3$, whereas the spinel phase, Ni_2TiO_4, and the pseudobrookite phase, $NiTi_2O_5$, are unstable relative to the phase assemblages $NiTiO_3$+NiO and $NiTiO_3$+TiO_2, respectively. The free energies of formation of the various end-member compounds from their oxide components were determined as follows:

$$2NiO+TiO_2 \rightarrow Ni_2TiO_4 \quad \Delta G^0 = -1.8 \pm 1.8 \text{ kcal}$$
$$NiO+TiO_2 \rightarrow NiTiO_3 \quad \Delta G^0 = -2.3 \pm 0.4 \text{ kcal}$$
$$NiO+2TiO_2 \rightarrow NiTi_2O_5 \quad \Delta G^0 = -2.0 \pm 0.4 \text{ kcal}$$
$$2MgO+TiO_2 \rightarrow Mg_2TiO_4 \quad \Delta G^0 = -5.8 \text{ kcal}$$
$$MgO+TiO_2 \rightarrow MgTiO_3 \quad \Delta G^0 = -5.1 \text{ kcal}$$
$$MgO+2TiO_2 \rightarrow MgTi_2O_5 \quad \Delta G^0 = -7.3 \text{ kcal}$$

INTRODUCTION

Relatively simple high-temperature equilibration techniques can be used to derive high-temperature thermodynamic data which are considerably more reliable and accurate than those derived by extrapolation of experimental data obtained at room temperature. Such equilibration methods have been used rather extensively in

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studies of oxide and silicate phases during recent years, and much insight has now been gained into the behavior of such systems at elevated temperatures. The present study extends such investigations to related substances, *viz.* the titanates of medium-sized divalent cations. The system MgO–NiO–TiO_2 was chosen as a model for such a study. Magnesium oxide is known to react with TiO_2 to form three stable phases of common titanate structures[1], *viz.* Mg_2TiO_4 (spinel structure), $MgTiO_3$ (geikielite, ilmenite structure), and $MgTi_2O_5$ (pseudobrookite structure) (see Fig. 1). Nickel oxide, on the other hand, is known to react with TiO_2 to form only one stable compound[2], $NiTiO_3$ (ilmenite structure), whereas the two hypothetical compounds Ni_2TiO_4 (spinel structure) and $NiTi_2O_5$ (pseudobrookite structure) are unknown and hence are assumed to be unstable. However, in view of the similarity in size of the two cations Mg^{2+} and Ni^{2+}, it is reasonable to expect that each of the solid-solution series starting at the MgO–TiO_2 side of the ternary system MgO–NiO–TiO_2 will extend for a considerable distance toward the analogous, hypothetical Ni compounds along the NiO–TiO_2 join of the system. By studying the activity–composition relations of these solid-solution series, one may not only gain knowledge of the thermodynamic behavior of important types of high-temperature solid-solution phases, one may also, by suitable extrapolations to the end members, be able to calculate free energies of formations of the phases (Ni_2TiO_4 and $NiTi_2O_5$) which have not been synthesized in their pure form. The present work was directed toward these two objectives.

The theoretical basis for evaluating activity–composition relations of solid solutions and free energies of formation of compounds from equilibria between a metal phase and selected pairs of solid-solution phases has been presented elsewhere[3–5]. The formulas applicable to the various phase assemblages of the present system can be derived by substituting the appropriate subscripts in the equations presented in these previous publications.

EXPERIMENTAL METHODS

The experimental methods used are similar to those described previously[4,6,7]. Directions of conjugation lines between coexisting solid-solution phases were determined by measuring the CO_2/CO ratios of a gas phase at which metallic nickel started to precipitate from the solid solutions, using two series of mixtures within the area of coexistence of the two solid solutions, one series having compositions close to one of the solid solutions, the other series having compositions close to the other solid solution. Specific details applicable to the present work are as follows.

The temperature of the investigation was chosen as 1400 °C. This is high enough to attain equilibrium within a reasonable period of time and low enough to avoid formation of a liquid phase.

"Fisher certified" analytical-grade reagents were used in preparing all mixtures. Mixtures of desired compositions were heated in air at 1400 °C for a minimum of 24 h, with an intermediate grinding. Following this pre-reaction, discs about onehalf inch diameter and one-eighth inch thick were made of each mixture, by using compacting pressures of about 10,000 psi. These discs were sintered at 1400°C for approximately 2 h. The discs were then broken into several small pieces suitable for wrapping in thin platinum wire and for suspension in a tube furnace for the final, equilibrium nickel precipitation runs.

Precautions were taken to check that equilibrium was attained. The samples were equilibrated for different lengths of time, and the progress of the reaction was followed. It was found that reaction was complete in 12 to 24 h. A few mixtures in which initially a small amount of metallic nickel had been precipitated were equilibrated in a CO_2/CO atmosphere slightly more oxidizing than that established by the precipitation runs, and the metal phase was found to disappear.

The temperature of the PtRh quench furnace was kept constant with commercial electronic controllers. Temperatures were measured with a Pt-90%Pt10%Rh thermocouple which was checked frequently against a reference Pt-90%Pt10%Rh thermocouple which was calibrated against the melting points of gold (1063°C) and diopside (1391.5°C). The accuracy of the temperature measurements is estimated to be ± 5°C.

The desired CO_2/CO ratios of the gas phase were obtained by use of differential flow meters as described previously[8].

RESULTS

General relations

Phase relations in the 1400°C isothermal section of the system $MgO-NiO-TiO_2$ are illustrated in Fig. 1. The geikielite solid solution is seen to be complete between the end members $MgTiO_3$ and $NiTiO_3$, whereas the spinel solid solution and the pseudobrookite solid solutions are incomplete, the former extending from Mg_2TiO_4 to about 42 mol% Ni_2TiO_4 along the $Mg_2TiO_4-Ni_2TiO_4$ join, and the latter extending from $MgTi_2O_5$ to about 82 mol% $NiTi_2O_5$ along the $MgTi_2O_5-NiTi_2O_5$ join.

Phase assemblages rutile+pseudobrookite, rutile+pseudobrookite+geikielite, rutile +geikielite

Results of equilibration runs for these phase assemblages (areas I, II and III of Fig. 1) are listed in Table I and shown graphically in Fig. 2. It is seen that the CO_2/CO ratios(and hence the NiO activities) are proportional to the mol fraction of $NiTi_2O_5$ over the whole concentration range of stability of the pseudobrookite solid solution, and hence the solution is ideal, within the estimated limits of error. Extrapolation of the straight line to the $NiTi_2O_5$ end member gives an a_{NiO}-value of 0.55 for the hypothetical phase assemblage $NiTi_2O_5+TiO_2$, and the free energy of formation of the hypothetical Ni-pseudobrookite end member from its oxide components according to the equations

$$NiO+2TiO_2 \rightarrow NiTi_2O_5 \qquad (1)$$

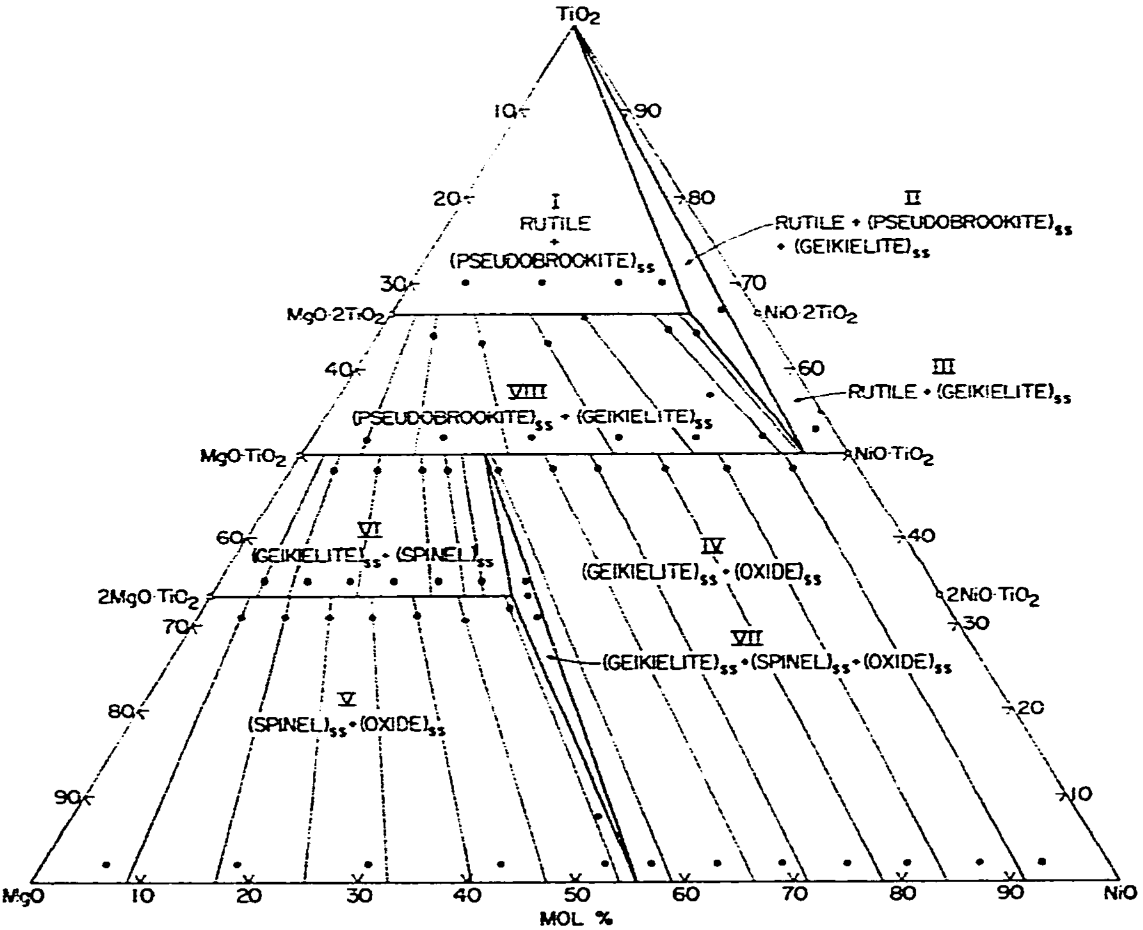

Fig. 1. Isothermal section of the system $MgO–NiO–TiO_2$ in contact with metallic nickel at 1400 °C. Solid circles respresent composition of the mixtures studied, and light solid lines are conjugation lines between coexisting solid-solution phases. The abbreviation ss denotes solid solution.

TABLE I

RESULTS OF EQUILIBRATION RUNS INVOLVING METALLIC NICKEL AND PHASE ASSEMBLAGES I (RUTILE + PSEUDOBROOKITE), II (RUTILE + PSEUDOBROOKITE + GEIKIELITE) AND III (RUTILE + GEIKIELITE) IN THE SYSTEM $MgO–NiO–TiO_2$ AT 1400 °C

Phase assemblage	*Composition (mol fraction)*			$\frac{N_{NiO}}{N_{NiO}+N_{MgO}}$	$r(CO_2/CO)$	a_{NiO}
	MgO	*NiO*	*TiO_2*			
I	0.250	0.050	0.700	0.167	2.4 ±0.4	0.09 ±0.01
	0.179	0.120	0.701	0.402	6.3 ±0.3	0.22 ±0.01
	0.109	0.190	0.701	0.635	10.2 ±0.3	0.35 ±0.01
	0.071	0.230	0.699	0.764	11.8 ±0.3	0.42 ±0.01
II	0.021	0.299	0.670	0.906	12.8 ±0.3	0.45 ±0.01
	0.016	0.455	0.529	0.967	13.9 ±0.4	0.49 ±0.01
III		[a]0.450	0.550	1.000	14.0 ±0.2	0.50 ±0.01

[a] This mixture is on the binary join $NiO–TiO_2$.

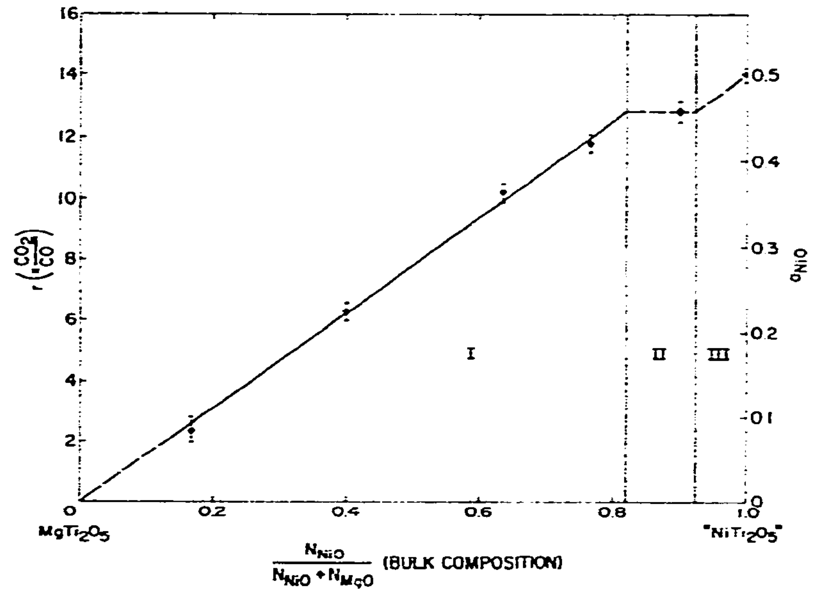

Fig. 2. Plot of CO_2/CO ratios and a_{NiO} *vs.* $N_{NiO}/(N_{NiO}+N_{MgO})$ for coexistence of metallic nickel and phase assemblages I (rutile + pseudobrookite), II (rutile + pseudobrookite + geikielite), III (rutile + geikielite) in the system MgO–NiO–TiO_2 at 1400 °C. The dashed vertical lines indicate compositions of the solid-solution phases in the three-phase triangle rutile + pseudobrookite + geikielite compare diagram in Fig. 1).

and

$$\Delta G^0 = 2.303\,RT\log_{10} a_{NiO} \tag{2}$$

is -2.0 ± 0.2 kcal.

From the CO_2/CO ratio determined for the last mixture in Table I, the free energy of formation of $NiTiO_3$ from the oxide components at 1400 °C is -2.3 ± 0.2 kcal, according to the equations

$$NiO + TiO_2 \rightarrow NiTiO_3 \tag{3}$$

and

$$\Delta G^0 = 2.303\,RT\log_{10} a_{NiO} \tag{4}$$

This is in good agreement with the value (-2.1 ± 0.1 kcal) obtained by an extrapolation of the data of Taylor and Schmalzried[9] from 1100 °C to 1400 °C.

Combination of the free-energy values for $NiTiO_3$ and $NiTi_2O_5$ gives for the reaction

$$NiTi_2O_5 \rightarrow NiTiO_3 + TiO_2 \tag{5}$$

a ΔG^0-value of -0.3 ± 0.4 kcal at 1400 °C. Hence, $NiTi_2O_5$ is unstable with respect to the phase assemblage $NiTiO_3$ plus TiO_2, in agreement with the phase relations shown in Fig. 1.

The activities of $NiTiO_3$ and $MgTiO_3$ in the geikielite solid solution will be calculated from results obtained for the phase assemblage pseudobrookite + geikielite (area VIII in Fig. 1), as described in a later section.

Phase assemblage geikielite + oxide solid solution

Equilibrium data for this phase assemblage (area IV of Fig. 1) are summarized in Table II. One set of mixtures (TiO_2 mol fraction 0.48) is located close to the spinel join, the other set of mixtures (TiO_2 mol fraction 0.02) is located close to the oxide join. These data, together with those obtained from a study of the equilibrium between metallic nickel and the phase assemblage spinel + oxide solid solution (see a later section), are shown graphically in Fig. 3 and in the form of conjugation lines in Fig. 1.

TABLE II

RESULTS OF EQUILIBRATION RUNS INVOLVING METALLIC NICKEL AND PHASE ASSEMBLAGE IV (GEIKIELITE + OXIDE SOLID SOLUTIONS) IN THE SYSTEM $MgO–NiO–TiO_2$ AT 1400 °C

Composition (mol fraction)			$\frac{N_{NiO}}{N_{NiO}+N_{MgO}}$	$r(CO_2/CO)$	a_{NiO}
MgO	*NiO*	*TiO_2*			
0.330	0.190	0.480	0.365	15.4 ±0.5	0.55 ±0.02
0.279	0.240	0.481	0.462	17.9 ±0.4	0.63 ±0.01
0.239	0.280	0.481	0.539	19.2 ±0.3	0.68 ±0.01
0.176	0.342	0.482	0.660	21.4 ±0.4	0.76 ±0.01
0.120	0.399	0.481	0.768	23.3 ±0.4	0.83 ±0.01
0.060	0.459	0.481	0.884	25.3 ±0.5	0.90 ±0.02
0.420	0.559	0.021	0.572	15.2 ±0.3	0.54 ±0.01
0.360	0.620	0.020	0.633	17.3 ±0.4	0.61 ±0.01
0.300	0.680	0.020	0.694	18.9 ±0.4	0.67 ±0.01
0.240	0.740	0.020	0.755	20.9 ±0.4	0.74 ±0.01
0.186	0.794	0.020	0.810	21.8 ±0.6	0.77 ±0.02
0.119	0.861	0.020	0.878	24.3 ±0.4	0.86 ±0.01
0.061	0.919	0.020	0.938	26.3 ±0.5	0.93 ±0.02

Extrapolation of the conjugation lines in phase assemblage IV (and in phase assemblage V, see the following section) to the MgO–NiO join give activities of NiO and MgO along this join as shown in Fig. 4. No solid solubility of TiO_2 in the MgO–NiO solution was detected at 1400 °C, and hence it is concluded that the latter solution shows a very small negative deviation from ideality. This is similar to the data of Hahn and Muan[10], which indicated ideal behavior within the wider limits of experimental error in the method used in their work.

Values of log C $\left(C = \frac{a_{NiO} \cdot N_{MgTiO_3}}{a_{MgO} \cdot N_{NiTiO_3}}\right)$ for the reaction

$$(MgO)+(NiTiO_3) \rightleftharpoons (NiO)+(MgTiO_3) \tag{6}$$

are shown graphically in Fig. 5. These data may be used to calculate activity coefficients of the $MgTiO_3$–$NiTiO_3$ solid solution and the change in free energy, $\Delta(\Delta G^0)$, for reaction (6) by methods which have been described previously[3–5]. The following equations apply to the present equilibrium:

$$\log \gamma_{MgTiO_3} = -N_{NiTiO_3} \log C + \int_0^{N_{NiTiO_3}} \log C \, dN_{NiTiO_3} \tag{7}$$

and

$$\log \gamma_{\mathrm{NiTiO_3}} = (1 - N_{\mathrm{NiTiO_3}}) \log C + \int_1^{N_{\mathrm{NiTiO_3}}} \log C \, \mathrm{d}N_{\mathrm{NiTiO_3}} \tag{8}$$

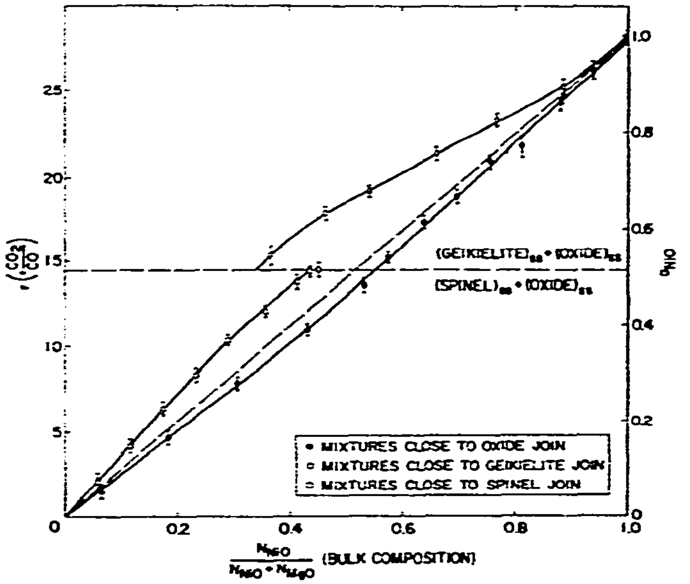

Fig. 3. Plot of CO_2/CO ratios and a_{NiO} *vs.* $N_{\mathrm{NiO}}/(N_{\mathrm{NiO}}+N_{\mathrm{MgO}})$ for coexistence of metallic nickel and assemblages IV (geikielite+oxide solid solution) and V (spinel+oxide solid solution) in the system MgO–NiO–TiO₂ at 1400 °C. The dashed line separates the area of phase assemblage IV from that of phase assemblage V.

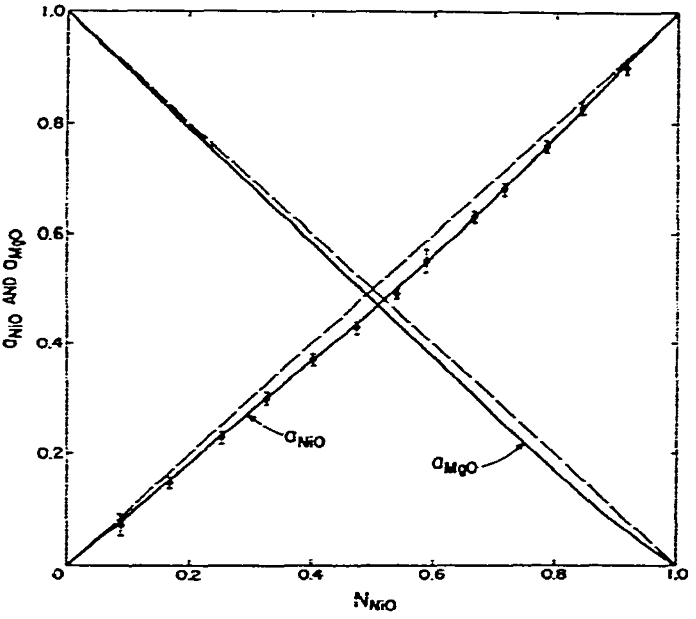

Fig. 4. Activity–composition relations along the MgO–NiO join in contact with metallic nickel at 1400 °C, as determined in the present investigation.

and

$$-\frac{\Delta(\Delta G^0)}{2.303\,RT} = \log C + \log \gamma_{MgTiO_3} - \log \gamma_{NiTiO_3} \tag{9}$$

where

$$\Delta(\Delta G^0) = \Delta G^0_{MgTiO_3} - \Delta G^0_{NiTiO_3} \tag{10}$$

and $\Delta G^0_{MgTiO_3}$ and $\Delta G^0_{NiTiO_3}$ are the free energies of formation of $MgTiO_3$ and $NiTiO_3$ from their oxide components, $MgO + TiO_2$ and $NiO + TiO_4$, respectively. The value of $\Delta(\Delta G^0)$ as determined from the above data is -2.8 ± 0.3 kcal. Combination of this with the free energy of formation of $NiTiO_3$ from its oxide components (see p. 125) gives a value of $\Delta G^0 = -5.1 \pm 0.5$ kcal for the free energy of formation of $MgTiO_3$ from its oxide components ($MgO + TiO_2 \rightarrow MgTiO_3$) at 1400°C. This is somewhat less negative than the value reported by Kelley[11] at 1400°C (-6.2 kcal), but in good agreement with the value (-4.8 kcal) determined recently for the same reaction at 1300°C from equilibria in the system MgO–CoO–TiO_4[12].

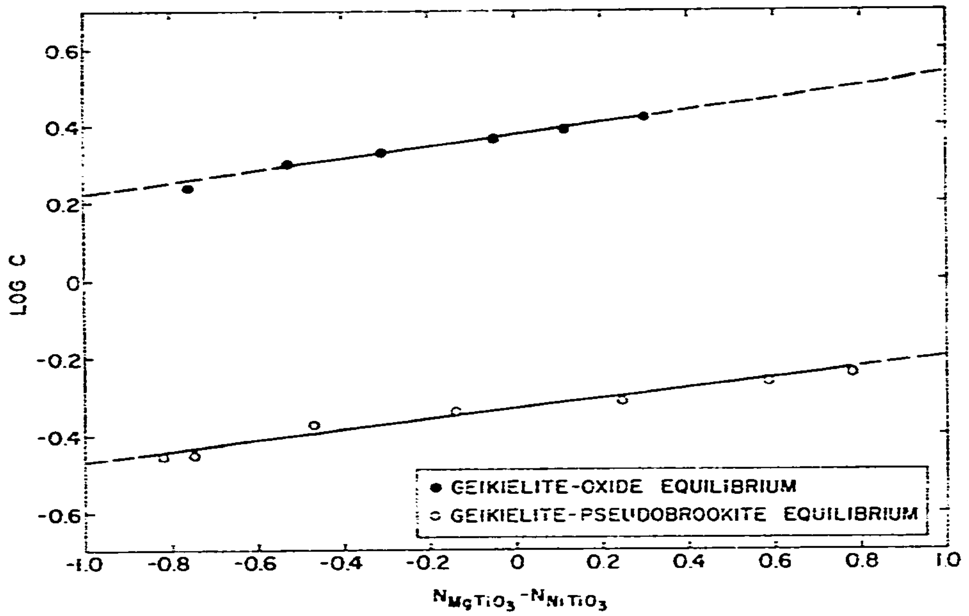

Fig. 5. Plot of log *C* *vs.* composition of geikielite, for equilibria in which geikielite coexists with metallic nickel and either oxide or pseudobrookite solid solutions (compare text).

The data from the geikielite+oxide equilibrium show that there is a slight positive deviation from ideality of the $MgTiO_3$–$NiTiO_3$ solid solution at 1400°C. The activity–composition curve for this join will be presented in a later section after independently checking these relations from data on the pseudobrookite+geikielite equilibrium.

Phase assemblage spinel+oxide solid solutions

Results of equilibrations involving mixtures within this field (area V of Fig. 1) are listed in Table III and shown graphically in Fig. 3, and in the form of conjugation lines in Fig. 1. Values of log C ($C = \frac{a_{NiO} \cdot N_{MgTi_{0.5}O_2}}{a_{MgO} \cdot N_{NiTi_{0.5}O_2}}$) as calculated for the reaction

$$(MgO)+(NiTi_{0.5}O_2) \rightleftharpoons (NiO)+(MgTi_{0.5}O_2) \qquad (11)$$

TABLE III

RESULTS OF EQUILIBRATION RUNS INVOLVING METALLIC NICKEL AND PHASE ASSEMBLAGE V (SPINEL+OXIDE SOLID SOLUTIONS) IN THE SYSTEM MgO–NiO–TiO_2 AT 1400 °C

Composition (mol fraction)			$\frac{N_{NiO}}{N_{NiO}+N_{MgO}}$	$r(CO_2/CO)$	a_{NiO}
MgO	*NiO*	*TiO_2*			
0.650	0.040	0.310	0.058	2.1 ±0.5	0.075 ±0.02
0.609	0.080	0.311	0.116	4.2 ±0.4	0.15 ±0.01
0.570	0.120	0.310	0.174	6.4 ±0.4	0.23 ±0.01
0.530	0.160	0.310	0.232	8.4 ±0.4	0.30 ±0.01
0.489	0.200	0.311	0.290	10.4 ±0.3	0.37 ±0.01
0.448	0.246	0.306	0.355	12.1 ±0.3	0.43 ±0.01
0.400	0.280	0.320	0.412	13.8 ±0.4	0.49 ±0.01
[a]0.377	0.290	0.333	0.435	14.4 ±0.3	0.51 ±0.01
[a]0.380	0.310	0.310	0.449	14.5 ±0.4	0.51 ±0.01
0.920	0.060	0.020	0.061	1.5 ±0.5	0.05 ±0.02
0.800	0.180	0.020	0.184	4.7 ±0.4	0.17 ±0.01
0.680	0.300	0.020	0.306	7.9 ±0.4	0.28 ±0.01
0.559	0.421	0.020	0.429	11.0 ±0.3	0.39 ±0.01
0.461	0.519	0.020	0.530	13.6 ±0.4	0.48 ±0.01
[b]0.500	0.500		0.500	13.0 ±0.4	0.46 ±0.01
0.441	0.483	0.076	0.523	14.0 ±0.3	0.50 ±0.01

[a] These mixtures are in the three-phase field geikielite+spinel+oxide. [b] This mixture is on the binary join NiO–MgO.

are shown in Fig. 6. The composition range over which C-values were obtained experimentally is too small to permit a reliable thermodynamic description of this solid-solution series. However, a definite trend in the data is apparent. The values of C decrease slightly with increasing N_{NiTiO_3}-values, suggesting a very small negative deviation from ideality of the spinel solid solution over the composition range studied. Further data and discussion of this solid solution will be presented in the following section dealing with results from phase assemblages VI, geikielite+spinel.

From the oxide–spinel equilibrium, the $\Delta(\Delta G^0)$-value for reaction (11) is calculated (by equations similar to those shown on p. 128) to be -1.9 ± 0.3 kcal at 1400 °C. Combination of this with the free energy of formation ($\Delta G^0_{Mg_2TiO_4}$) of Mg_2TiO_4 from its oxide components ($2MgO+TiO_2$) will yield an approximate value of the free energy of formation of Ni_2TiO_4 from its oxide components ($2NiO+TiO_2$), according to the relationship

$$\Delta G^0_{Ni_2TiO_4} = \Delta G^0_{Mg_2TiO_4} + 2\Delta(\Delta G^0) \qquad (12)$$

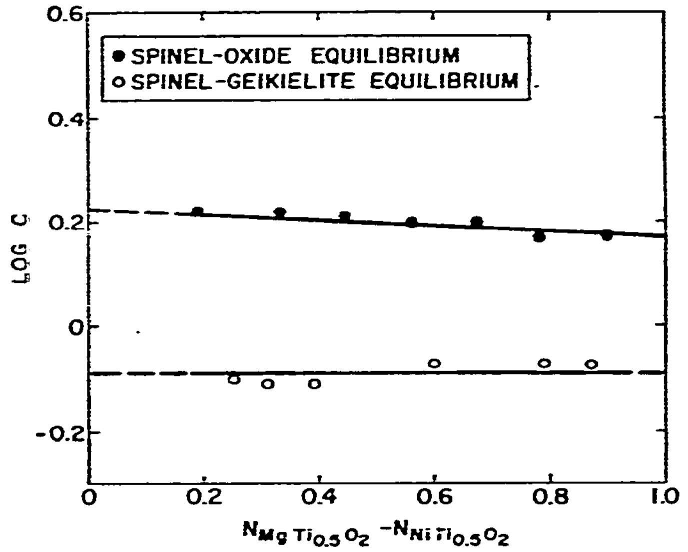

Fig. 6. Plot of log *C* *vs*. composition of spinel, for equilibria in which spinel coexists with metallic nickel and either oxide or pseudobrookite solid solutions (compare text).

The value of $\Delta G^0_{Mg_2TiO_4}$ at 1300°C has been determined recently (−5.1 kcal) from a study of the equilibrium between oxide and spinel solid solutions in the system MgO–CoO–TiO_2[12]. It was shown in that study that the oxide and spinel solid solutions deviate very little from ideality, and that a plot of log *C* *vs*. composition for this equilibrium is close to a straight line, and that the value of log *C* at $N_{CoTi_{0.5}O_2} = N_{MgTi_{0.5}O_2} = 0.5$ therefore gives a good measure of the value of $\Delta(\Delta G^0)$ for the reaction attending the distribution of Mg^{2+} and Co^{2+} between the two coexisting solid solutions[5]. In order to obtain a value of $\Delta G^0_{Mg_2TiO_4}$ at the temperature of the present investigation, 1400°C, a couple of determinations were made of directions of conjugation lines between coexisting spinel and oxide solid-solution phases in the system MgO–CoO–TiO_2 at 1400°C. The two samples which were run yielded conjugation lines that intercepted the Mg_2TiO_4–Co_2TiO_4 join close to, but on opposite sides of the point where $N_{CoTi_{0.5}O_2} = N_{MgTi_{0.5}O_2}$. The value of the intercept is 0.08, which gives a value of −1.2 ±0.6 kcal for the difference between the ΔG^0-values of Mg_2TiO_4 and Co_2TiO_4. From the work of Brežný and Muan[13], ΔG^0 for the reaction $2CoO + TiO_2 \rightarrow Co_2TiO_4$ at 1400°C is −4.6 ±0.3 kcal. Hence, the free energy of formation of Mg_2TiO_4 from 2 MgO and TiO_2 at 1400°C is found to be −5.8 ±0.9 kcal. This is in satisfactory agreement with the value (−5.1 kcal) determined by Brežný and Muan at 1300°C[12] in their study of the system MgO–CoO–TiO_2, but considerably less negative than the value (−9.3 kcal) calculated by Kelley from room-temperature data[1].

The free energy of formation of Ni_2TiO_4 from its oxide components according to the reaction

$$2NiO + TiO_2 \rightarrow Ni_2TiO_4 \qquad (13)$$

as calculated on the basis of the data obtained in the present investigation is $\Delta G^0 = -2.0 \pm 1.5$ kcal. This is in good agreement with data obtained in recent studies of the systems MnO–NiO–TiO_2[14] and ZnO–NiO–TiO_2[15]. Combining this with the free energy of formation of $NiTiO_3$, −2.3 kcal, we calculate for the reaction

$$Ni_2TiO_4 \rightarrow NiO + NiTiO_3 \qquad (14)$$

a ΔG^0-value of -0.3 ± 0.7 kcal at 1400°C. This is in agreement with the observed instability of Ni_2TiO_4 relative to the phase assemblage $NiO + NiTiO_3$.

Phase assemblage geikielite + spinel solid solutions

Results of equilibration runs for this phase assemblage (area VI of Fig. 1) are listed in Table IV and shown graphically in Fig. 7, and in the form of conjugation lines in Fig. 1. Values of log C ($C = \frac{a_{NiTiO_3} \cdot N_{MgTi_{0.5}O_2}}{a_{MgTiO_3} \cdot N_{NiTi_{0.5}O_2}}$) as calculated for the reaction

$$(MgTiO_3) + (NiTi_{0.5}O_2) \rightleftharpoons (NiTiO_3) + (MgTi_{0.5}O_2) \qquad (15)$$

TABLE IV

RESULTS OF EQUILIBRATION RUNS INVOLVING METALLIC NICKEL AND PHASE ASSEMBLAGE VI (GEIKIELITE + SPINEL SOLID SOLUTION) IN THE SYSTEM MgO–NiO–TiO_2 AT 1400°C

Composition (mol fraction)			$\frac{N_{NiO}}{N_{NiO}+N_{MgO}}$	$r(CO_2/CO)$	a_{NiO}
MgO	*NiO*	*TiO_2*			
0.480	0.040	0.480	0.077	2.9 ±0.5	0.10 ±0.02
0.440	0.080	0.480	0.154	6.6 ±0.3	0.23 ±0.01
0.399	0.120	0.481	0.231	10.0 ±0.3	0.36 ±0.01
0.378	0.143	0.479	0.275	12.0 ±0.3	0.43 ±0.01
0.609	0.040	0.351	0.062	2.0 ±0.4	0.07 ±0.01
0.569	0.080	0.351	0.123	4.2 ±0.4	0.15 ±0.01
0.531	0.119	0.350	0.183	6.4 ±0.3	0.23 ±0.01
0.490	0.159	0.351	0.245	8.4 ±0.3	0.30 ±0.01
0.450	0.200	0.350	0.308	10.5 ±0.3	0.37 ±0.01
0.410	0.240	0.350	0.369	13.2 ±0.4	0.47 ±0.01
[a]0.370	0.280	0.350	0.431	14.4 ±0.3	0.51 ±0.01

[a] This mixture is in the three-phase triangle geikielite + spinel + oxide.

are shown graphically as part of Fig. 6. The C-values do not vary significantly with composition over the stability range of the spinel solid solution, and the latter may be assumed to be close to ideal over the composition range studied. This observation is in reasonable agreement with that made from the oxide + spinel equilibrium which suggested a very slight negative deviation from ideality. The $\Delta(\Delta G^0)$-value calculated for reaction (15) is 0.7 ± 0.3 kcal at 1400°C. Combination of this with the free energies of formation of $NiTiO_3$, Mg_2TiO_4 and $MgTiO_3$ from their oxide components at

1400 °C (−2.3, −5.8 and −5.1 kcal, respectively, see previous section), gives a ΔG^0-value for the reaction

$$2NiO+TiO_2 \rightarrow Ni_2TiO_4 \qquad (16)$$

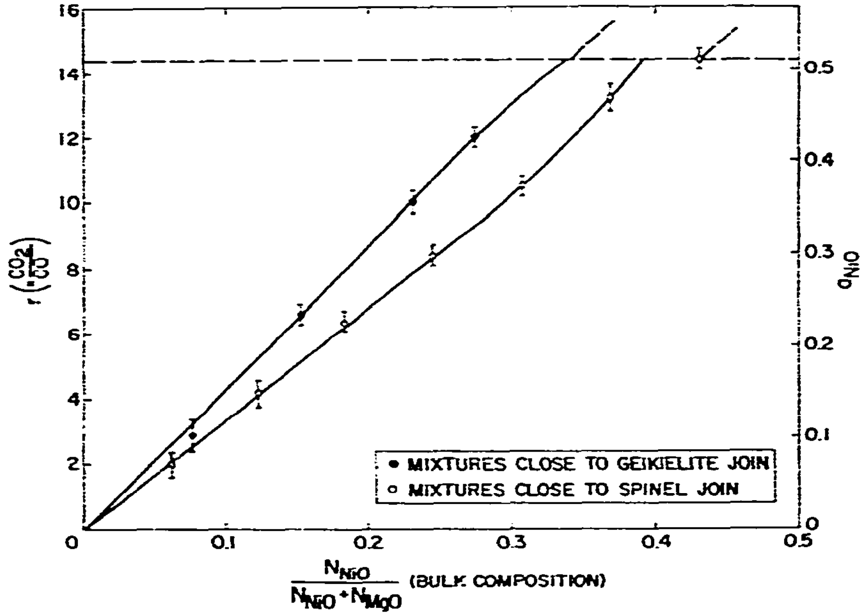

Fig. 7. Plot of CO_2/CO ratios and a_{NiO} vs. $N_{NiO}/(N_{NiO}+N_{MgO})$ for coexistence of metallic nickel and phase assemblage VI (geikielite+spinel solid solution) in the system MgO–NiO–TiO_2 at 1400 °C The horizontal line separates the area of phase assemblage VI from the area of phase assemblage IV.

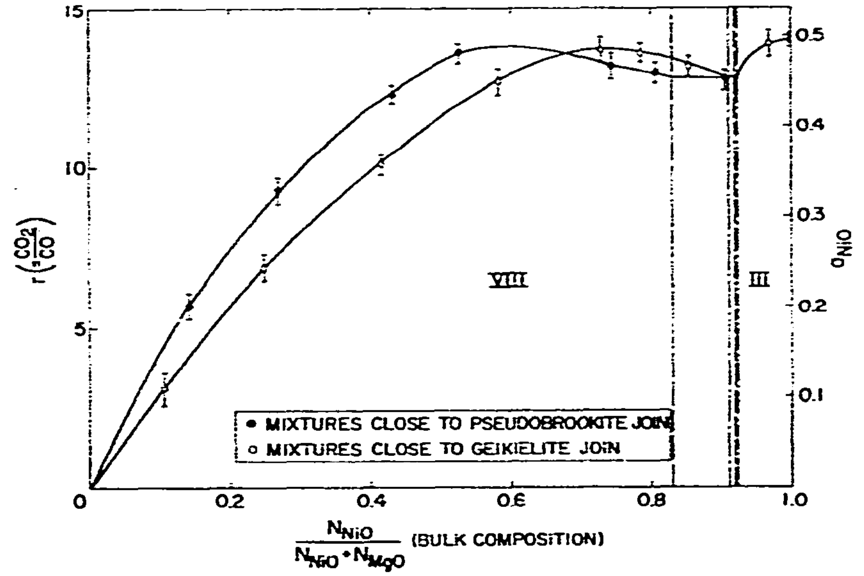

Fig. 8. Plot of CO_2/CO ratios and a_{NiO} vs. $N_{NiO}/(N_{NiO}+N_{MgO})$ for coexistence of metallic nickel and phase assemblages VIII (pseudobrookite+geikielite) and III (rutile+geikielite) in the system MgO–NiO–TiO_2 at 1400 °C. The areas enclosed by vertical dashed lines and vertical dashed-dot lines represent the widths of the three-phase field rutile+pseudobrookite+geikielite near the pseudobrookite and the geikielite joins, respectively.

of −1.6 ±2.1 kcal. This is in satisfactory agreement with the value determined from phase assemblage V, −2.0 ±1.5 kcal.

Phase assemblage geikielite + pseudobrookite

Equilibrium data for mixtures within this phase assemblage (area VIII of Fig. 1) are summarized in Table V and illustrated graphically in Fig. 8, and shown in the form of conjugation lines in Fig. 1.

TABLE V

RESULTS OF EQUILIBRATION RUNS INVOLVING METALLIC NICKEL AND PHASE ASSEMBLAGE VIII (PSEUDOBROOKITE + GEIKIELITE) IN THE SYSTEM $MgO-NiO-TiO_2$ AT 1400 °C

Composition (mol fraction)			$\frac{N_{NiO}}{N_{NiO}+N_{MgO}}$	$r(CO_2/CO)$	a_{NiO}
MgO	*NiO*	*TiO₂*			
0.310	0.051	0.639	0.141	5.7 ±0.4	0.20 ±0.01
0.270	0.100	0.630	0.270	9.3 ±0.4	0.33 ±0.01
0.210	0.160	0.630	0.432	12.3 ±0.3	0.44 ±0.01
0.161	0.179	0.660	0.526	13.6 ±0.3	0.48 ±0.01
0.091	0.262	0.647	0.742	13.2 ±0.4	0.47 ±0.01
0.069	0.290	0.641	0.808	13.0 ±0.3	0.46 ±0.01
[a]0.031	0.299	0.670	0.906	12.8 ±0.3	0.45 ±0.01
0.431	0.051	0.518	0.106	3.1 ±0.5	0.11 ±0.02
0.360	0.120	0.520	0.250	6.9 ±0.4	0.24 ±0.01
0.279	0.200	0.521	0.417	10.1 ±0.3	0.36 ±0.01
0.200	0.280	0.520	0.583	12.7 ±0.4	0.45 ±0.01
0.130	0.350	0.520	0.730	13.7 ±0.4	0.49 ±0.01
0.091	0.339	0.570	0.788	13.6 ±0.3	0.48 ±0.01
0.069	0.410	0.521	0.855	13.2 ±0.3	0.47 ±0.01

[a] This mixture is in the three-phase field rutile + pseudobrookite + geikielite.

Using the ideality of the pseudobrookite solid solution as a starting point (see previous section on equilibria for phase assemblage I), activity–composition relations for the geikielite join are derived as illustrated in Fig. 9. A slight positive deviation from ideality is observed, confirming the conclusions made from the oxide + geikielite equilibrium.

The $\Delta(\Delta G^0)$-value calculated for the reaction

$$(MgTi_2O_5)+(NiTiO_3) \rightleftharpoons (NiTi_2O_5)+(MgTiO_3) \qquad (17)$$

at 1400 °C is 2.5 ±0.3 kcal. Combination of this with the previously determined free energies of formation of the other compounds from their oxide components at 1400 °C ($NiTi_2O_5$, −2.0 kcal; $MgTiO_3$, −5.1 kcal; $NiTiO_3$, −2.3 kcal) gives for the reaction

$$MgO+2TiO_2 \rightarrow MgTi_2O_5$$

at 1400 °C a ΔG^0-value of −7.3 ±0.8 kcal. This is somewhat less negative than the value (−8.75 kcal) listed by Kelley[11], but in satisfactory agreement with the value (−6.8 kcal) derived recently from equilibria in the system $MgO-CoO-TiO_2$ at 1300 °C[12].

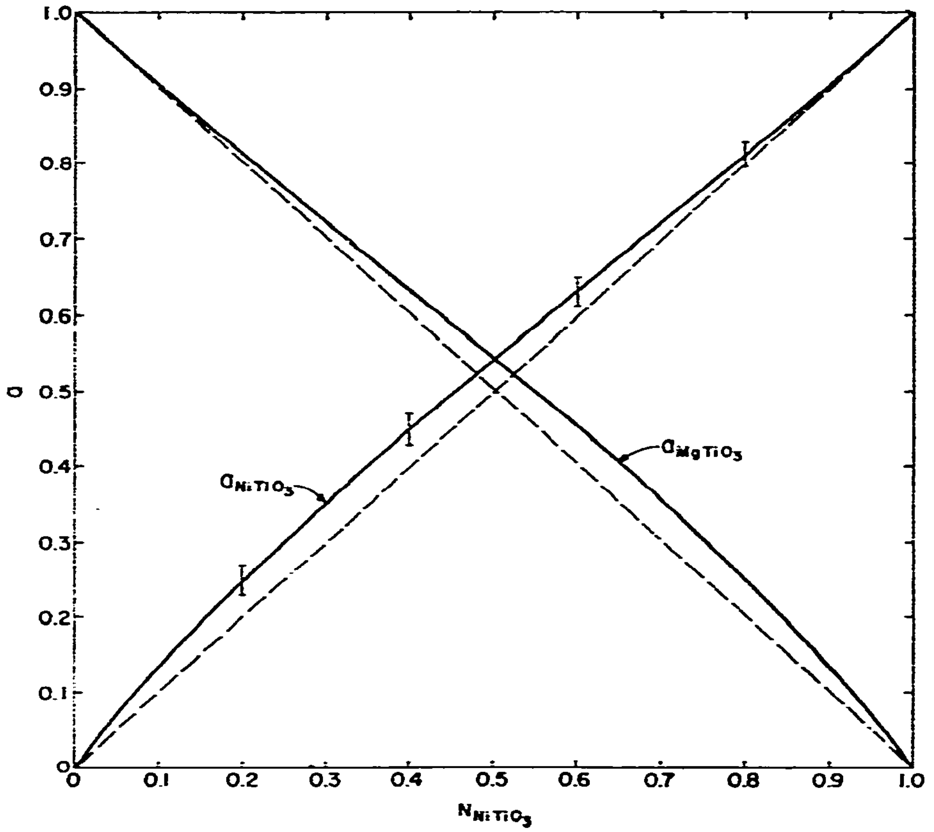

Fig. 9. Activities of $MgTiO_3$ and $NiTiO_3$ as a function of composition along the geikielite join of the system MgO–NiO–TiO_2 at 1400°C.

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