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ACTIVITY–COMPOSITION RELATIONS OF SOLID SOLUTIONS AND STABILITIES OF Mg_2TiO_4, $MgTiO_3$ AND $MgTi_2O_5$ AS DETERMINED FROM EQUILIBRIA IN THE SYSTEM MgO–CoO–TiO_2 AT 1300°C*

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ABSTRACT

Directions of conjugation lines between pairs of coexisting solid-solution phases in the system MgO–CoO–TiO_2 in contact with metallic Co at 1300°C are used to calculate activity–composition relations in the three solid-solution series Mg_2TiO_4–Co_2TiO_4, $MgTiO_3$–$CoTiO_3$ and $MgTi_2O_5$–$CoTi_2O_5$. Combinations of these data with known free energies of formation of the cobalt titanates Co_2TiO_4, $CoTiO_3$ and $CoTi_2O_5$ permit calculation of the free energies of formation of Mg_2TiO_4, $MgTiO_3$ and $MgTi_2O_5$ from their oxide components at 1300°C.

The Mg_2TiO_4–Co_2TiO_4 solid solution shows a slight positive deviation from ideality, the $(Mg,Co)TiO_3$ solid solution a slight negative deviation from ideality, and the $(Mg,Co)Ti_2O_5$ solid solution is practically ideal. The following free energies of formation were determined for the various magnesium titanates from their oxide components at 1300°C:

$$2MgO + TiO_2 \rightarrow Mg_2TiO_4 \quad \Delta G^0 = -5.1 \pm 0.5 \text{ kcal}$$
$$MgO + TiO_2 \rightarrow MgTiO_3 \quad \Delta G^0 = -4.8 \pm 1.0 \text{ kcal}$$
$$MgO + 2TiO_2 \rightarrow MgTi_2O_5 \quad \Delta G^0 = -6.8 \pm 1.0 \text{ kcal}$$

INTRODUCTION

The available free-energy data for the various magnesium titanates at elevated temperatures have been calculated from room-temperature heats of formation and entropy and specific-heat data[1]. The uncertainty limits of high-temperature data obtained by this method are relatively large, and it is desirable to develop methods by which these free-energy data can be calculated from equilibrium measurements carried out at elevated temperatures. Such experimental methods are not readily available for the magnesium titanates, because both oxide components (MgO and TiO_2) are very stable relative to their elements. However, experimental methods are

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readily available for determination of the stabilities of the analogous compounds of cobalt, Co_2TiO_4, $CoTiO_3$ and $CoTi_2O_5$[2]. The latter compounds form complete solid-solution series with the magnesium titanate analogues. A study of activity–composition relations in these solid solutions at elevated temperatures permit calculation of the free energies of formation of the magnesium titanates.

The 1300-°C isothermal section of the system MgO–CoO–TiO_2 is presented in Fig. 1, showing the four solid-solution series Mg_2TiO_4–Co_2TiO_4 (spinel), $MgTiO_3$–$CoTiO_3$ (geikielite), $MgTi_2O_5$–$CoTi_2O_5$ (pseudobrookite), and MgO–CoO (oxide). The latter solution has been shown[3] to be ideal at 1200 °C.

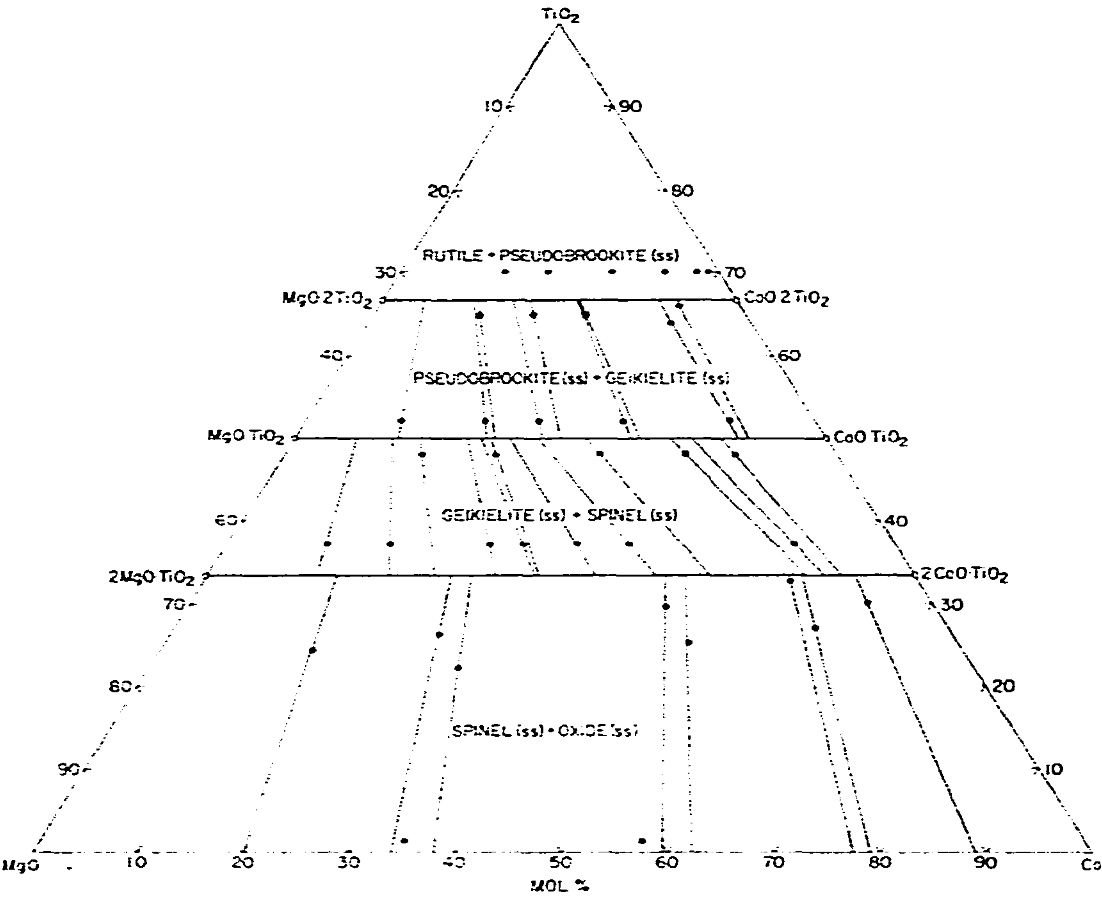

Fig. 1. Isothermal section of the system MgO–CoO–TiO_2 at 1300 °C, showing compositions of mixtures studied (solid dots), the solid-solution series occurring in the system, and experimentally determined conjugation lines (light lines) between coexisting solid-solution phases. The abbreviation ss denotes solid solution.

Free energies of formation of Co_2TiO_4 and $CoTiO_3$ from their oxide components were determined in the temperature range of 900–1200 °C by Taylor and Schmalzried[4], using EMF measurements involving ZrO_2–CaO solid electrolytes. Free energies of formation of Co_2TiO_4, $CoTiO_3$, and $CoTi_2O_5$ from their oxide components at 1300°C were determined recently by the present authors[2], using oxide–metal–gas equilibration techniques. The ΔG^0-values of Co_2TiO_4, $CoTiO_3$ and $CoTi_2O_5$ (from their oxide components) at 1300°C were found to be -5.6 kcal, -3.4 kcal and -4.2 kcal, respectively. Based on room-temperature data, Kelley[1] has reported the following free energies of formation of magnesium titanates from their oxide components at 1300°C: Mg_2TiO_4, -8.8 kcal; $MgTiO_3$, -6.1 kcal; $MgTi_2O_5$, -9.9 kcal.

The theoretical basis for evaluating activity–composition relations of solid solutions and free energies of formation of compounds from experimentally determined CO_2/CO ratios of a gas phase coexisting with metallic cobalt and selected pairs of solid-solution phases has been presented elsewhere[5–7]. 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. Using as an example the oxide+spinel equilibrium (see area I of Fig. 1) according to the equation

$$(CoO)+(MgTi_{0.5}O_2) \rightleftharpoons (MgO)+(CoTi_{0.5}O_2) \tag{1}$$

the activity coefficients γ of the spinel solid solution are determined from the expressions

$$\log \gamma_{CoTi_{0.5}O_2} = -N_{MgTi_{0.5}O_2} \log C + \int_0^{N_{MgTi_{0.5}O_2}} \log C \, dN_{MgTi_{0.5}O_2} \tag{2}$$

and

$$\log \gamma_{MgTi_{0.5}O_2} = (1-N_{MgTi_{0.5}O_2}) \log C + \int_{N_{MgTi_{0.5}O_2}}^{1} \log C \, dN_{MgTi_{0.5}O_2} \tag{3}$$

where the N's with appropriate subscripts are mol fractions and C is the quotient

$$C = \frac{a_{MgO} \cdot N_{CoTi_{0.5}O_2}}{a_{CoO} \cdot N_{MgTi_{0.5}O_2}} \tag{4}$$

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

$$(CoO)+(MgTi_{0.5}O_2) \rightleftharpoons (MgO)+(CoTi_{0.5}O_2) \tag{5}$$

is then calculated from the equation

$$-\frac{\Delta(\Delta G^0)}{2.303\,RT} = \log C + \log \gamma_{CoTi_{0.5}O_2} - \log \gamma_{MgTi_{0.5}O_2} \tag{6}$$

Here

$$\Delta(\Delta G^0) = \tfrac{1}{2}\Delta G^0_{Co_2TiO_4} - \tfrac{1}{2}\Delta G^0_{Mg_2TiO_4} \tag{7}$$

where $\Delta G^0_{Mg_2TiO_4}$ and $\Delta G^0_{Co_2TiO_4}$ are the free energies of formation of the compounds Mg_2TiO_4 and Co_2TiO_4, respectively, from their oxide components. Hence, if

$\Delta G^0_{Co_2TiO_4}$ is known, the value of $\Delta G^0_{Mg_2TiO_4}$ may be calculated from the above equilibrium.

Analogous expressions apply to the other equilibria dealt with in the present study.

EXPERIMENTAL METHODS

The experimental methods used are similar to those described previously[6, 8–10], and only specific details applicable to the present work will be discussed here.

Mixtures of desired compositions were sintered in air at 1350°C for 24 h. The mixtures were contained in Pt crucibles which had been presaturated with cobalt under the prevailing experimental conditions, in order to minimize loss of cobalt from the oxide phases during the heat treatment. Following this heat treatment, the mixtures were finely ground and pressed into pellets of 1 cm diameter and 0.5 cm height (compacting pressure ~ 10,000 psi). These pellets were then sintered in air at 1350°C for 15 h, in the same Pt crucibles as above. Each pellet was subsequently broken into several small pieces suitable for suspension with very thin (0.004 inch diameter) Pt wire in a vertical tube furnace for final equilibration experiments. The latter were carried out at constant temperature (1300°C) and chosen CO_2/CO ratios of the gas phase, and the equilibrated samples were quenched to room temperature and examined under the microscope for presence or absence of metallic cobalt as a phase. The following procedure was used to check attainment of equilibrium between the oxide phases and metallic cobalt: prereacted pellets of each mixture were suspended in the vertical quench furnace at 1300°C for 12 h at an oxygen pressure sufficiently low to cause precipitation of a small amount of metallic cobalt. Final equilibrations to establish the CO_2/CO ratios at which just a trace of metallic cobalt was present in each mixture were then made with two samples side by side in the furnace, one sample which had been prereduced to contain metallic cobalt, the other without metallic cobalt as a phase.

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[11].

RESULTS

Phase assemblage spinel solid solution + oxide solid solution

Results of equilibration runs for this phase assemblage are listed in Table I and shown graphically in Fig. 2. Conjugation lines constructed from these data are shown in Fig. 1, and calculated C-values ($C = \frac{a_{MgO} \cdot N_{CoTi_{0.5}O_2}}{a_{CoO} \cdot N_{MgTi_{0.5}O_2}}$) for the reaction

$$(CoO)+(MgTi_{0.5}O_2) \rightleftharpoons (MgO)+(CoTi_{0.5}O_2) \qquad (8)$$

are listed in Table I and shown graphically in Fig. 3.

TABLE I

RESULTS OF EQUILIBRATION RUNS FOR THE PHASE ASSEMBLAGE SPINEL SOLID SOLUTION + OXIDE SOLID SOLUTION IN THE SYSTEM $MgO–CoO–TiO_2$ AT 1300 °C

Composition of mixture (mol fraction)			*Composition of oxide phase*		*Composition of spinel phase*		*r(CO₂/CO)*	*log C*
MgO	*CoO*	*TiO_2*	N_{MgO}	N_{CoO}	$N_{MgTi_{0.5}O_2}$	$N_{CoTi_{0.5}O_2}$		
0.613	0.145	0.242	0.80	0.20	0.81	0.19	1.10	−0.03
0.483	0.255	0.262	0.66	0.34	0.66	0.34	1.95	0.00
0.485	0.293	0.222	0.62	0.38	0.62	0.38	2.20	0.00
0.253	0.452	0.295	0.40	0.60	0.35	0.65	3.45	0.09
0.254	0.494	0.252	0.38	0.62	0.32	0.68	3.50	0.11
0.120	0.555	0.325	0.22	0.78	0.17	0.83	4.50	0.14
0.125	0.605	0.270	0.21	0.79	0.15	0.85	4.60	0.18
0.060	0.640	0.300	0.11	0.89	0.08	0.92	5.15	0.15
	0.700	0.300		1.00		1.00	5.85	
[a]0.642	0.343	0.015	0.65	0.35			2.00	
[a]0.420	0.565	0.015	0.43	0.57			3.35	

[a] These mixtures are located close to the MgO–CoO join, and were used to establish that no appreciable amounts of TiO_2 dissolve in the oxide (MgO–CoO) solid solution, and that the activities of MgO and CoO are the same (within limits of experimental errors) as those for binary MgO–CoO mixtures of the same MgO/CoO ratios.

The MgO–CoO solid solution has been found previously[3] to be ideal. In view of the importance of this assumption as a starting point for the derivations in the present paper, these activity–composition relations were checked by the same method as used for the other solid-solution series of the present study. The ideality of the oxide solid solutions within the limits of experimental error was confirmed at 1150 °C. These data are listed in Table II.

TABLE II

RESULTS OF EQUILIBRATION RUNS FOR CHECKING OF ACTIVITY–COMPOSITION RELATIONS IN THE SYSTEM MgO–CoO AT 1150 °C

N_{CoO}	*r(CO₂/CO)*	a_{CoO}
0.35	3.16	0.35 ±0.01
0.50	4.40	0.49 ±0.01
0.58	5.35	0.58 ±0.04
1.00	9.06	1.00

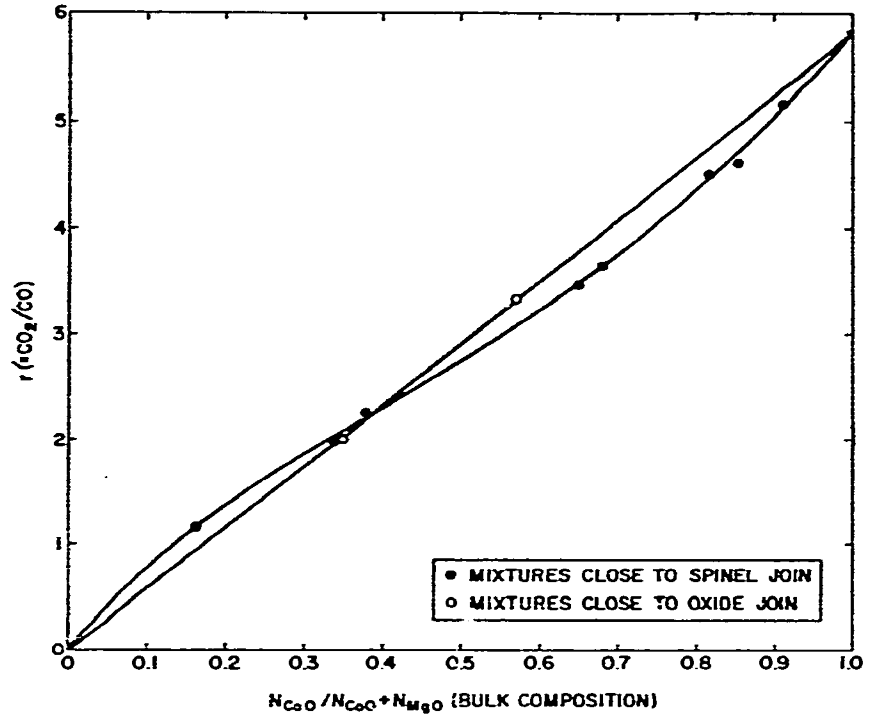

Fig. 2. Diagram showing CO_2/CO ratios at which spinel and oxide solid solutions coexist with metallic cobalt at 1300°C, as a function of composition.

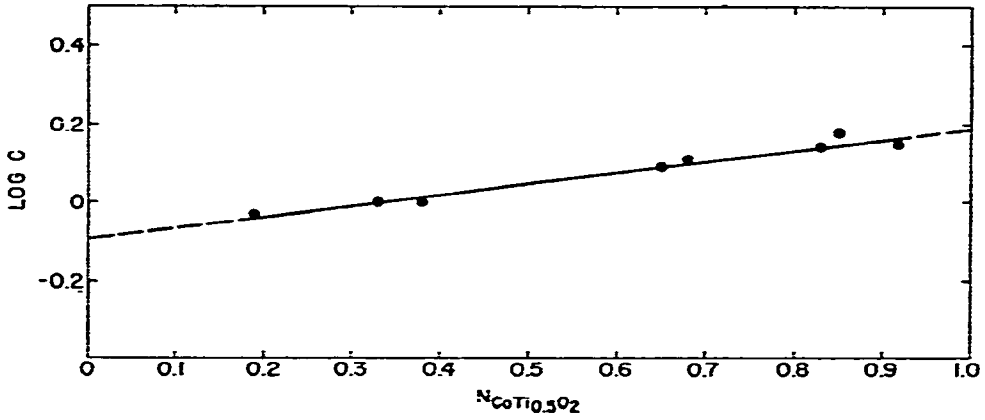

Fig. 3. Diagram showing values of log C ($C = \frac{a_{MgO} \cdot N_{CoTi_{0.5}O_2}}{a_{CoO} \cdot N_{MgTi_{0.5}O_2}}$), *vs.* composition for the coexistence of spinel and oxide solid solutions, in the presence of metallic cobalt, in the system MgO–CoO–TiO_2 at 1300°C.

Activity–composition relations in the Mg_2TiO_4–Co_2TiO_4 solid solution as derived by previously known equations (5–7) (compare p. 109) and the data of Table I are shown in Fig. 4. There is a slight positive deviation from ideality, although the deviation is not much larger than the estimated limits of experimental error. The value of $\Delta(\Delta G^0)$ is -0.25 kcal. Combining this value with the known

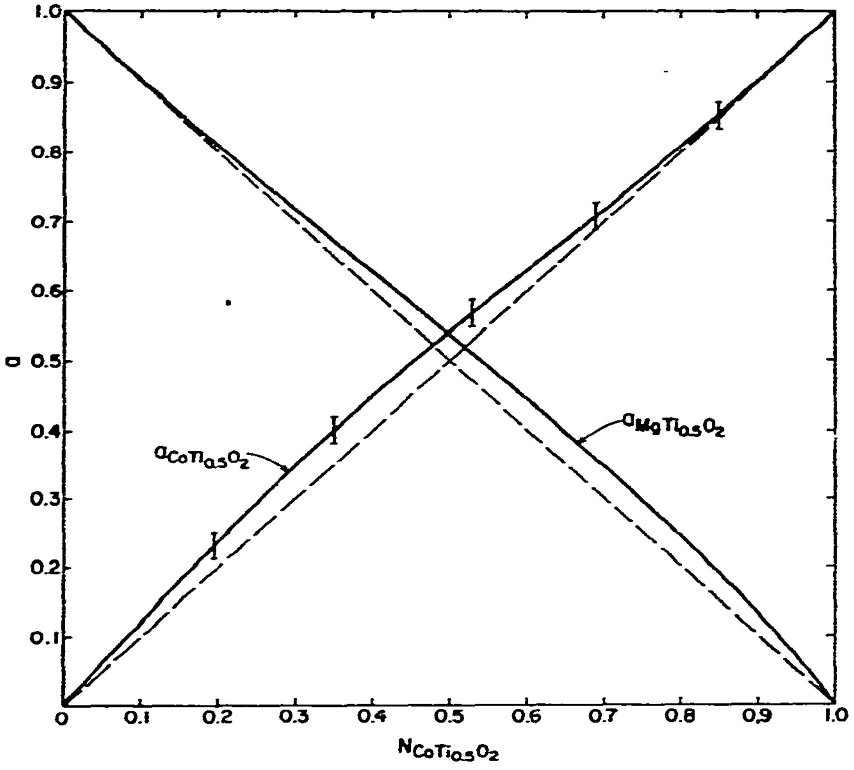

Fig. 4. Activity–composition relations along the spinel join in the system MgO–CoO–TiO_2 at 1300 °C. Vertical lines indicate estimated limits of error.

free energy of formation of Co_2TiO_4 from its oxide components (−5.6 kcal at 1300 °C[2]), we obtain for the reaction

$$2MgO + TiO_2 \rightarrow Mg_2TiO_4 \qquad (9)$$

at 1300 °C a ΔG^0-value of −5.1 ±0.5 kcal. This is considerably less negative than the value (−8.8 kcal) listed by Kelley[1]. Our new value is consistent with unpublished results obtained recently in our laboratory in studies of the systems MgO–NiO–TiO_2[12] and MgO–"FeO"–TiO_2[13].

Phase assemblage geikielite solid solution + spinel solid solution

Results of equilibration runs for this phase assemblage are listed in Table III and shown graphically in Fig. 5. Conjugation lines constructed from these data are shown in Fig. 1, and calculated C-values ($C = \frac{a_{MgTi_{0.5}O_2} \cdot N_{CoTiO_3}}{a_{CoTi_{0.5}O_2} \cdot N_{MgTiO_3}}$) for the reaction

$$(CoTi_{0.5}O_2) + (MgTiO_3) \rightleftharpoons (MgTi_{0.5}O_2) + (CoTiO_3) \qquad (10)$$

are listed in Table III and shown graphically in Fig. 6.

Activity–composition relations in the $MgTiO_3$–$CoTiO_3$ solid solution as derived from these data are shown as a dash-dot curve in Fig. 7. (Activity–composition relations along this join can also be calculated from the geikielite–pseudobrookite equilibrium, as described in a later section.) The value of $\Delta(\Delta G^0)$ is $+1.65$ kcal.

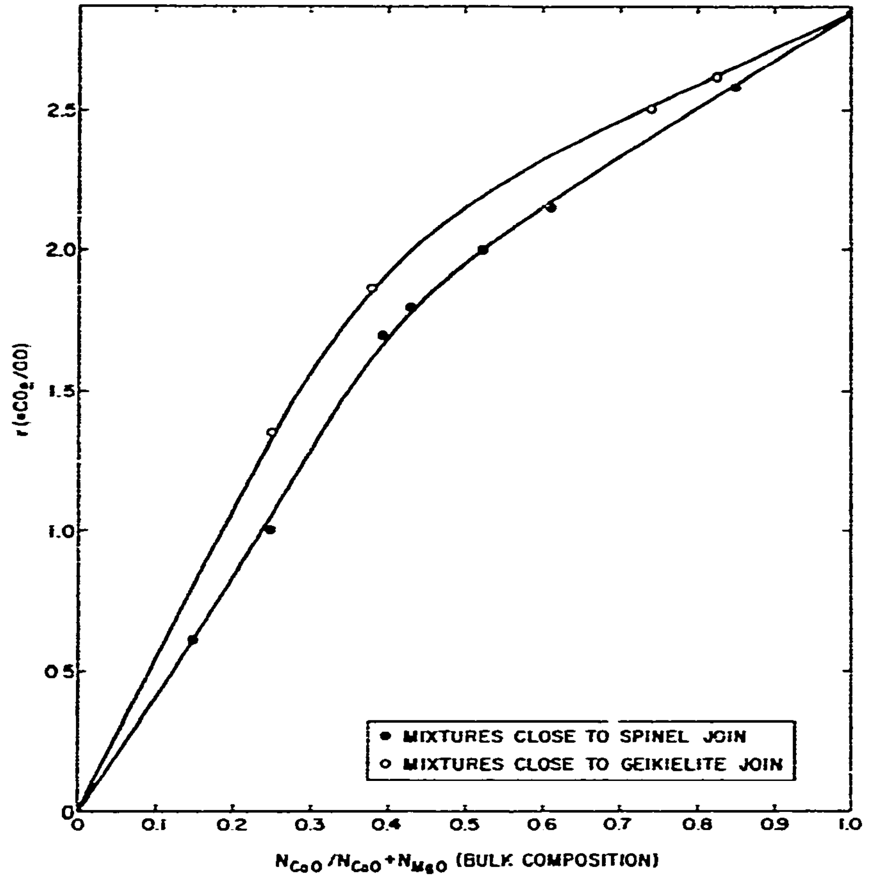

Fig. 5. Diagram showing CO_2/CO ratios at which geikielite and spinel solid solutions coexist with metallic cobalt at 1300 °C, as a function of composition.

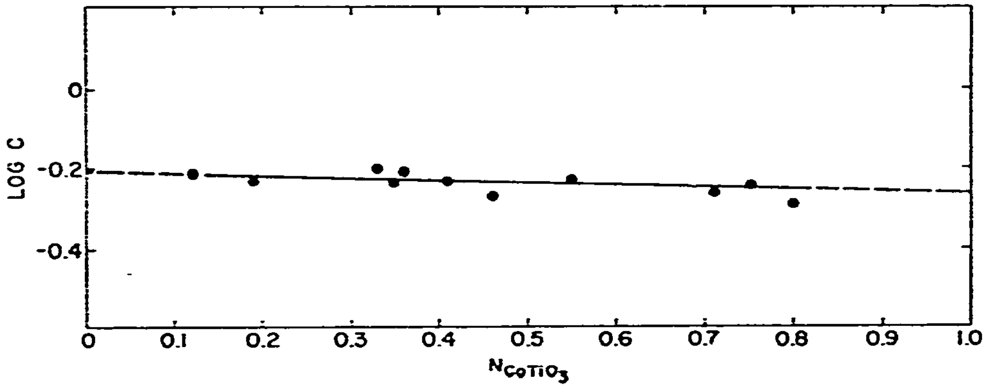

Fig. 6. Diagram showing values of log C ($C = \dfrac{a_{MgTi_{0.5}O_2} \cdot N_{CoTiO_3}}{a_{CoTi_{0.5}O_2} \cdot N_{MgTiO_3}}$) *vs.* composition for the coexistence of geikielite and spinel solid solutions, in the presence of metallic cobalt, in the system MgO–CoO–TiO_2 at 1300 °C.

Combination of this with the known free energies of formation of $CoTiO_3$, Co_2TiO_4, and Mg_2TiO_4 from their oxide components [−3.4[2], −5.6[2], and −5.1 kcal (this work), respectively] gives for the reaction

$$MgO + TiO_2 \rightarrow MgTiO_3 \tag{11}$$

a value of −4.8 kcal at 1300°C. The value at 1300°C as estimated by Kelley from low-temperature data is −6.1 kcal. Our new value is consistent with results obtained in our studies of the systems $MgO–NiO–TiO_2$[12] and MgO–"FeO"–TiO_2[13].

TABLE III

RESULTS OF EQUILIBRATION RUNS FOR THE PHASE ASSEMBLAGE GEIKIELITE SOLID SOLUTION + SPINEL SOLID SOLUTION IN THE SYSTEM $MgO–CoO–TiO_2$ AT 1300°C

Composition of mixture (mol fraction)			*Composition of spinel phase*		*Composition of geikielite phase*		$r(CO_2/CO)$	*log C*
MgO	*CoO*	TiO_2	$N_{MgTi_{0.5}O_2}$	$N_{CoTi_{0.5}O_2}$	N_{MgTiO_3}	N_{CoTiO_3}		
0.535	0.095	0.370	0.84	0.16	0.88	0.12	0.61	−0.21
0.475	0.155	0.370	0.74	0.26	0.81	0.19	1.00	−0.23
0.380	0.250	0.370	0.59	0.41	0.67	0.33	1.71	−0.20
0.350	0.280	0.370	0.53	0.47	0.65	0.35	1.80	−0.23
0.300	0.330	0.370	0.45	0.55	0.59	0.41	2.00	−0.23
0.250	0.380	0.370	0.37	0.63	0.54	0.46	2.15	−0.27
0.095	0.535	0.370	0.13	0.87	0.25	0.75	2.58	−0.24
0.390	0.130	0.480	0.68	0.32	0.76	0.24	1.35	−0.23
0.320	0.200	0.480	0.52	0.48	0.63	0.37	1.87	−0.21
0.220	0.300	0.480	0.29	0.71	0.45	0.55	2.30	−0.23
0.135	0.385	0.480	0.15	0.85	0.29	0.71	2.50	−0.26
0.095	0.425	0.480	0.09	0.91	0.20	0.80	2.62	−0.29
	0.520	0.480					2.85	

Phase assemblage rutile + pseudobrookite solid solutions

Results of equilibration runs involving this phase assemblage are listed in Table IV.

For the equilibrium

$$(CoTi_2O_5) + CO \rightleftharpoons Co + 2TiO_2 + CO_2 \tag{12}$$

the activities of $CoTi_2O_5$ are calculated from the expression

$$a_{CoTi_2O_5} = \frac{r}{r_0} \tag{13}$$

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. Activities of $CoTi_2O_5$ along the $MgTi_2O_5–CoTi_2O_5$ join as calculated on this

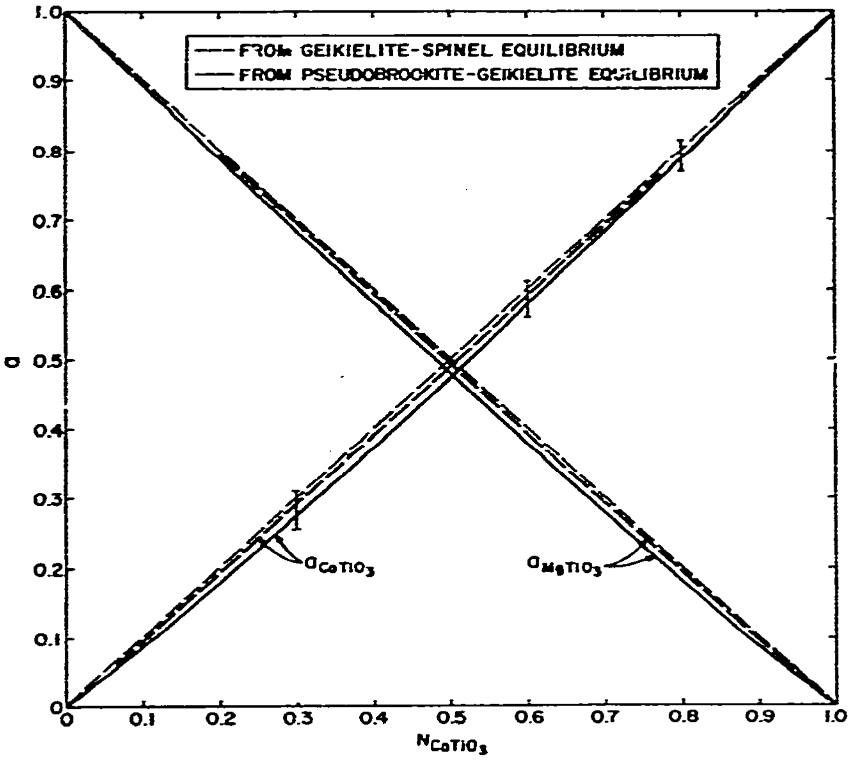

Fig. 7. Activity–composition relations along the geikielite join in the system $MgO–CoO–TiO_2$ at 1300°C. The heavy dash curves represent data obtained from the geikielite+spinel equilibrium, heavy solid curves represent data obtained from the pseudobrookite+geikielite equilibrium, and the light dash curves represent relations according to Raoult's law. Vertical lines indicate estimated limits of error.

basis are listed in Table IV and plotted in Fig. 8. It is seen that the activity–composition curve is ideal, within the estimated limits of error.

TABLE IV

RESULTS OF EQUILIBRATION RUNS FOR THE PHASE ASSEMBLAGE RUTILE + PSEUDOBROOKITE SOLID SOLUTION IN THE SYSTEM $MgO–CoO–TiO_2$ AT 1300°C

Composition of mixture (mol fraction)			$\frac{N_{CoO}}{N_{CoO}+N_{MgO}}$	$r(CO_2/CO)$	$a_{CoTi_2O_5}$
N_{MgO}	N_{CoO}	N_{TiO_2}			
0.202	0.098	0.70	0.33	0.51	0.33
0.16	0.14	0.70	0.47	0.68	0.44
0.10	0.20	0.70	0.67	1.00	0.65
0.05	0.25	0.70	0.83	1.28	0.83
0.02	0.28	0.70	0.93	1.42	0.93
0.01	0.29	0.70	0.97	1.50	0.98
	0.30	0.70	1.00	1.54	1.00

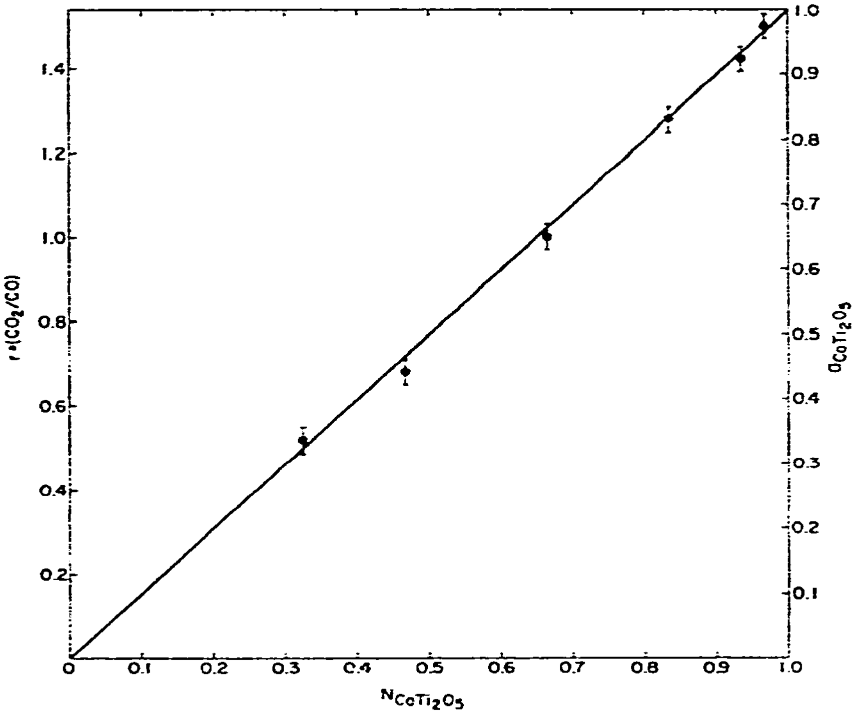

Fig. 8. Activity–composition relations along the pseudobrookite join of the system MgO–CoO–TiO_2 at 1300°C. Vertical lines indicate estimated limits of error.

Phase assemblage pseudobrookite solid solution + geikielite solid solution

Results of equilibration runs for this phase assemblage are listed in Table V and shown graphically in Fig. 9. Conjugation lines constructed from these data are shown in Fig. 1, and values of C ($C = \frac{a_{MgTi_2O_5} \cdot N_{CoTiO_3}}{a_{CoTi_2O_5} \cdot N_{MgTiO_3}}$) for the reaction

$$(CoTi_2O_5) + (MgTiO_3) \rightleftharpoons (MgTi_2O_5) + (CoTiO_3) \qquad (14)$$

are listed in Table V and shown graphically in Fig. 10.

Activity–composition relations in the $MgTiO_3$–$CoTiO_3$ solid solution as derived from these data are shown as part of Fig. 7 (heavy solid curve).

The agreement between the data obtained from the pseudobrookite + geikielite equilibrium and the previous data obtained from the spinel + geikielite equilibrium is quite satisfactory, considering that two equilibration steps are involved in each case (rutile to pseudobrookite to geikielite in the former case, oxide to spinel to geikielite in the latter case), and considering that there may be a slight amount of ternary solubility to either side of the solid-solution series involved. A slight negative deviation from ideality along this join is suggested by the data, although the degree of negative deviation is within the estimated limits of experimental error. The value of $\Delta(\Delta G^0)$ is -1.2 kcal. Combination of this with the known free energies of formation of

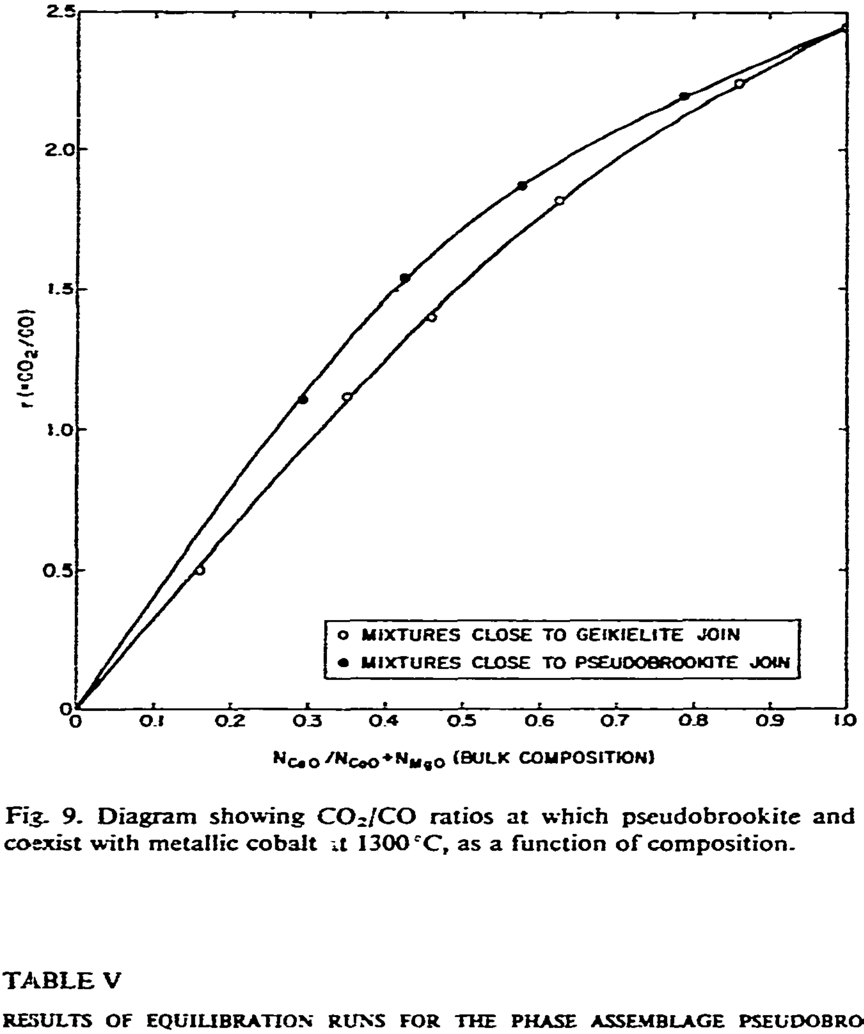

Fig. 9. Diagram showing CO_2/CO ratios at which pseudobrookite and geikielite solid solutions coexist with metallic cobalt at 1300°C, as a function of composition.

TABLE V

RESULTS OF EQUILIBRATION RUNS FOR THE PHASE ASSEMBLAGE PSEUDOBROOKITE SOLID SOLUTION + GEIKIELITE SOLID SOLUTION IN THE SYSTEM $MgO–CoO–TiO_2$ AT 1300°C

Composition of mixture (mol fraction)			*Composition of pseudobrookite phase*		*Composition of geikielite phase*		*r(CO₂/CO)*	*log C*
MgO	*CoO*	*TiO₂*	$N_{MgTi_2O_5}$	$N_{CoTi_2O_5}$	N_{MgTiO_3}	N_{CoTiO_3}		
0.39	0.09	0.52	0.88	0.12	0.81	0.19	0.50	0.24
0.31	0.17	0.52	0.73	0.27	0.64	0.36	1.12	0.18
0.26	0.22	0.52	0.63	0.37	0.53	0.47	1.40	0.18
0.18	0.30	0.52	0.44	0.56	0.37	0.63	1.86	0.13
0.08	0.40	0.52	0.19	0.81	0.16	0.84	2.25	0.09
0.25	0.10	0.65	0.72	0.28	0.62	0.38	1.11	0.20
0.20	0.15	0.65	0.59	0.41	0.50	0.50	1.55	0.16
0.15	0.20	0.65	0.43	0.57	0.35	0.65	1.88	0.13
0.075	0.285	0.64	0.22	0.78	0.16	0.84	2.20	0.17
0.055	0.285	0.66	0.16	0.84	0.14	0.86	2.24	0.07
	0.36	0.64					2.44	

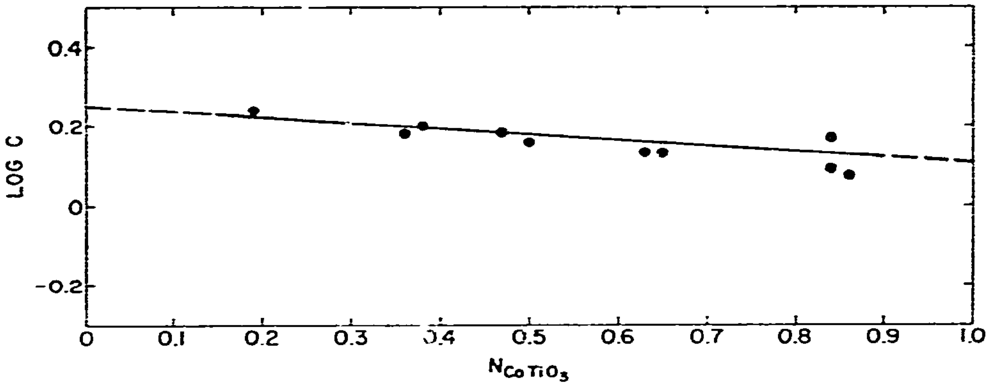

Fig. 10. Diagram showing values of log C ($C = \frac{a_{MgTi_2O_5} \cdot N_{CoTiO_3}}{a_{CoTi_2O_5} \cdot N_{MgTiO_3}}$) *vs.* composition for the coexistence of pseudobrookite and geikielite solid solutions, in the presence of metallic cobalt, in the system MgO–CoO–TiO_2 at 1300°C.

$CoTiO_3$, $MgTiO_3$, and $CoTi_2O_5$ from their oxide components [−3.4 kcal[2], −4.8 kcal (this work) and −4.2 kcal[2], respectively] gives for the reaction

$$MgO + 2TiO_2 \rightarrow MgTi_2O_5 \qquad (15)$$

at 1300°C a ΔG^0-value of −6.8 kcal. This is considerably less negative than the value (−9.9 kcal) estimated by Kelley[1] from room-temperature calorimetric data. Data obtained in studies of the systems MgO–NiO–TiO_2[12] and MgO–"FeO"–TiO_2[13] in our laboratory confirm the revised ΔG^0-value for the $MgTi_2O^5$ phase.

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