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ACTIVITY–COMPOSITION RELATIONS OF SOLID SOLUTIONS AND STABILITIES OF MANGANESE AND NICKEL TITANATES AT 1250°C AS DERIVED FROM EQUILIBRIA IN THE SYSTEMS $MnO-CoO-TiO_2$ AND $MnO-NiO-TiO_2$*

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ABSTRACT

Equilibria between a metal phase (either cobalt or nickel), a gas phase of known oxygen pressures, and pairs of solid-solution phases in the systems $MnO-CoO-TiO_2$ and $MnO-NiO-TiO_2$ are used to calculate activity–composition relations in the solid-solution series $Mn_2TiO_4-Co_2TiO_4$, $MnTiO_3-CoTiO_3$, $MnTi_2O_5-CoTi_2O_5$, $Mn_2TiO_4-Ni_2TiO_4$ and $MnTiO_3-NiTiO_3$, and free energies of formation of the manganese titanates Mn_2TiO_4, $MnTiO_3$ and $MnTi_2O_5$ and of nickel orthotitanate, Ni_2TiO_4.

The spinel solid solutions ($Mn_2TiO_4-Co_2TiO_4$ and $Mn_2TiO_4-Ni_2TiO_4$) show negative deviations from ideality, the pyrophanite solid solutions ($MnTiO_3-CoTiO_3$ and $MnTiO_3-NiTiO_3$) show small positive deviations from ideality, and the pseudobrookite solid solution $MnTi_2O_5-CoTi_2O_5$ probably displays a very small positive deviation from ideality.

The following free energies of formation were determined for the various manganese and nickel titanates from their oxide components at 1250°C:

$$\begin{aligned}
&2MnO+TiO_2 \rightleftharpoons Mn_2TiO_4 && \Delta G^0 = -7.6 \pm 0.5 \text{ kcal}\\
&MnO+TiO_2 \rightleftharpoons MnTiO_3 && \Delta G^0 = -7.0 \pm 0.8 \text{ kcal}\\
&MnO+2TiO_2 \rightleftharpoons MnTi_2O_5 && \Delta G^0 = -6.3 \pm 0.8 \text{ kcal}\\
&2NiO+TiO_2 \rightleftharpoons Ni_2TiO_4 && \Delta G^0 = -1.0 \pm 1.0 \text{ kcal}
\end{aligned}$$

INTRODUCTION

The present investigation is part of a series of studies aimed at expanding our knowledge of the energetics of compound formation and solid-solution behavior of oxidic materials of common structure types. In the present paper, we extend previous studies of silicate and titanate systems at elevated temperatures to the titanates of manganese, for which no thermodynamic data have been available previously.

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The 1250°C isothermal sections through the two systems MnO-CoO-TiO_2 and MnO–NiO–TiO_2 are shown in Figs. 1 and 2, respectively. Manganese oxide and titanium oxide form two compounds at elevated temperatures, *viz.* Mn_2TiO_4 with spinel structure and $MnTiO_3$ with geikielite structure. Each of these compounds forms a complete solid-solution series with the analogous cobalt compounds for which stability data are available from previous studies[1]. Similarly, $MnTiO_3$ forms a complete solid-solution series with the analogous nickel compound, $NiTiO_3$, for which stability data are available from previous studies[2], and Mn_2TiO_4 is the starting point for a solid-solution series extending partway toward the hypothetical nickel analogue, Ni_2TiO_4, which is not stable in its pure form and for which approximate instability data have been derived in previous studies[2]. Finally, there is a partial solid solution from the stable cobalt compound $CoTi_2O_5$ toward the unstable, hypothetical manganese analogue, $MnTi_2O_5$. By studying the activity–composition

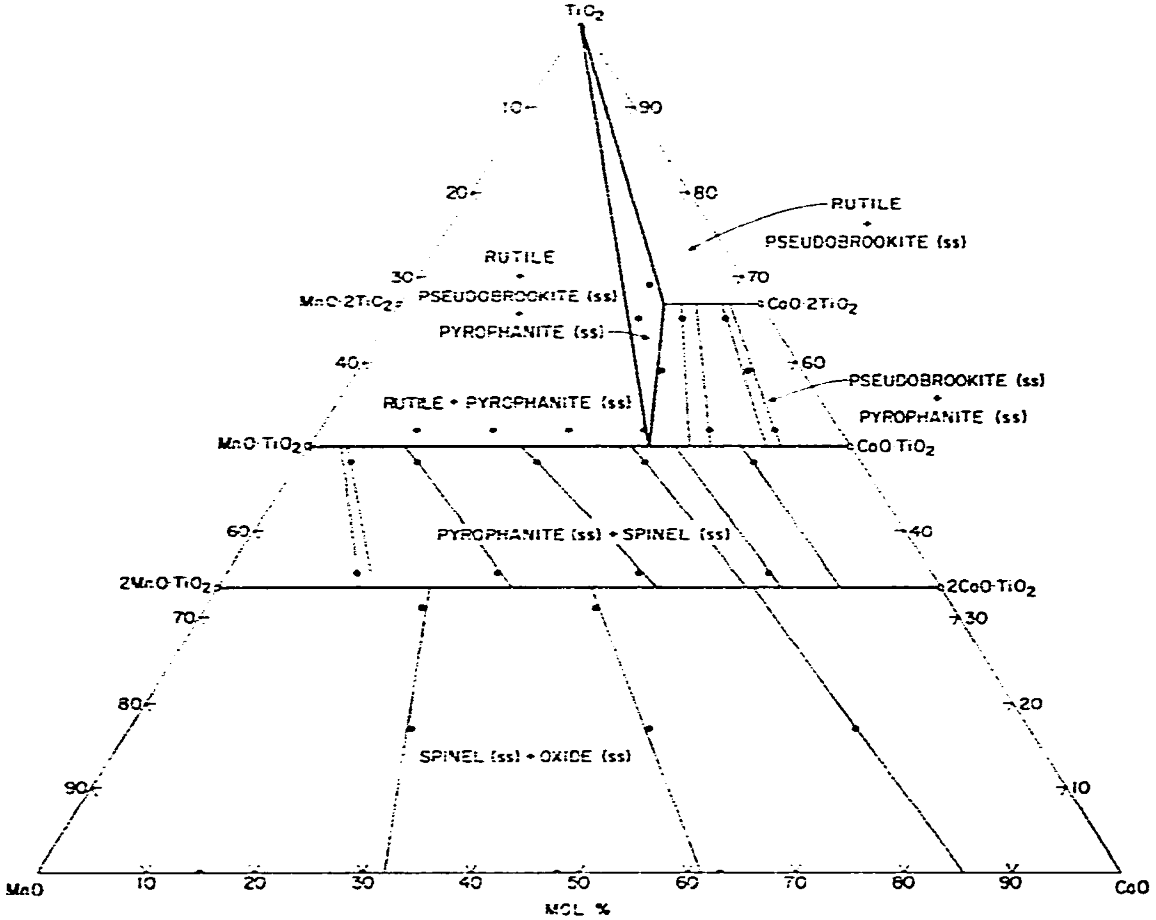

Fig. 1. The 1250°C isothermal section of the system MnO–CoO–TiO_2, showing the extent of the various solid solutions, and conjugation lines between coexisting solid-solution phases (light lines). Solid dots represent compositions of mixtures studied.

relations of these solid solutions, and knowing the free energies of formation of one of the end members of each solution, the free energy of formation of the other end member, from its oxide components, may be calculated.

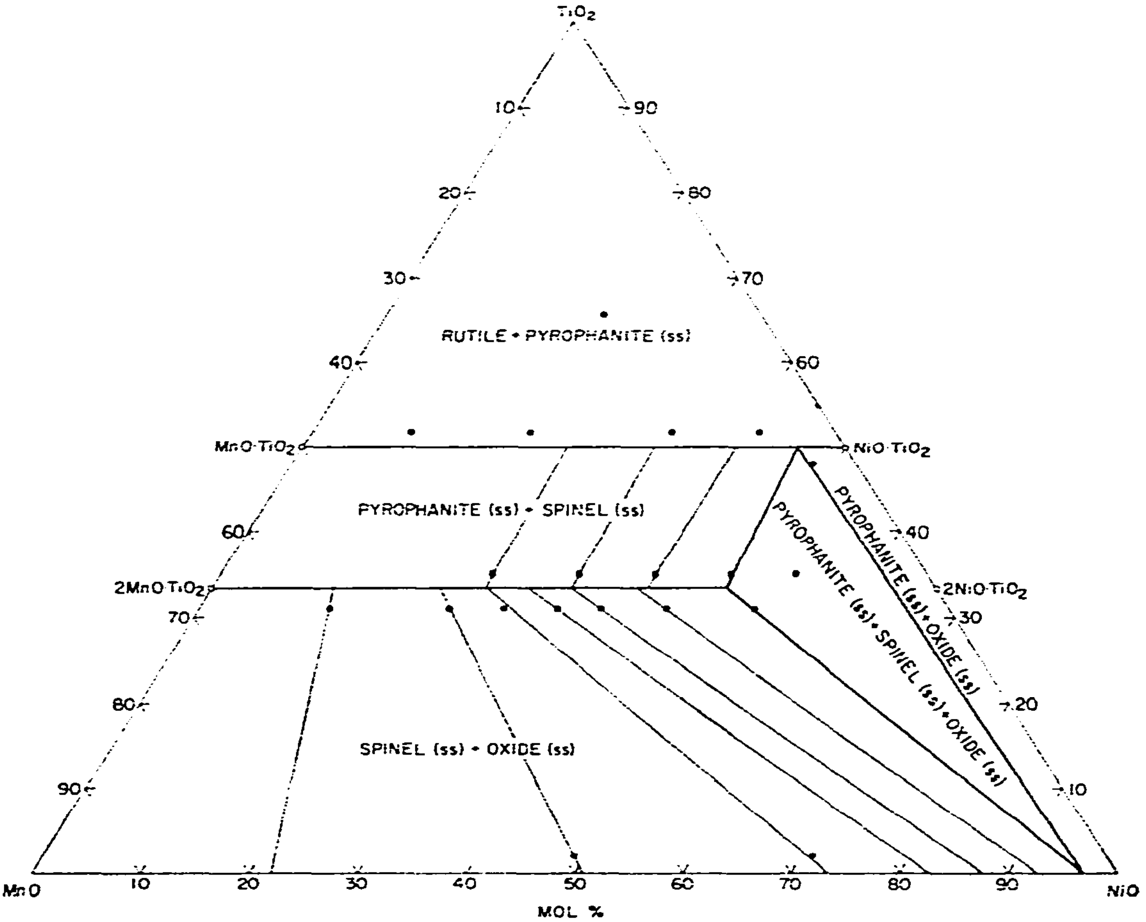

Fig. 2. The 1250 °C isothermal section of the system MnO–NiO–TiO_2, showing the extent of the various solid solutions, and conjugation lines between coexisting solid-solution phases (light lines). Solid dots represent compositions of mixtures studied.

Activity–composition relations in the two systems MnO–CoO and MnO–NiO have been determined previously. The system MnO–CoO at 1200 °C was found to be close to ideal[3], whereas the system MnO–NiO displays a considerable positive deviation from ideality in the temperature range of 1100–1300 °C. (Ref. 4).

The free energies of formation of the various cobalt titanates (Co_2TiO_4, $CoTiO_3$ and $CoTi_2O_5$) at elevated temperatures have been determined by two groups of investigators by different experimental techniques[1,5], and with satisfactory agreement among the results. The stability of $NiTiO_3$ has also been determined with good accuracy[2], whereas only approximate free energies of formation of the two unstable, hypothetical nickel titanates, Ni_2TiO_4 and $NiTi_2O_5$, have been calculated from solid-solution equilibria in the system MgO–NiO–TiO_2 (Ref. 2).

The approach in the present work will be to use equilibrium data from the system MnO–CoO–TiO_2 in conjunction with the known stabilities of the cobalt titanates to calculate the stabilities of the manganese titanates. The latter will then be used, in conjunction with equilibrium data for the system MnO–NiO–TiO_2, to calculate free energies of formation of the nickel titanates. The results for the latter will be compared with those previously obtained from equilibria in the system MgO–NiO–TiO_2.

The theoretical basis for evaluating activity–composition relations and stabilities of end-member compounds from metal–oxide–gas equilibria have been described elsewhere[6,7]. 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. For the solid solutions of the present systems, the activity expressions will be

$$a_{\mathrm{MeTi_{0.5}O_2}} = N_{\mathrm{MeTi_{0.5}O_2}} \cdot \gamma_{\mathrm{MeTi_{0.5}O_2}} = a_{\mathrm{MeO}} \cdot a_{\mathrm{TiO_2}}^{1/2} \tag{1}$$

$$a_{\mathrm{MeTiO_3}} = N_{\mathrm{MeTiO_3}} \cdot \gamma_{\mathrm{MeTiO_3}} = a_{\mathrm{MeO}} \cdot a_{\mathrm{TiO_2}} \tag{2}$$

and

$$a_{\mathrm{MeTi_2O_5}} = N_{\mathrm{MeTi_2O_5}} \cdot \gamma_{\mathrm{MeTi_2O_5}} = a_{\mathrm{MeO}} \cdot a_{\mathrm{TiO_2}}^{2} \tag{3}$$

for the spinel, pyrophanite and pseudobrookite solid solutions, respectively, where Me represents one of the elements Mn, Co, or Ni, and the *a*'s, *N*'s and γ's with appropriate subscripts represent activities, mol fractions and activity coefficients, respectively.

EXPERIMENTAL METHODS

The experimental methods used were similar to those described previously[2,6], and only a brief account of the main procedure and of specific details applicable to the present study will be given here.

Mixtures of desired compositions were made up from reagent-grade ("Baker Analyzed") oxides and pre-reacted in CO_2–CO atmospheres at ~1250°C to yield the coexisting pairs of oxide phases corresponding to the equilibrium relations in the systems MnO–CoO–TiO_2 and MnO–NiO–TiO_2 (see Figs. 1 and 2). In order to attain homogeneity of each of the coexisting solid solutions, the prereaction was continued for considerable periods of time (one to four days) with one or more intermediate grindings.

The pre-reacted, densely sintered mixtures were broken into chunks suitable for suspension with a thin (0.004" diameter) platinum wire into a vertical tube quench furnace for the final equilibration runs at 1250°C under carefully controlled oxygen pressures of the atmosphere. The latter was achieved by mixing CO_2 and CO in desired proportions[8]. The oxygen pressure was decreased in small increments until a point was reached where a trace of metal (either cobalt or nickel) was present in contact with the oxide phases. The pattern of precipitation of the metal phase was used as a means of judging whether the phases of the pre-reacted sample had attained satisfactory homogeneity: when the metal phase precipitated in the form of tiny bright specks uniformly distributed over the whole section, the samples were considered homogeneous. If, on the other hand, larger metal particles were precipitated locally, it was taken as a sign of heterogeneity in the pre-reacted mixtures, and such mixtures were returned for further pre-reaction treatment. The reversibility of the reaction between the oxide phases, the metal phase and the gas phase was checked by approaching the equilibrium also in the opposite direction. This was done by increasing in small increments the oxygen pressures of the gas phase in equilibrium with samples from which a small amount of metal had been precipitated. This caused the metal phase to disappear at or only slightly above the oxygen pressure determined from the metal precipitation runs.

The temperatures in the equilibration runs were measured with a Pt *vs.* 90%Pt–10%Rh thermocouple calibrated against the melting points of gold (1063 °C) and synthetic diopside (1391.5 °C). The overall accuracy of the temperature measurement is estimated to be within ±5 °C.

RESULTS

The system MnO–CoO–TiO_2

Phase assemblage oxide solid solution + spinel solid solution

Results of equilibration runs involving this phase assemblage are listed in Table I and shown in the form of conjugation lines in Fig. 1. For the equilibrium

$$(\mathrm{MnO}) + (\mathrm{CoTi_{0.5}O_2}) \rightleftharpoons (\mathrm{CoO}) + (\mathrm{MnTi_{0.5}O_2}) \tag{4}$$

the activity coefficients are calculated from the Eqns.[6,7,9]

$$\log \gamma_{\mathrm{MnTi_{0.5}O_2}} = -N_{\mathrm{CoTi_{0.5}O_2}} \log C + \int_0^{N_{\mathrm{CoTi_{0.5}O_2}}} \log C \, \mathrm{d}N_{\mathrm{CoTi_{0.5}O_2}} \tag{5}$$

and

$$\log \gamma_{\mathrm{CoTi_{0.5}O_2}} = (1 - N_{\mathrm{CoTi_{0.5}O_2}}) \log C + \int_1^{N_{\mathrm{CoTi_{0.5}O_2}}} \log C \, \mathrm{d}N_{\mathrm{CoTi_{0.5}O_2}} \tag{6}$$

where C is the quotient

$$C = \frac{a_{\mathrm{CoO}} \cdot N_{\mathrm{MnTi_{0.5}O_2}}}{a_{\mathrm{MnO}} \cdot N_{\mathrm{CoTi_{0.5}O_2}}} \tag{7}$$

The activity–composition relations of the MnO–CoO solid solution [a_{CoO} and a_{MnO} in Eqn. (7)] at 1250 °C were determined by the same method as used for the other solid-solution series of the present study. The results are listed in Table II and shown graphically in Fig. 3. A moderate positive deviation is observed. This is a refinement of the data of Aukrust and Muan[3]. Their data also suggested a small

TABLE I

EXPERIMENTALLY DETERMINED CO_2/CO RATIOS OF GAS PHASE IN EQUILIBRIUM WITH METALLIC COBALT AND PAIRS OF OXIDIC PHASES IN THE SYSTEM $MnO–CoO–TiO_2$ AT 1250 °C

Phase assemblage	*Composition of mixture (mol fraction)*			*r(= CO_2/CO)*
	MnO	*CoO*	*TiO_2*	
Spinel(ss) + oxide(ss)	0.49	0.20	0.31	2.46
	0.33	0.36	0.31	4.30
	0.57	0.26	0.17	2.41
	0.35	0.48	0.17	4.30
	0.16	0.67	0.17	5.77
Rutile + pyrophanite(ss)	0.39	0.09	0.52	0.48
	0.32	0.16	0.52	0.82
	0.25	0.23	0.52	1.18
	0.18	0.30	0.52	1.41
Pyrophanite(ss) + spinel(ss)	0.47	0.05	0.48	1.11
	0.41	0.11	0.48	1.88
	0.30	0.22	0.48	2.45
	0.20	0.32	0.48	2.68
	0.10	0.42	0.48	2.88
	0.53	0.12	0.35	1.03
	0.40	0.25	0.35	1.86
	0.27	0.38	0.35	2.43
	0.15	0.50	0.35	2.76
Pseudobrookite(ss) + pyrophanite(ss)	0.08	0.27	0.65	1.58
	0.04	0.31	0.65	1.95
	0.13	0.28	0.59	1.48
	0.05	0.36	0.59	2.00
	0.12	0.36	0.52	1.70
	0.06	0.42	0.52	2.02
Rutile + pseudobrookite(ss) + pyrophanite(ss)	0.09	0.23	0.68	1.44
	0.12	0.23	0.65	1.43

TABLE II

RESULTS OF EQUILIBRATION RUNS FOR DETERMINING ACTIVITY–COMPOSITION RELATIONS IN THE SYSTEM $MnO–CoO$ AT 1250 °C

N_{CoO}	*r(= CO_2/CO)*	a_{CoO}
0.15	1.25	0.18
0.30	2.3	0.34
0.48	3.5	0.52
0.63	4.4	0.65
1.00	6.7	1.00

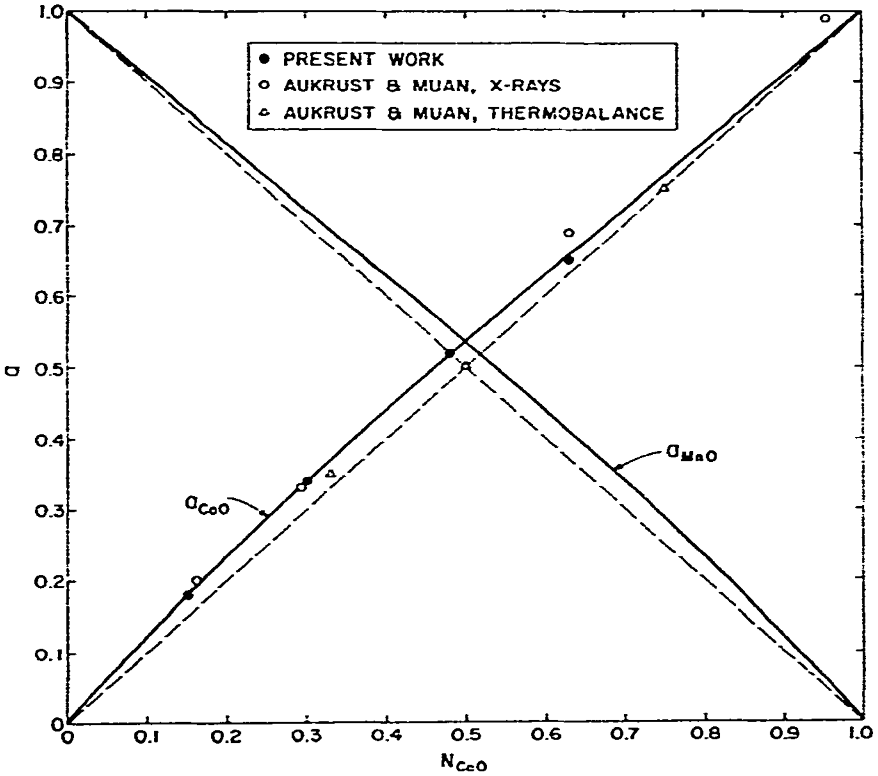

Fig. 3. Activity–composition relations in the system MnO–CoO at 1250°C, as determined in the present investigation. The curve for MnO was obtained by Gibbs–Duhem integration. The light dashed line shows relations according to Raoult's law. Data from previous work[3] are included for comparison.

positive deviation from ideality, but the deviation was within the somewhat wider limits of error associated with their experimental method.

Values of log C as calculated for Reaction (4) are shown as part of Fig. 4, and

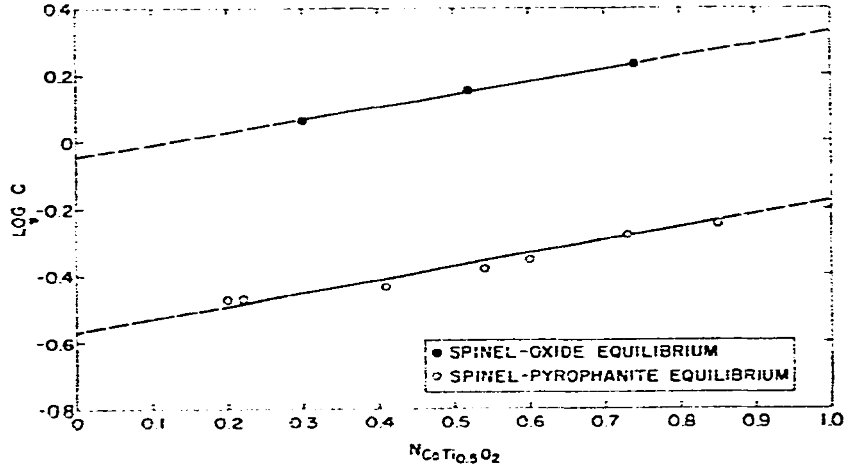

Fig. 4. Plot of log C *vs.* composition for coexistence of spinel solid solutions with either oxide solid solutions (solid circles) or pyrophanite solid solutions (open circles) in the system MnO–CoO–TiO_2 at 1250°C.

activities for the spinel solid solution as derived from these data are shown in Fig. 5. (The latter diagram is based also on more extensive activity data for this solid solution as derived from the pyrophanite–spinel equilibrium, as discussed in a later section.)

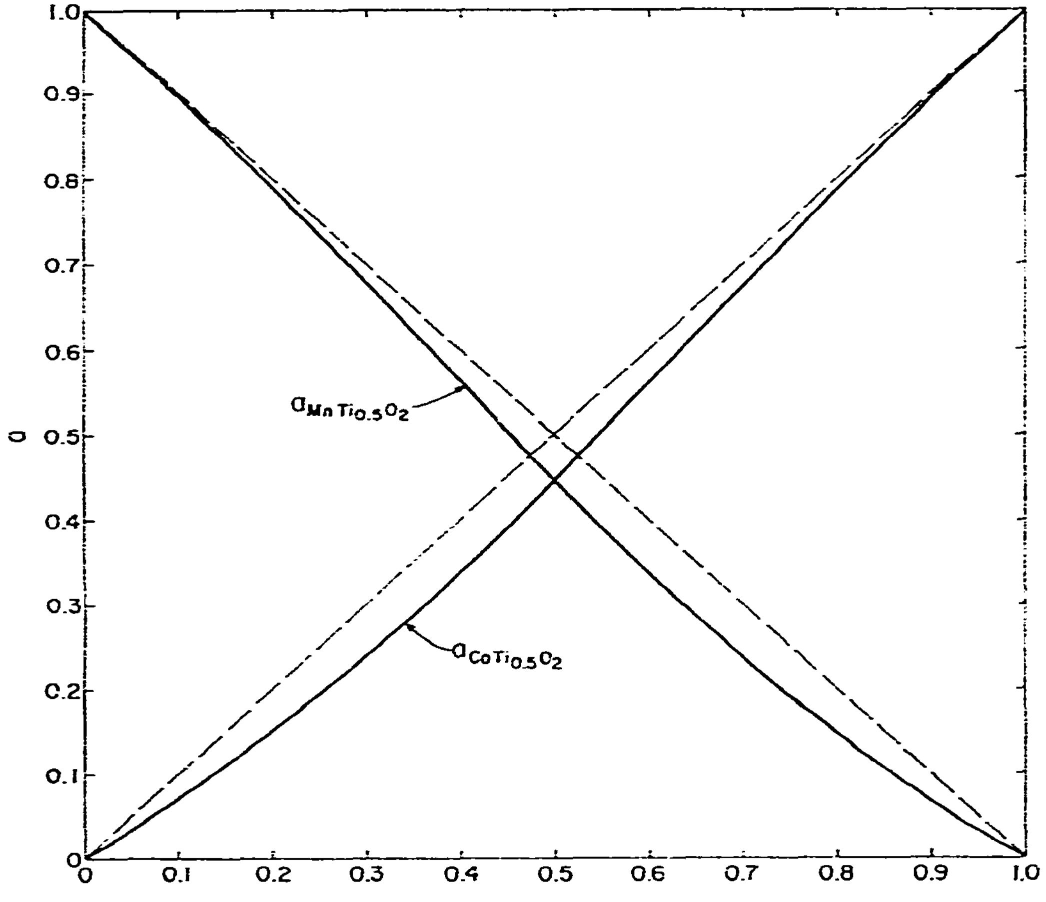

Fig. 5. Activity–composition relations in Mn_2TiO_4–Co_2TiO_4 solid solutions at 1250 °C, as calculated from directions of conjugation lines between coexisting oxide and spinel solid solutions, and from directions between coexisting pyrophanite and spinel solid solutions. The light dashed line shows relations according to Raoult's law.

The change in standard free energy, $\Delta(\Delta G^0)$, for Reaction (4)

$$\Delta(\Delta G^0) = \tfrac{1}{2}\Delta G^0_{Mn_2TiO_4} - \tfrac{1}{2}\Delta G^0_{Co_2TiO_4} \qquad (8)$$

is then calculated from the equation

$$-\frac{\Delta(\Delta G^0)}{2.303\,RT} = \log C + \log \gamma_{MnTi_{0.5}O_2} - \log \gamma_{CoTi_{0.5}O_2} \qquad (9)$$

Knowing $\Delta G^0_{Co_2TiO_4}$, and determining $\Delta(\Delta G^0)$ experimentally, the value of $\Delta G^0_{Mn_2TiO_4}$ is obtained as

$$\Delta G^0_{Mn_2TiO_4} = \Delta G^0_{Co_2TiO_4} + 2\Delta(\Delta G^0) \qquad (10)$$

The value of $\Delta(\Delta G^0)$ for Reaction (4) as calculated from Eqn. (9) is -1.0 kcal, and the free energy of formation of Mn_2TiO_4 from its oxide components according to the equation

$$2MnO + TiO_2 \rightleftharpoons Mn_2TiO_4 \qquad (11)$$

is $\Delta G^0 = -7.6$ kcal at 1250°C, based on a value of -5.6 kcal for $\Delta G^0_{Co_2TiO_4}$ at 1250°C[1].

Phase assemblage rutile + pyrophanite solid solution

The results of equilibration runs involving this phase assemblage are listed in Table I. For the equilibrium

$$(CoTiO_3) + CO \rightleftharpoons Co + TiO_2 + CO_2 \qquad (12)$$

the activities of $CoTiO_3$ in the pyrophanite solid solution are calculated from the expression

$$a_{CoTiO_3} = \frac{r}{r_0} \qquad (13)$$

where r and r_0 are the CO_2/CO ratios of the equilibrium above and of the equilibrium between $CoTiO_3$, TiO_2 and metallic cobalt in the binary system CoO–TiO_2, respectively. The latter phase assemblage is not stable at 1250°C, but the r_0-value is readily calculated from the free-energy data available[1] for each of the compounds involved in the equilibrium. The plot of r *vs.* $N_{CoO}/(N_{CoO} + N_{MnO})$ in Fig. 6 indicate sa moderate positive deviation from ideality of the pyrophanite solid solution.

Phase assemblage pyrophanite solid solution + spinel solid solution

Equilibrium data for this phase assemblage are listed in Table I and shown in the form of conjugation lines in Fig. 1. Using the known activity–composition relations of the pyrophanite solid solution, as determined from the pyrophanite–rutile equilibrium, values of log C $[C = (a_{CoTiO_3} \cdot N_{MnTi_{0.5}O_2})/(a_{MnTiO_3} \cdot N_{CoTi_{0.5}O_2})]$ as calculated for the reaction

$$(MnTiO_3) + (CoTi_{0.5}O_2) \rightleftharpoons (CoTiO_3) + (MnTi_{0.5}O_2) \qquad (14)$$

from the above data are obtained as shown in Fig. 4. It is seen that the slopes of the two curves in Fig. 4 are practically identical, and hence the deviations from ideality of the spinel solid solution as determined from the present equilibrium are in agreement with those determined from the oxide + spinel equilibrium. Activities of the components of the spinel solid solution are shown in Fig. 5. A considerable negative deviation from ideality is observed.

The value of $\Delta(\Delta G^0)$ for reaction (14) as calculated from these data is 2.6 kcal. Combining this with the known values of the free energies at 1250°C of the other components involved in the pyrophanite + spinel equilibrium (Co_2TiO_4, -5.6 kcal[1];

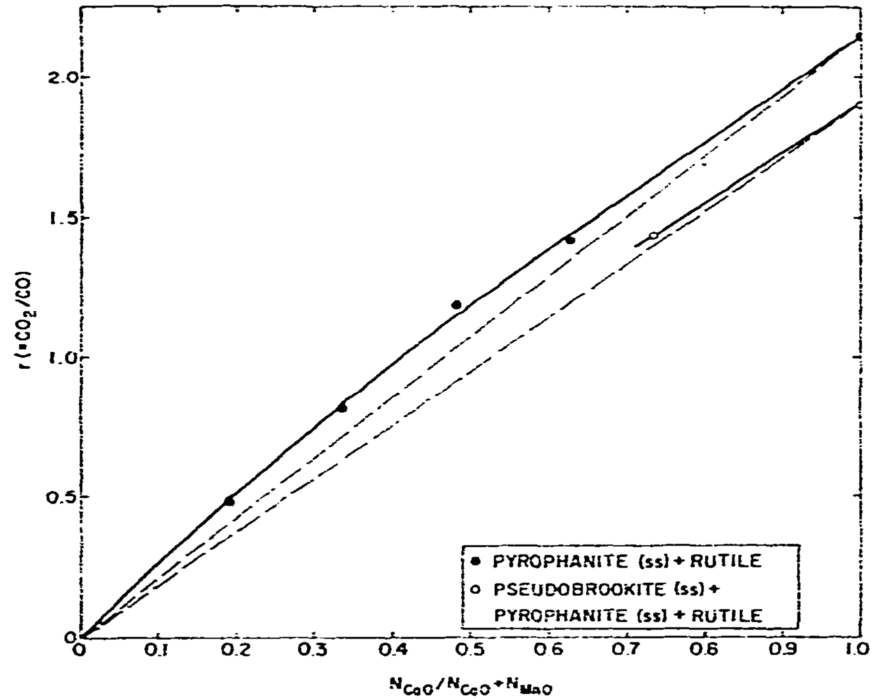

Fig. 6. Plot of CO_2/CO ratios (r) vs. composition for pyrophanite solid solutions (solid circles) and pseudobrookite solid solutions (open circles) in equilibrium with rutile and metallic cobalt in the system MnO–CoO–TiO_2 at 1250 °C.

Mn_2TiO_4, −7.6 kcal, this work; $CoTiO_3$, −3.4 kcal[1]), we obtain for the free energy of formation of $MnTiO_3$ from its oxide components according to the reaction

$$MnO + TiO_2 \rightleftharpoons MnTiO_3 \qquad (15)$$

a $\Delta G^0_{MnTiO_3}$-value of −7.0 kcal at 1250 °C.

Phase assemblage pseudobrookite solid solution + pyrophanite solid solution

Equilibrium data for this phase assemblage are listed in Table I and shown in the form of conjugation lines in Fig. 1. Values of log C $[C = (a_{CoTiO_3} \cdot N_{MnTi_2O_5})/(a_{MnTiO_3} \cdot N_{CoTi_2O_5})]$ as calculated for the reaction

$$(MnTiO_3) + (CoTi_2O_5) \rightleftharpoons (CoTiO_3) + (MnTi_2O_5) \qquad (16)$$

are shown in Fig. 7. The activities of $CoTiO_3$ and $MnTiO_3$ used in the expression for C were those determined from the rutile + pyrophanite equilibrium. The composition range of the pseudobrookite solid solution is too small, and the number of points obtained is too small, to permit a reliable and accurate description of the behavior of this solid solution. However, the C-values change very little with composition, and the data suggest that the pseudobrookite solid solution shows a very small positive deviation from ideality.

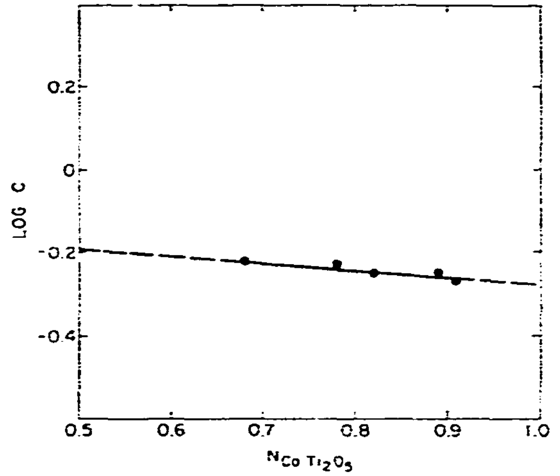

Fig. 7. Plot of log C *vs.* composition for coexistence of pseudobrookite and pyrophanite solid solutions in the system MnO–CoO–TiO_2 at 1250 °C.

The value of $\Delta(\Delta G^0)$ for Reaction (16) at 1250 °C is 1.3 kcal. Combination of this value with the known free energies of formation of the other components involved in Reaction (16) ($CoTiO_3$, −3.4 kcal[1]; $CoTi_2O_5$, −4.0 kcal[1]; $MnTiO_3$, −7.0 kcal, this work) gives for the free energy of formation of $MnTi_2O_5$ from its oxide components according to the equation

$$MnO + 2TiO_2 \rightleftharpoons MnTi_2O_5 \qquad (17)$$

a ΔG^0-value of −6.3 kcal at 1250 °C. Because of the long extrapolation involved, this figure is quite uncertain. The value is consistent with the observed instability of $MnTi_2O_5$ in the binary system MnO–TiO_2, inasmuch as the ΔG^0-value calculated for the reaction

$$MnTi_2O_5 \rightleftharpoons MnTiO_3 + TiO_2$$

is −0.7 kcal, based on the data obtained in the present investigation.

Phase assemblage rutile + pseudobrookite solid solution + pyrophanite solid solution

Results of equilibration runs involving this phase assemblage are included in Table I and in Fig. 6. The pseudobrookite phase of this assemblage is the end point of a solid-solution series starting at $CoTi_2O_5$ and extending part-way toward the hypothetical compound $MnTi_2O_5$. For this solution, we may write

$$(CoTi_2O_5) + Co \rightleftharpoons Co + 2TiO_2 + CO_2 \qquad (18)$$

and activities of $CoTi_2O_5$ are calculated from the expression

$$a_{CoTi_2O_5} = \frac{r}{r_0} \qquad (19)$$

where r and r_0 are the CO_2/CO ratios of the equilibrium above and of the equilibrium between $CoTi_2O_5$, TiO_2 and metallic cobalt in the binary system CoO–TiO_2, respectively. The composition range over which the pseudobrookite solution is stable is too small to derive accurately the properties of this solution, but the data suggest (see Fig. 6) that the solution has a small positive deviation from ideality, confirming the conclusion reached from the pyrophanite–pseudobrookite equilibrium (see preceding section).

The system MnO–NiO–TiO$_2$

Phase assemblage oxide solid solution + spinel solid solution

Results of equilibration runs for this phase assemblage are listed in Table III and shown in the form of conjugation lines in Fig. 2. Values of log C $[C = (a_{\mathrm{NiO}} \cdot N_{\mathrm{MnTi_{0.5}O_2}})/(a_{\mathrm{MnO}} \cdot N_{\mathrm{NiTi_{0.5}O_2}})$ for the reaction

$$(\mathrm{MnO}) + (\mathrm{NiTi_{0.5}O_2}) \rightleftharpoons (\mathrm{NiO}) + (\mathrm{MnTi_{0.5}O_2}) \qquad (20$$

TABLE III

EXPERIMENTALLY DETERMINED CO_2/CO RATIOS OF GAS PHASE IN EQUILIBRIUM WITH METALLIC NICKEL AND PAIRS OF OXIDIC PHASES IN THE SYSTEM MnO–NiO–TiO_2 AT 1250°C

Phase assemblage	*Composition of mixture (mol fraction)*			*r(= CO_2/CO)*
	MnO	*NiO*	*TiO$_2$*	
Spinel(ss) + oxide(ss)	0.57	0.12	0.31	11.6
	0.46	0.23	0.31	21.5
	0.41	0.28	0.31	26.1
	0.36	0.33	0.31	29.3
	0.32	0.37	0.31	31.3
	0.26	0.43	0.31	32.8
	0.18	0.51	0.31	34.2
	0.49	0.49	0.02	21.4
	0.27	0.71	0.02	26.5
Rutile + pyrophanite(ss)	0.13	0.20	0.67	13.7
	0.00	0.45	0.55	19.5
	0.39	0.09	0.52	6.0
	0.28	0.20	0.52	10.7
	0.15	0.33	0.52	15.2
	0.07	0.41	0.52	17.7
Pyrophanite(ss) + spinel(ss)	0.40	0.25	0.35	15.5
	0.32	0.33	0.35	21.1
	0.25	0.40	0.35	28.0
	0.18	0.47	0.35	33.6
Pyrophanite(ss) + spinel(ss) + oxide(ss)	0.12	0.53	0.35	34.2
Pyrophanite(ss) + oxide(ss)	0.04	0.48	0.48	34.5

as calculated from the above data are shown graphically in Fig. 8. Activity–composition relations for the spinel solid solution within its stability range, based on the

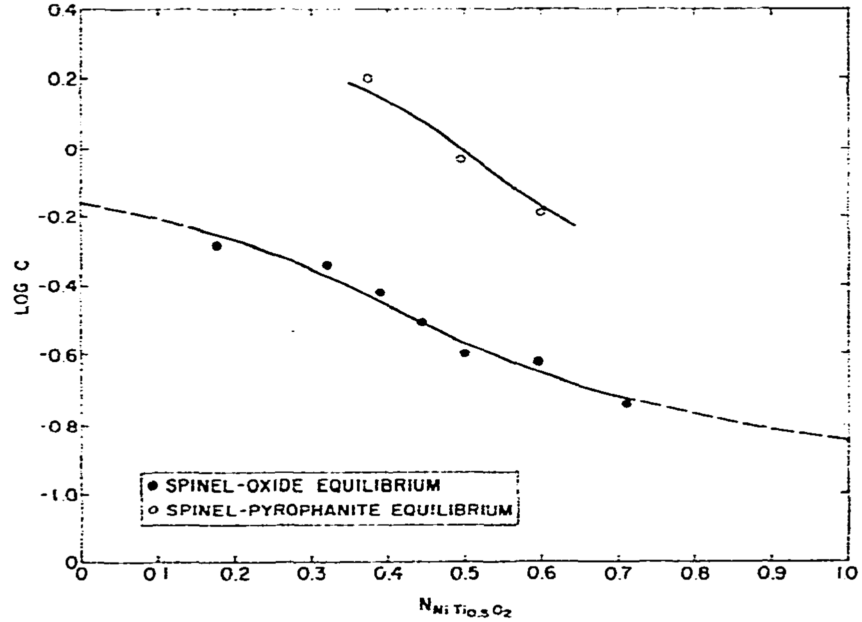

Fig. 8. Plot of log *C* *vs.* compsoition for the coexistence of spinel solid solutions with either oxide solid solutions (solid circles) or pyrophanite solid solutions (open circles) in the system MnO–NiO–TiO_2 at 1250°C.

analogues of Eqns. (5) and (6) (see p. 281) are illustrated in Fig. 9. The solution displays a considerable negative deviation from ideality. The value of $\Delta(\Delta G^0)$ for Reaction (20) is −3.6 kcal. Combination of this value with the previously determined ΔG^0-value for Mn_2TiO_4 at 1250°C (−7.6 kcal) from the MnO–CoO–TiO_2 equilibrium data gives a value of −0.5 kcal for the free energy of formation of Ni_2TiO_4 from its oxide components according to the reaction

$$2NiO+TiO_2 \rightleftharpoons Ni_2TiO_4 \tag{21}$$

This is in reasonable agreement with the value (−1.9 ±1.8 kcal) previously determined for this compound at 1400°C from equilibria in the system MgO–NiO–TiO_2[2] and with the value (−1.7 ±1.0 kcal) determined for this compound at 1050°C from equilibria in the system ZnO–NiO–TiO_2[10].

Phase assemblage rutile + pyrophanite solid solution

Results of equilibrations involving this phase assemblage are listed in Table III. For the equilibrium

$$(NiTiO_3)+CO \rightleftharpoons Ni+TiO_2+CO_2 \tag{22}$$

the activities of $NiTiO_3$ in the $MnTiO_3$–$NiTiO_3$ solid solution are calculated from the expression

$$a_{NiTiO_3} = \frac{r}{r_0} \tag{23}$$

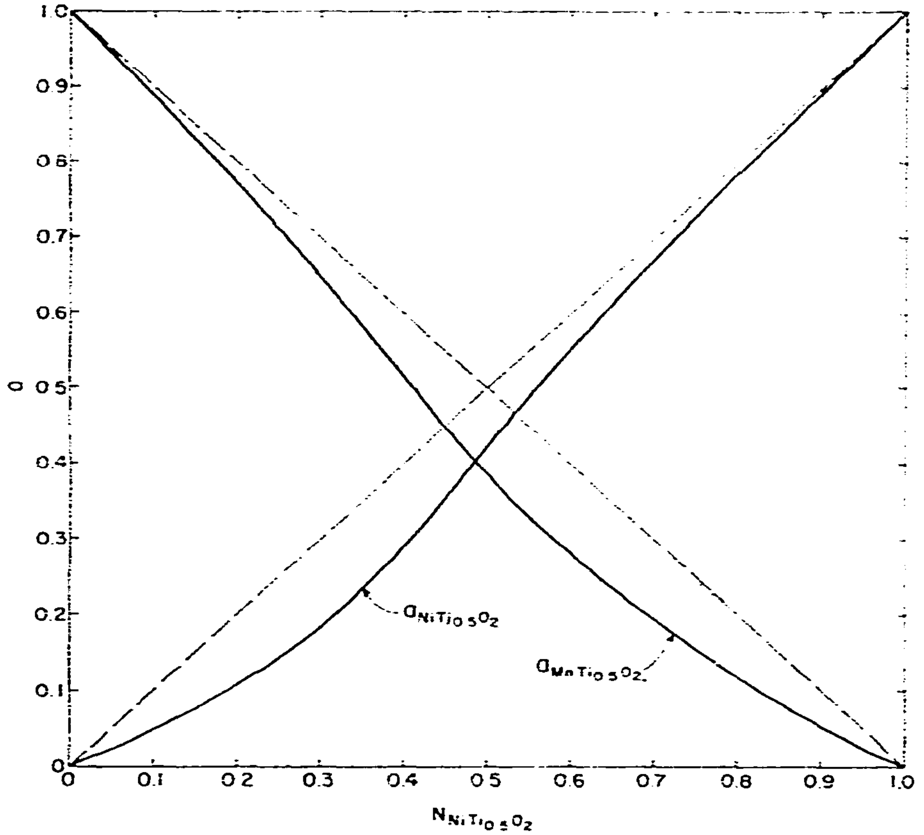

Fig. 9. Activity–composition relations along the spinel solid-solution series (Mn_2TiO_4–Ni_2TiO_4) in the system MnO–NiO–TiO_2 at 1250°C.

where r and r_0 are the CO_2/CO ratios of the equilibrium above, and of the equilibrium between $NiTiO_3$, TiO_2 and metallic nickel in the binary system NiO–TiO_2, respectively. Activity–composition relations along the $MnTiO_3$–$NiTiO_3$ join, as calculated on this basis, are illustrated graphically in Fig. 10. The system shows a considerable positive deviation from ideality.

Phase assemblage spinel + pyrophanite solid solution

The data for this phase assemblage may be used to check the consistency between the data for the spinel solid solution, as obtained from the oxide + spinel phase assemblage, and the data for the pyrophanite solid solution, as determined from the rutile + pyrophanite phase assemblage. Results of equilibration runs for a few mixtures having spinel and pyrophanite as the coexisting phases are listed in Table III and shown in the form of conjugation lines in Fig. 2. Values of log C [$C = (a_{NiTiO_3} \cdot N_{MnTi_{0.5}O_2})/(a_{MnTiO_3} \cdot N_{NiTi_{0.5}O_2})$] for the reaction

$$(MnTiO_3) + (NiTi_{0.5}O_2) \rightleftharpoons (NiTiO_3) + MnTi_{0.5}O_2) \tag{24}$$

as calculated from the above data are included in Fig. 8. In these calculations, the activity–composition relations used for the pyrophanite solid solution were those

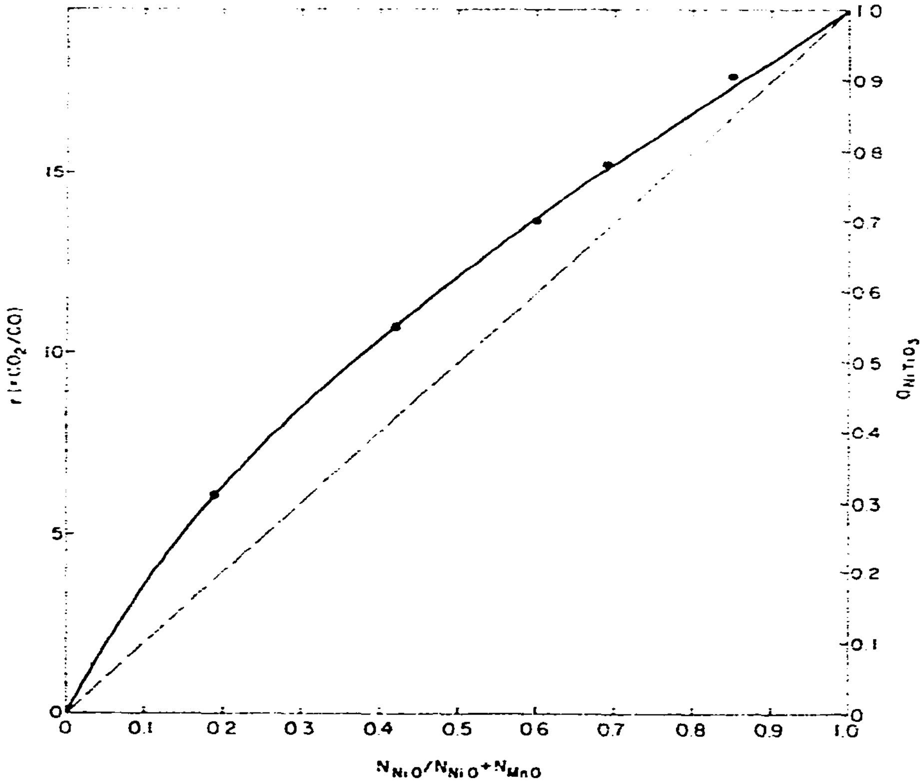

Fig. 10. Plot of CO_2/CO ratios (r) and activities of $NiTiO_3$ *vs.* composition for pyrophanite solid solutions in equilibrium with rutile and metallic nickel in the system $MnO-NiO-TiO_2$ at 1250°C.

determined from the rutile+pyrophanite equilibrium. Taking the value of log C at $N_{NiTi_{0.5}O_2} = N_{MnTi_{0.5}O_2} = 0.5$ as an approximate measure of $\Delta(\Delta G^0)$ for Reaction (24)[7], and using ΔG^0-values determined previously for the other species of Eqn. (24) ($MnTi_{0.5}O_2$, -3.8 kcal, this work; $NiTiO_3$, -2.3 kcal[2]; $MnTiO_3$, -7.0 kcal, this work), we calculate from this equilibrium a ΔG^0-value of -1.6 kcal for the formation of the hypothetical compound Ni_2TiO_4 from its end members at 1250°C. This is in excellent agreement with the data for this compound as obtained from the systems $MgO-NiO-TiO_2$[2] and $ZnO-NiO-TiO_2$[10], and in satisfactory agreement with the data obtained from the oxide+spinel equilibrium in the present work. The slope of the curves showing log C *vs.* composition in Fig. 8 is a measure of the deviation from ideality of the spinel solid solution. It is seen that the slopes of the two curves over the composition ranges studied for both equilibria are similar, and hence the limited data obtained for the spinel+pyrophanite equilibrium tend to confirm the negative deviation from ideality of the spinel solid solution and demonstrate the internal consistency of the data.

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