American Mineralogist, Volume 72, pages 280–291, 1987

Free energies of formation of NiO, CoO, Ni_2SiO_4, and Co_2SiO_4

HUGH ST. C. O'NEILL*
Research School of Earth Sciences, Australian National University, Canberra, Australia

ABSTRACT

The chemical potentials of oxygen defined by the reactions

$$2Ni + O_2 = 2NiO$$
$$2Co + O_2 = 2CoO$$
$$2Ni + SiO_2 + O_2 = Ni_2SiO_{4(olivine)}$$
$$2Co + SiO_2\ ;+ O_2 = Co_2SiO_{4(olivine)}$$

have been measured using an electrochemical technique. The results are (μ_{O_2} in J·mol^{-1}, T in kelvins)

for Ni + NiO,

$$\mu_{O_2}\,(\pm 120) = -480\,104 + 244.700T - 9.167T \ln T \qquad (800 < T < 1420),$$

for Co + CoO,

$$\mu_{O_2}\,(\pm 120) = -491\,649 + 508.527T - 53.284T \ln T + 0.025\,18T^2 \qquad (800 < T < 1397),$$

for $Co_2SiO_4 + Co + SiO_{2(qz)}$,

$$\mu_{O_2}\,(\pm 130) = -491\,141 + 122.815T + 3.5527T \ln T \qquad (960 < T < 1397),$$

for $Ni_2SiO_4 + Ni + SiO_{2(qz)}$,

$$\mu_{O_2}\,(\pm 180) = -516\,690 + 362.97T - 22.297T \ln T \qquad (960 < T < 1820),$$

where the given uncertainties are plus or minus one standard deviation.

For all the equilibria except $Ni_2SiO_4 + Ni + SiO_2$, the results are in excellent agreement with the calorimetric data. Ni_2SiO_4 breaks down to NiO + SiO_2 (cristobalite = crs) at 1820 ± 5 K. Since for the two equilibria involving SiO_2 both quartz (qz) and cristobalite were used, some information is also given for the reaction

$$SiO_{2(qz)} = SiO_{2(crs)}.$$

INTRODUCTION

Ni and Co are both compatible trace elements, in that they readily substitute for Mg and Fe^{2+} in common rock-forming silicates, and both are siderophile (that is, they are easily reduced to the metallic state and incorporated into Fe-rich metal). The combination of these properties makes Ni and Co important in understanding some of the processes involved in the formation and evolution of the terrestrial planets and meteorite parent bodies, in particular the segregation of metal and the consequent formation of planetary cores. In the accessible regions of the terrestrial planets and in the unreduced portion of meteorites, most of the Ni and Co occur in olivine, $(Mg,Fe^{2+})_2SiO_4$, as the components Ni_2SiO_4 and Co_2SiO_4, which are the only binary phases found in the systems NiO-SiO_2 and CoO-SiO_2 at atmospheric pressure.

The aim of this paper is to provide a sound thermodynamic basis for the description of the reduction of Ni and Co by measuring the chemical potential of oxygen defined by the reactions

$$2Ni + O_2 = 2NiO \tag{1}$$
$$2Co + O_2 = 2CoO \tag{2}$$
$$2Ni + SiO_2 + O_2 = Ni_2SiO_4 \tag{3}$$
$$2Co + SiO_2 + O_2 = Co_2SiO_4 \tag{4}$$

using an electrochemical method with calcia-stabilized zirconia (CSZ) as an oxygen-specific electrolyte.

With the recent measurements on the heat capacities of Ni_2SiO_4 and Co_2SiO_4 from 5 to 1000 K (Robie et al., 1982, 1984), there now exist accurate calorimetric data for all substances in Reactions 1 to 4, which may be used to provide a check on the consistency of the experimental determinations of these reactions. Most of the previous work is in fact not very consistent with the calorimetric

---

* Present address: C.R.A. Research, P.O. Box 42, Boolaroo, N.S.W. 2284, Australia.

0003–004X/87/0304–0280$02.00

data. There are, moreover, considerable differences between many of the previous studies, and it is not always apparent which, if any, of these are to be preferred. Accurate calibration of Ni + NiO and Co + CoO is particularly desirable as these equilibria have been widely used as oxygen buffers in the double-capsule technique in hydrothermal experiments (Eugster, 1957), and as reference electrodes in electrochemical experiments, and therefore bear on a large body of other data. The Ni + NiO equilibrium has also often been used as a calibrant or a check in gas-mixing furnaces or in H_2-membrane experiments. Earlier work on the Ni + NiO and Co + CoO equilibria from this laboratory using a similar electrochemical technique but with air as the reference has been reported by Holmes et al. (1986); the present results, although being in good agreement with those of Holmes et al., are believed to be slightly more accurate.

EXPERIMENTAL METHOD AND STRATEGY

A full description of the method, apparatus, and procedure used in this study is given in O'Neill (1987), together with a discussion of some of the potential errors involved. Briefly, an electrochemical cell is constructed consisting of two electrodes, A and B, each defining chemical potential oxygen, $\mu^A_{O_2}$ and $\mu^B_{O_2}$, separated by the oxygen-specific electrolyte calcia-stabilized zirconia (CSZ). Under ideal conditions (e.g., zero electronic conductivity) the open-circuit emf, *E*, developed by such a cell is related to the difference in μ_{O_2} between the two electrodes by

$$4FE = \mu^B_{O_2} - \mu^A_{O_2}$$

where *F* is the Faraday constant (96 484.56 coulomb·mol^{-1}).

As the method measures the difference between the chemical potentials of the two electrodes, one, with known μ_{O_2}, must be chosen as a reference. Since one of the potential problems in the method is the possible transfer of oxygen from the electrode with the higher μ_{O_2} to the electrode with the lower—whether by small amounts of electronic conductivity or by other causes such as permeability of the electrolyte—it is desirable to bracket the unknown by doing two sets of experiments, one with a reference electrode with higher μ_{O_2}, and another with a lower. In this study, Fe + "FeO" mixtures were used for the lower μ_{O_2} reference electrode; for the determination of the Ni + NiO equilibrium, Cu + Cu_2O was used as the higher μ_{O_2} reference electrode. The μ_{O_2} values defined by the Fe + "FeO" and the Cu + Cu_2O equilibria have been recently redetermined to a high degree of accuracy in this laboratory (O'Neill, in prep.) using air (the μ_{O_2} of which is of course precisely and independently known) as the reference electrode and have been taken to be (in J·mol^{-1}; *T* in kelvins) for Fe + "FeO" (±90)

$$-605\,812 + 1366.718T - 182.7955T\ln T + 0.103\,592T^2 \quad (833 < T < 1042)$$

$$-519\,357 + 59.427T + 8.9276T\ln T \quad (1042 < T < 1184)$$

$$-551\,159 + 259.404T - 16.9484T\ln T \quad (1184 < T < 1450)$$

and for Cu + Cu_2O (±40)

$$-347\,705 + 246.096T - 12.9053T\ln T \quad (750 < T < 1330)$$

The reference pressure for oxygen is 1 bar (10^5 Pa), and the uncertainty given in parentheses is one standard deviation. These values are in good agreement with the earlier results from this laboratory of Holmes et al. (1986).

As a check on the consistency of the above data, the emf's of cells with Cu + Cu_2O as the sample electrode and Fe + "FeO" as the reference, and vice versa, were measured with completely satisfactory results (i.e., agreement to within ±100 J·mol^{-1}). The distinction between the "sample" and "reference" electrodes is somewhat artificial, but follows from the particular experimental arrangement used (see Fig. 1 in O'Neill, 1987).

There are two reasons why air was not further used as a reference electrode.

1. The high μ_{O_2} of air and its high oxygen content exacerbates the problem of polarization caused by oxygen transfer into the sample either from the finite electronic conductivity or permeability of the CSZ electrolyte. The more reactive the sample, the less the problem. Some experiments by Worrell and Iskoe (1973) have shown that the overvoltages produced by passing a small current through a symmetrical cell of the type

$$M + MO_x|CSZ|M + MO_x$$

decrease by approximately an order of magnitude at any one temperature in the order M = Cu < Fe < Ni. Similar experiments by Iwase et al. (1981) show that the Mo + MoO_2 electrode polarizes even more than Ni + NiO, and it is surely to be expected that a three-phase mixture involving silicates would be very much less reactive than these simple two-phase metal + metal oxide mixtures. Thus it is hoped that, by choosing the two most reactive metal + metal oxide mixtures available (i.e., Cu + Cu_2O and Fe + "FeO") for the primary experiments against air, this problem may be minimized.

2. The μ_{O_2} vs. *T* slope of air is very different from that of most solid oxygen buffers, most of which (all, in this study) have quite similar slopes. Hence, if a suitable metal + metal oxide mixture is used as the reference electrode, any absolute error in temperature measurement translates into a much smaller error in the μ_{O_2} of the unknown than if air were the reference.

Although the Cu + Cu_2O electrode appears to be the most reactive solid reference electrode available and is also the most precisely known, it does have some disadvantages. Most importantly, the eutectic melting temperature of Cu + Cu_2O is relatively low (~1330 K). Molten mixtures cannot be used as reference electrodes in the present apparatus, as they combine rapidly with the Pt lead wires, which not only contaminates the electrode, but may also break the electrical circuit. In addition, the spring loading of the electrode against the electrolyte (see Fig. 1 in O'Neill, 1987) would squeeze out any liquid material, disrupting the cell. However, it is at these higher temperatures that oxygen transfer is observed to become a problem, and consequently where it is particularly desirable to bracket the unknown by measurements against electrodes with both higher and lower μ_{O_2} values. Hence, after determining the μ_{O_2} of the Ni + NiO equilibrium against both Fe + "FeO" and Cu + CuO, Ni + NiO was thereafter used as the higher-μ_{O_2} reference electrode for the other reactions. Also Cu + Cu_2O invariably sticks to the electrolyte tube, and although there is no evidence of any chemical reaction (the Cu + Cu_2O may be cleaned off with acid), this does mean that the tube often breaks on taking the cell apart and so cannot be used again. Ni + NiO never sticks, and Fe + "FeO" only rarely, when evidence of oxidation is present.

EXPERIMENTAL DETAILS

Materials

The metal–metal oxide electrodes were made from mixtures of Cu and Cu_2O, Fe and "FeO," Ni and NiO, and Co and CoO in the molar ratio 3:1. Cu_2O was prepared from Cu and CuO and "FeO" from Fe and Fe_2O_3, mixed in almost the appropriate ratio but with a slight excess of metal, and sintered at 1000°C for ~16 h under a flowing stream of Ar, which was purified by passing successively over activated charcoal, phosphorus pentoxide, and Ti chips at 800°C. CoO was prepared from Co_3O_4 by heating at 1000°C under a flowing stream of unpurified Ar for ~16 h. NiO was sintered in air at 1000°C for ~16 h. The metals were used as supplied, in the powder form with grain size less than 20 μm. All reagents were stated by the manufacturers to be of 99.9% purity or greater, with the exception of Fe and Co metals, which were 99.5%.

Two forms of SiO_2 were used: quartz from a large natural crystal of gem quality, with no inclusions visible under the optical microscope; and cristobalite from amorphous $SiO_2 \cdot xH_2O$, sintered in air at 1550°C for 3 d.

Co_2SiO_4 olivine was synthesized from Co_3O_4 and amorphous SiO_2, dried at 700°C, by sintering in air for 1 d at 1200°C, grinding under acetone, and sintering again for 3 d at 1200°C. This treatment gave pure olivine, with no excess CoO or SiO_2 detectable either by X-ray diffraction or optical examination. This material was used for all the runs (with both quartz and cristobalite) using Fe + "FeO" as the reference electrode, but unfortunately was entirely used up in the process; therefore, for the run with the Ni + NiO reference electrode, some Co_2SiO_4 from the stock of substances that exist in this laboratory was used. It was made at 1330°C, other conditions unknown, and contained about 2% excess CoO.

Ni_2SiO_4 olivine proved rather difficult to synthesize. Attempts using NiO and dried amorphous SiO_2 never reacted completely, even at 1500°C for 1 week with one intermediate grinding. However, a gel method using $Ni(NO_3)_2 \cdot 6H_2O$ and tetraethyl orthosilicate proved very successful. The gel was sintered at 1500°C for 2 d, and the final product contained a very small amount of excess SiO_2 in the form of cristobalite. This material was used for run Ni-OL 1. For all the other runs, Ni_2SiO_4 commercially supplied by Tem-Pres was used. The conditions of synthesis are unknown.

Performance of the electrochemical cells

The cells involving metal–metal oxide equilibria alone came rapidly to equilibrium, with the recorded emf generally being within ±5 mV of the final value as soon as the initial temperature was reached. These cells were then left at the initial temperature for about 24 h before the first reading was recorded, by which time the emf had been observed to be stable to within ±0.2 mV and with no detectable drift for at least 12 h. Thereafter the emf generally changed almost instantaneously to the new equilibrium value on increasing temperature, and within a few hours on decreasing temperature. The lower temperature limit above which the cells were found to operate satisfactorily was about 800 K; below this temperature, the resistance of the cells becomes high comparable to the impedance of the measuring device. At high temperatures, the emf of the cell may be observed to decrease slowly but inexorably with time; this normally does not occur below about 1250–1350 K, the actual temperature limit varying from run to run. Hence, readings at these higher temperatures were taken as rapidly as possible, and when any untoward decrease of emf with time was noted, either the temperature was lowered or the run abandoned.

The cells used to measure the Co_2SiO_4 + Co + SiO_2 equilibrium behaved similarly, except that rather longer was needed to reach equilibrium initially, and stable emf's could not be achieved below ~950 K. For the run with Ni + NiO as the reference electrode, in which the Co_2SiO_4 contained some excess CoO, the emf initially reached a plateau corresponding to the Co + CoO equilibrium, at which it stayed for ~5 h before increasing fairly rapidly to the final value, which was achieved in a total of ~36 h.

The behavior of the various Ni_2SiO_4-containing cells differed markedly according to the provenance of the Ni_2SiO_4. The cells using Ni_2SiO_4 commercially supplied by Tem-Pres achieved equilibrium quite rapidly and generally performed similarly to those with Co_2SiO_4. Those with Ni_2SiO_4 made from a gel approached equilibrium very slowly, and reasonable results could not be obtained below 1150 K, the apparent μ_{O_2} being anomalously low (i.e., more reducing) at lower temperatures. Attempts using Ni_2SiO_4 made from NiO and amorphous SiO_2 (which was known to be incompletely reacted) also gave anomalously low μ_{O_2} values, which is opposite to the effect that might be expected if the μ_{O_2} were buffered by NiO + Ni. The emf's from these cells were very unsteady, in marked contrast to all other cells used in this study, and hence no attempt was made to record any data from them.

Equilibrium was demonstrated by (1) obtaining data after both increasing and decreasing temperature, (2) passing a small current through the cell, (3) evacuating one or other of the electrode compartments and filling with an oxidizing or reducing gas such as air or Ar + CH_4, before refilling with purified Ar.

Especially at lower temperatures, the cell sometimes does not return to equilibrium after procedure 3, which was therefore used sparingly, and only toward the end of the run.

Temperatures were measured to ±0.1 K with Pt-$Pt_{90}Rh_{10}$ thermocouples calibrated against the melting point of Au using the IPTS-68 scale. Temperatures are reported to the nearest degree to allow for errors in calibration and measurement. The cell emf's were measured to ±0.01 mV, and have been reported to the nearest 0.1 mV. The performance of all cell assemblies was checked by measuring the emf of symmetrical cells of the type

$$\text{Pt, M} + \text{MO}_x|\text{CSZ}|\text{M} + \text{MO}_x\text{, Pt,}$$

where M = Fe, Cu, or Ni. These emf values were confirmed to be effectively zero (<0.2 mV) for all cells except those involving Cu + Cu_2O; these latter showed small (<1.0 mV), reproducible emf's which were thought to be due to incorrect positioning of the cell in the constant temperature zone of the furnace. Since, to a first approximation, such thermoelectric emf's are expected to be independent of the composition of the sample electrode, they were subtracted from the final readings obtained with the Cu + Cu_2O cells. In writing cell assemblages, the convention has been adopted of putting the sample electrode on the left-hand side and the reference on the right; to avoid confusion, all cell emf's have therefore been reported without +ve or −ve signs, the actual polarity of the cells being in all cases obvious.

RESULTS

Ni + NiO

It was felt to be particularly important that the measurements on the Ni + NiO equilibrium should be as accurate and reliable as possible because Ni + NiO was subsequently used as a reference electrode for the determinations of the three other reactions in this work. Therefore, three types of cells were studied:

$$\text{Pt, Ni} + \text{NiO}|\text{CSZ}|\text{Cu} + \text{Cu}_2\text{O, Pt} \qquad \text{(I)}$$

$$\text{Pt, Ni} + \text{NiO}|\text{CSZ}|\text{Fe} + \text{“FeO”, Pt} \qquad \text{(II)}$$

$$\text{Pt, Fe} + \text{“FeO”}|\text{CSZ}|\text{Ni} + \text{NiO, Pt.} \qquad \text{(III)}$$

TABLE 1. Results from the cells used to measure the free energy of formation of NiO

T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)
NiO 1: Ni + NiO vs. Fe + "FeO"							
884	243.8	932	249.5	1007	258.8	1332	291.7
901	245.8	948	251.3	1034	262.0	1382	296.7
917	247.8	978	255.4	1279	286.4		
NiO 2: Ni + NiO vs. Fe + "FeO"							
977	255.1	838	238.9	1061	264.8	1100	268.7
1034	261.8	1126	271.3	1048	263.4	1138	272.5
1006	258.7	1138	272.5	1020	260.4	1187	277.4
977	255.4	1163	275.1	991	256.9	1210	279.6
947	251.9	1199	278.8	962	253.8	1222	280.7
915	248.3	1151	274.1	1175	276.2	1233	281.8
882	244.3	1114	270.2	1126	271.3	1256	284.0
848	240.1	1088	267.5	1074	266.0	1200	278.5
NiO 3: Ni + NiO vs. Fe + "FeO"							
881	243.5	962	253.3	1062	264.8	1177	276.9
898	245.4	977	255.2	1076	266.2	1201	279.1
914	247.5	992	256.9	1089	267.6	1225	281.4
931	249.9	1007	258.7	1102	269.1	1165	275.2
914	248.0	1021	260.3	1128	271.8	1140	272.7
897	245.9	1035	261.9	1152	274.2	1189	277.5
946	251.4	1049	263.5				
NiO 4: Fe + "FeO" vs. Ni + NiO							
1148	273.8	1098	268.4	1257	284.6	1344	293.1
1124	271.3	1111	269.8	1234	282.2	1334	292.0
1098	268.6	1124	271.1	1187	277.5	1323	290.9
1072	265.7	1137	272.5	1210	279.8	1301	288.7
1044	262.8	1149	273.7	1312	290.4	1279	286.4
1016	259.7	1161	275.0	1333	292.5	1257	284.2
988	256.6	1174	276.2	1355	294.7	1211	279.7
1002	258.0	1198	278.6	1375	296.8	1163	275.0
1016	259.7	1221	280.9	1396	298.9	1268	285.3
1031	261.1	1245	283.3	1416	301.0	1290	287.5
1044	262.6	1267	285.5	1406	299.8	1312	289.7
1058	264.0	1289	287.9	1385	297.6	1334	291.9
1072	265.7	1278	286.8	1365	295.4	1355	294.1
1085	267.1						
NiO 5: Ni + NiO vs. Cu + Cu_2O							
918	285.6	965	282.1	1210	264.2	1225	263.1
934	284.4	980	281.0	1246	261.7	1201	264.7
950	283.2	995	279.9	1270	260.1		
NiO 6: Ni + NiO vs. Cu + Cu_2O							
904	286.5	1027	277.8	1096	272.5	1226	262.7
920	285.6	1041	276.4	1123	270.4	1249	261.1
953	283.5	1055	275.3	1149	268.3	1273	259.5
983	281.1	1069	274.3	1176	266.2	1296	257.8
1013	279.2	1082	273.4	1201	264.4	1318	256.3
NiO 7: Ni + NiO vs. Cu + Cu_2O							
914	286.1	880	288.4	1085	273.6	1174	267.0
880	288.6	888	287.9	1098	272.6	1185	266.2
863	289.8	896	287.2	1111	271.8	1197	265.4
845	291.2	905	286.6	1124	270.9	1210	264.5
826	292.5	913	286.1	1136	270.1	1221	263.5
817	293.3	929	284.9	1149	269.2	1233	262.7
807	294.0	945	283.7	1111	271.7	1245	262.0
797	294.8	960	282.6	1084	273.6	1257	261.1
807	293.9	975	281.5	1058	275.6	1268	260.2
817	293.2	990	280.4	1029	277.6	1234	262.3
826	292.4	1004	279.3	1000	279.8	1187	265.7
835	291.8	1019	278.3	971	282.1	1279	258.9
844	291.1	1033	277.3	986	280.9	1291	258.1
853	290.5	1045	276.3	1015	278.8	1301	257.3
863	289.7	1059	275.3	1043	276.7	1312	256.5
871	289.1	1072	274.4	1161	268.0	1323	255.6

Note: The order is that in which the measurements were made.

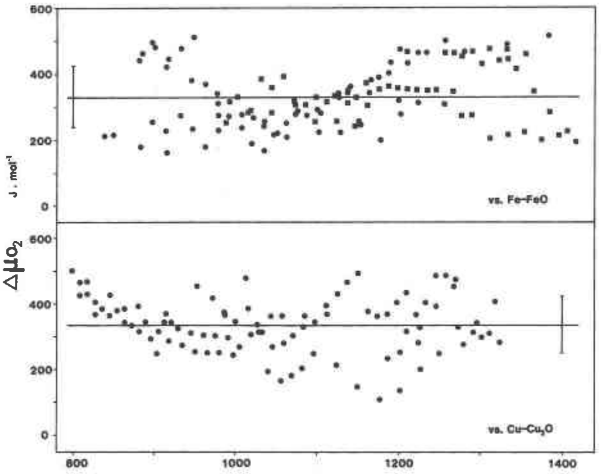

Fig. 1. Comparison of the results obtained from the present work for free energy of the reaction $2Ni + O_2 = 2NiO$ with those of Holmes et al. (1986). Top: vs. Fe + "FeO"; ●, runs Ni 1–3; ■, run Ni 4. Bottom: vs. Cu + Cu_2O, runs Ni 5–7.

The difference between cells II and III is that in the former the Ni + NiO electrode occupies the sample position and Fe + "FeO" the reference, and vice versa in the latter. Three separate runs were done with cells of types I and II, and one run with type III.

The results are given in Table 1 and plotted as function of temperature in Figure 1, using the previous determination from this laboratory of Holmes et al. (1986) as a reference. It may be seen that all three types of cells give a μ_{O_2} that is slightly lower than that of Holmes et al. (1986). For the runs vs. Cu + Cu_2O, linear regression analysis of this difference ($\Delta\mu_{O_2}$) as a function of temperature gives (in J·mol⁻¹)

$$\Delta\mu_{O_2}\,(\pm 85) = -424\,(\pm 62) + 0.084\,(\pm 0.059)\,T$$

and for the runs vs. Fe + "FeO"

$$\Delta\mu_{O_2}\,(\pm 97) = -52\,(\pm 101) - 0.2505\,(\pm 0.094)\,T.$$

Since in the one case, this slope is slightly positive and in the other, slightly negative—and in both cases is very small—it was assumed that the difference between the results of the present work and those of Holmes et al. (1986) is independent of temperature, and is given by

$$\Delta\mu_{O_2} = -334 \pm 90.$$

As the error estimated in Holmes et al. (1986) is ±400 J·mol⁻¹, agreement between the two studies may be said to be excellent. The present results are, however, believed to be more accurate, as the experimental method employed here minimizes any systematic errors due to the following causes: (1) temperature measurement, as the temperature dependence of the cell emf's reported here is nearly an order of magnitude less than for cells using air as the reference; (2) temperature gradients, as the presence of these has been checked for using the symmetric

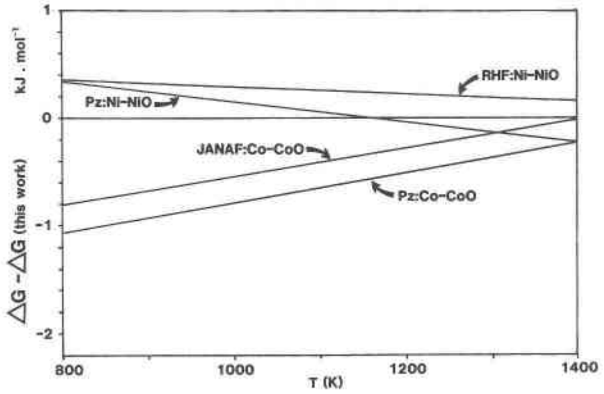

Fig. 2. Comparison of the present results for the free energy of the reactions $2Ni + O_2 = 2NiO$ and $2Co + O_2 = 2CoO$ with that derived from calorimetric data as assessed in Pankratz (1982; Pz), Robie et al. (1978; RHF), and Chase et al. (1974; JANAF). The curves are smoothed representations of values tabulated at 100-K intervals.

TABLE 2. Results from the cells used to measure the free energy of formation of CoO

T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)
Co 1: Co + CoO vs. Fe + "FeO"							
865	183.6	1008	187.3	1152	189.9	917	185.2
883	184.0	1021	187.6	1176	190.2	933	185.5
899	184.6	1035	187.8	1188	190.4	949	186.0
916	184.9	1049	188.1	1200	190.5	965	186.4
932	185.3	1063	188.4	1223	190.7	1009	187.5
948	185.7	1076	188.6	1246	191.0	1090	188.7
963	186.1	1102	189.2	866	183.7	1116	189.1
978	186.5	1128	189.7	901	184.7	1141	189.4
993	186.9						
Co 2: Co + CoO vs. Fe + "FeO"							
1103	188.8	1355	193.5	1202	190.8	1406	195.1
1375	194.3	1395	194.8	1166	190.2	1416	195.4
1153	190.0	1376	194.2	1142	189.9	1426	195.7
1201	190.7	1356	193.7	1117	189.6	1386	194.5
1224	191.0	1334	193.1	1178	190.2	1366	193.9
1248	191.2	1313	192.6	1214	190.6	1345	193.3
1269	191.5	1292	192.1	1237	190.9	1324	192.8
1291	191.8	1270	191.7	1260	191.2	1303	192.2
1313	192.2	1248	191.3	1366	193.8	1406	194.9
1334	192.8	1225	191.0	1386	194.4		
Co 3: Co + CoO vs. Ni + NiO							
893	60.9	850	57.1	942	65.4	1070	77.1
876	59.4	859	57.8	957	66.8	1096	79.3
859	57.9	867	58.6	972	68.3	1122	81.4
841	56.3	876	59.4	987	69.8	1082	78.1
823	54.6	885	60.2	1001	71.1	1172	85.7
804	52.8	893	61.1	1015	72.3	1196	87.8
813	53.6	901	61.9	1029	73.5	1220	89.8
823	54.5	910	62.6	1043	74.7	1159	84.8
832	55.4	926	64.0	1056	75.9	1243	91.6
841	56.3						
Co 4: Co + CoO vs. Ni + NiO							
958	67.2	1058	76.3	1185	87.0	1311	97.0
974	68.5	1111	80.7	1209	89.1	1332	98.7
989	69.9	1137	82.9	1266	93.5	1311	97.4
1003	71.2	1148	83.6	1289	95.5	1353	100.6
1031	73.7	1160	84.7				

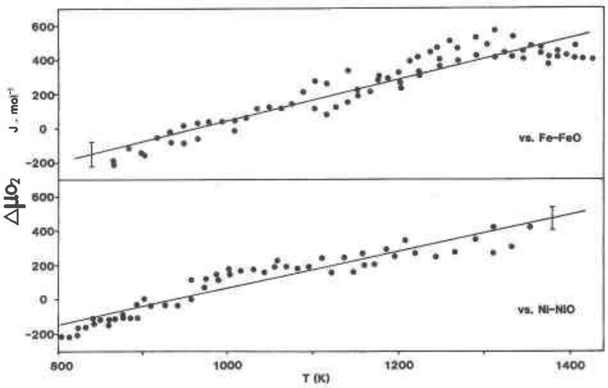

Fig. 3. Comparison of the results obtained from the present work for the free energy of the reaction $2Co + O_2 = 2CoO$ with those of Holmes et al. (1986). Top: vs. Fe + "FeO." Bottom: vs. Ni + NiO.

cells and the appropriate correction has been made where necessary (i.e., for those cells with Cu + Cu_2O as the reference electrode); and, most importantly, (3) polarization of the Ni + NiO electrode from oxygen leakages. The Fe + "FeO" reference electrode is more reducing than Ni + NiO, and Cu + Cu_2O more oxidizing, so that the good agreement of the results from both types of cell implies that oxygen transfer across the CSZ electrolyte cannot have been a significant source of error. Furthermore, the similarly good agreement of the results from cells of type II and III argues against any significant penetration of oxygen from the atmosphere into either the sample or reference electrode compartments.

Accordingly, the equation for μ_{O_2} of Ni + NiO (in J·mol⁻¹; T in kelvins) given in Holmes et al. has been modified to

$$\mu_{O_2}(\pm 120) = -480\,104 + 244.700T - 9.167T \ln T \quad (800 < T < 1420)$$

where the uncertainty in parentheses (±120 J·mol⁻¹) is the estimated one-standard-deviation uncertainty derived from the observed statistical uncertainty in the experiments (±90 J·mol⁻¹), coupled with those for the Cu + Cu_2O and Fe + "FeO" reference electrodes (±40 and ±90 J·mol⁻¹, respectively).

The above expression is compared in Figure 2 to those given in the compilations of thermodynamic data of Robie et al. (1978) and Pankratz (1982), which are both derived exclusively from calorimetric measurements (i.e., low-temperature heat capacities, high-temperature heat contents, and an enthalpy of formation determined by combustion calorimetry). From this it may be seen that agreement with the calorimetric data is excellent. The difference in the μ_{O_2} vs. T slope of the present work with that of the equation given in Pankratz is only +0.8 J·K⁻¹·mol⁻¹ and with the tabulations of Robie et al. (1978) is even less, +0.3 J·K⁻¹·mol⁻¹. It is interesting to note that the difference between the two compilations is comparable in magnitude to the difference between either and the present work and, as the sources of the data in both are the same, seems to result solely from fitting the high-temperature heat-content measurements to different forms of the extended Maier-Kelley empirical heat-capacity equations. Moreover, when comparing the calorimetric data with the present work, it should be borne in mind that the standard entropy of NiO is derived from heat-capacity measurements that extend down to only 54 K (King, 1957) and that the heat-content measurements (King and Christensen, 1958) were interpreted by King and Christensen, and consequently by Robie et al. (1978) and Pankratz (1982), to show not only the well-established transition at the Néel temperature (525 K) but a further transition, of unknown origin, at 565 K. The existence of this second transition (which has actually been given the status of being labeled as a $\beta \rightarrow \gamma$ transition in most thermodynamic compilations) has recently been shown to be probably an artifact of the data (Bergman and Ågren 1985). It may therefore be concluded that the present results are in very good agreement with the calorimetric data, such as they are. The appropriate amendment to the standard enthalpy of formation of NiO calculated by the third-law method by Holmes et al. (1986) yields

$$\Delta H^0_{f,298.15} = -240.28\ \mathrm{kJ \cdot mol^{-1}}.$$

This value—considering that in addition to the uncertainty in the experimental data, it is also subject to the uncertainties in the calorimetric data for the standard entropies and high-temperature heat capacities of NiO, Ni, and O_2—compares very favorably with that measured by combustion calorimetry (-239.74 ± 0.42 kJ·mol^{-1}; Boyle et al., 1954).

Since a fairly comprehensive comparison with previous work on the Ni + NiO equilibrium has been given in Holmes et al. (1986), this exercise will not be repeated here. However, it should be noted that the often-quoted results of Huebner and Sato (1970) deviate from those of the present work by -555 J·mol^{-1} at 800 K to $+4091$ J·mol^{-1} at 1400 K, which thus also indicates a very large discrepancy between the results of Huebner and Sato (1970) and the calorimetric data. The recent work by Comert and Pratt (1984) shows a deviation from the present results in exactly the opposite direction, from $+1962$ J·mol^{-1} at 800 K to -452 J·mol^{-1} at 1275 K.

Co + CoO

Measurements on the Co + CoO equilibrium were obtained from two types of cells:

$$\mathrm{Pt, Co + CoO|CSZ|Fe + \text{“FeO”}, Pt} \qquad \text{(IV)}$$
$$\mathrm{Pt, Co + CoO|CSZ|Ni + NiO, Pt.} \qquad \text{(V)}$$

Two separate runs were done with each type of cell. The results are given in Table 2 and have been treated in the same way as those for Ni + NiO by plotting them as a function of temperature referred to the previous determination of Holmes et al. (1986) in Figure 3. Again, agreement with the latter is quite good. Linear regression of the difference between the present work and that of Holmes et al. (1986) as a function of temperature gives, for the runs with Fe + "FeO" as the reference electrode (in J·mol^{-1}),

$$\Delta\mu_{O_2}\,(\pm 75) = +1157\,(\pm 63) - 1.200\,(\pm 0.053)\,T,$$

and for the runs with Ni + NiO,

$$\Delta\mu_{O_2}\,(\pm 64) = +1000\,(\pm 57) - 1.065\,(\pm 0.055)\,T.$$

The very good agreement between the results from the two types of cell is a powerful demonstration of the extraordinarily high internal precision of these measurements. Taken together, the results, which cover the temperature range 800–1420 K, give

$$\Delta\mu_{O_2}\,(\pm 71) = +1075\,(\pm 40) - 1.133\,(\pm 0.036)\,T,$$

which has been used to amend the expression for Co + CoO (in J·mol^{-1}) given in Holmes et al. (1986) to

$$\mu_{O_2}\,(\pm 120) = -491\,649 + 508.527T - 53.284T \ln T + 0.025\,18T^2 \qquad (800 < T < 1397).$$

The accompanying error has been estimated in the same way as for Ni + NiO. This expression has been compared in Figure 2 with the tabulated calorimetrically derived values given in the JANAF tables (Chase et al., 1974) and by Pankratz (1982) [the values given in Robie et al. (1978) contain an error caused by the high-temperature heat-capacity equation for CoO not being constrained so as to join smoothly with the heat capacity at 298.15 K]. The present work shows a difference in μ_{O_2} vs. T slope compared to the JANAF values of 1.29 J·K^{-1}·mol^{-1}, and 1.44 J·K^{-1}·mol^{-1} with the values in Pankratz. Thus, if the present data are correct, the calorimetrically determined entropy of CoO has been underestimated by approximately 0.7 J·K^{-1}·mol^{-1} (assuming the entropies of Co and O_2 are accurate), which is rather larger than the quoted uncertainty in the measurement of the standard entropy of CoO at 298.15 K (±0.33 J·K^{-1}·mol^{-1}, King, 1957). However, as for NiO, the standard entropy of CoO was determined from heat-capacity measurements that extend down to only 54 K (King, 1957). Moreover, the Curie point of CoO occurs at ~287 K, and therefore the anomaly in the heat capacity occurs inconveniently near to where the low-temperature adiabatic heat-capacity measurements must be joined to the high-temperature heat-content measurements of King and Christensen (1958). That the discrepancy for Co + CoO is in the opposite sense to the rather smaller one noted above for Ni + NiO at least indicates that it is not due to any systematic error in the emf measurements.

Some additional evidence that it is the calorimetric entropy of CoO rather than the present results that may be slightly in error comes from assessment of the thermodynamics of the reaction

$$3\mathrm{CoO} + \tfrac{1}{2}\mathrm{O_2} = \mathrm{Co_3O_4}, \qquad (5)$$

the data for which were presented in O'Neill (1985), where it was noted that, at temperatures <1100 K, there was a rather large discrepancy of 4.01 J·K⁻¹·mol⁻¹ of Co_3O_4 between the emf results and the calorimetrically determined μ_{O_2} vs. T slope of the reaction. If the data given in O'Neill (1985) are re-examined using the new values for the Cu + Cu_2O reference electrode used in this paper (which make but a small difference) and the standard entropy for CoO increased by 0.7 J·K⁻¹·mol⁻¹, this discrepancy is reduced to 0.9 ± 0.3 J·K⁻¹·mol⁻¹, which is a great improvement and could perhaps be reduced to nothing if the possible nonstoichiometry of CoO in equilibrium with Co_3O_4 were taken into account (see the discussion in O'Neill, 1985).

The present results imply a slight correction to the preferred value for the enthalpy of formation of CoO given by Holmes et al. (1986):

$$\Delta H^0_{f,298.15} = -236.86 \text{ kJ}\cdot\text{mol}^{-1}.$$

This value is slightly less negative than the value of −238.49 ± 1.26 kJ·mol⁻¹ obtained from combustion calorimetry by Boyle et al. (1954), as amended in the JANAF tables (Chase et al., 1974) to take into account the presence of Co_3O_4 and Co_2SiO_4 in the combustion products.

As for Ni + NiO, an extensive comparison with previous studies of the Co + CoO equilibrium is given in Holmes et al. (1986).

TABLE 3. Results for the reaction $Co_2SiO_4 = 2Co + SiO_2 + O_2$

T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)
Co-OL 1: Co_2SiO_4 + Co + $SiO_{2(qz)}$ vs. Fe + "FeO"							
1010	141.4	1037	143.1	1167	150.0	1091	146.4
1024	142.2	1051	143.8	1179	150.6	1065	145.2
1038	143.1	1065	144.6	1191	151.2	1104	147.0
1010	141.6	1078	145.2	1202	151.7	1130	147.7
980	139.8	1091	146.0	1214	152.3	1154	148.9
965	138.6	1104	146.8	1226	152.7	1225	152.6
980	139.5	1117	147.5	1237	153.3	1248	153.4
995	140.5	1130	148.2	1143	148.8	1293	156.1
1010	141.4	1143	148.8	1117	147.6	1314	157.3
1024	142.2	1154	149.4				
Co-OL 2: Co_2SiO_4 + Co + $SiO_{2(crs)}$ vs. Fe + "FeO"							
1334	158.6	1175	149.8	1180	150.3	1345	159.6
1315	157.2	1156	148.4	1192	151.0	1156	148.7
1293	156.1	1105	145.4	1250	154.1	1204	151.2
1272	154.9	1204	151.5	1272	155.1	1227	152.4
1250	153.6	1227	152.8	1294	156.3	1241	153.4
1227	152.5	1239	153.4	1262	154.3	1358	160.0
1204	151.3	1204	151.5				
Co-OL 3: Co_2SiO_4 + Co + $SiO_{2(qz)}$ vs. Ni + NiO							
1152	124.5	1061	119.7	1269	130.6	1220	127.3
1101	121.7	1074	120.5	1291	131.5	1188	126.8
1200	127.1	1088	121.3	1314	132.4	1212	127.3
1224	128.3	1101	122.0	1335	133.2	1292	132.0
1005	116.8	1114	122.5	1292	131.2	1314	132.0
1019	117.5	1127	123.3	1248	129.4	1335	133.7
1033	118.2	1176	125.9	1223	128.2	1356	134.4
1047	119.0	1247	129.6				

Co_2SiO_4 + Co + SiO_2

Three types of cell were examined:

$$\text{Pt, } Co_2SiO_4 + Co + SiO_{2(qz)}|\text{CSZ}|\text{Fe} + \text{“FeO,” Pt} \quad \text{(VI)}$$

$$\text{Pt, } Co_2SiO_4 + Co + SiO_{2(crs)}|\text{CSZ}|\text{Fe} + \text{“FeO,” Pt} \quad \text{(VII)}$$

$$\text{Pt, } Co_2SiO_4 + Co + SiO_{2(qz)}|\text{CSZ}|\text{Ni} + \text{NiO, Pt.} \quad \text{(VIII)}$$

The results are given in Table 3. Those involving SiO_2 in the cristobalite (crs) form will be treated later; all the other data were analyzed to give the standard enthalpy of Reaction 4 at 298.15 K by the third-law method:

$$\Delta_r H^0_{m,298.15} = \Delta_r G^0_{m,T} - \int_{298.15}^{T} \Delta_r C^0_{P,m}\, dT + T\left(\Delta_r S^0_{m,298.15} + \int_{298.15}^{T} (\Delta_r C^0_{P,m}/T)\, dT\right) \quad (6)$$

using the calorimetric data listed in Table 4. The calculated values of $\Delta_r H^0_{m,298.15}$ have been plotted against the temperature of the datum in Figure 4. Such a plot should give a horizontal line (i.e., $\Delta_r H^0_{m,298.15}$ should be independent of temperature if both the emf measurements and all the calorimetric data are correct). For the results obtained with Fe + "FeO" as the reference electrode, which cover the temperature range 965–1314 K, regression analysis on $\Delta_r H^0_{m,298.15}$ gives (in J·mol⁻¹)

$$-501\,579\ (\pm 179) + 0.025\ (\pm 0.160)\ T\ (\pm 89)$$

or, independent of T,

$$-501\,551 \pm 88,$$

and, for the results obtained with Ni + NiO as the reference electrode (1019–1356 K),

$$-501\,232\ (\pm 157) - 0.185\ (\pm 0.132)\ T$$

or

$$-501\,452\ (\pm 76).$$

Thus the small discrepancy discernible in Figure 4 between the two sets of measurements is not statistically significant. Combination of all measurements gives

$$-501\,621\ (\pm 130) + 0.100\ (\pm 0.113)\ T\ (\pm 97)$$

or, independent of temperature,

$$-501\,507\ (\pm 96).$$

(The uncertainties given in parentheses are the statistical uncertainties in the experimental data only and do not include the uncertainties in the data for the reference electrodes, nor those of the calorimetric data used in the calculation.)

The present results are thus in almost perfect agreement with the calorimetric data. They consequently indicate that the small discrepancy noted in the previous section between the emf results and the calorimetric data for the Co + CoO equilibrium is probably not due to errors in the calorimetric data for Co. The above value

TABLE 4. Results for the reaction $Ni_2SiO_4 = 2Ni + SiO_2 + O_2$

T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)
Ni-OL 1: $Ni_2SiO_4 + Ni + SiO_{2(qz)}$ vs. $Ni + NiO$							
1269	14.4	1137	19.0	1246	14.9	1358	12.2
1223	15.4	1149	18.3	1291	13.9	1379	11.6
1199	16.2	1162	17.5	1314	13.4	1400	10.7
1175	17.0	1186	16.5	1336	12.9	1326	13.1
1149	18.2	1210	15.9				
Ni-OL 2: $Ni_2SiO_4 + Ni + SiO_{2(qz)}$ vs. $Ni + NiO$							
972	24.1	1069	20.4	1172	17.0	1197	16.2
987	23.5	1083	20.0	1184	16.7	1256	14.7
1001	23.0	1096	19.5	1196	16.4	1289	13.8
1015	22.5	1109	19.0	1208	16.1	1311	13.1
1029	22.0	1122	18.5	1220	15.7	1245	14.8
1043	21.5	1135	17.9	1232	15.4	1150	17.6
1014	22.3	1147	17.6	1244	15.1	1111	18.9
1056	20.9	1159	17.3	1267	14.5		
Ni-OL 3: $Ni_2SiO_4 + Ni + SiO_{2(crs)}$ vs. $Ni + NiO$							
1071	22.4	1099	20.7	1138	19.5	1259	15.7
1044	23.9	1073	21.8	1150	19.1	1269	15.4
1059	23.2	1045	23.1	1162	18.7	1280	15.1
1072	22.4	1016	25.0	1182	17.9	1292	14.8
1085	21.6	1031	24.3	1199	17.6	1303	14.5
1099	21.1	1045	23.4	1211	17.2	1314	14.1
1112	20.6	1059	22.7	1223	16.9	1335	13.4
1125	20.1	1072	22.2	1199	17.6	1356	12.8
1138	19.4	1085	21.6	1175	18.2	1377	12.1
1149	19.0	1099	21.0	1223	16.7	1398	11.3
1162	18.5	1112	20.4	1235	16.4	1418	10.5
1175	18.2	1125	19.9	1247	16.1	1325	13.7
1125	19.8						
Ni-OL 4: $Ni_2SiO_4 + Ni + SiO_{2(qz)}$ vs. Fe + "FeO"							
981	230.7	1088	247.4	1163	257.5	1126	252.8
966	228.7	1101	249.2	1175	259.1	1101	249.4
950	226.3	1114	251.0	1188	260.6	1074	245.5
994	232.4	1126	252.7	1200	262.4	1047	241.5
1008	234.6	1139	254.5	1139	254.5	1020	237.1
1022	236.9	1114	251.2	1163	257.5	1033	239.0
1036	239.1	1088	247.7	1175	259.1	1047	241.0
1049	241.2	1061	244.0	1187	260.6	1060	243.0
1062	243.3	1126	252.7	1199	262.1	1073	244.8
1075	245.4	1151	256.0	1211	263.6	1087	246.7

for $\Delta_r H^0_{m,298.15}$ was therefore adopted and was combined with the calorimetric data to calculate values for the free energy of reaction at 20-K intervals between 900 and 1400 K, which were then used to obtain the following equation for $Co_2SiO_4 + Co + SiO_{2(qz)}$:

$$\mu_{O_2}\,(\pm 130) = -491\,141 + 122.815T + 3.5527T \ln T.$$

This, when combined with the data for the Co + CoO equilibrium, gives the following values for the free energy of formation of Co_2SiO_4 from the oxides (in $J \cdot mol^{-1}$):

$$\Delta_f G^0_{m,Co_2SiO_4,oxides}\,(\pm 120) = -31\,224 + 13.4475T \quad (900 < T < 1400).$$

The standard enthalpy of formation of Co_2SiO_4 from the oxides is then calculated to be

$$\Delta_f H^0_{m,oxides} = -27.79 \text{ kJ} \cdot \text{mol}^{-1},$$

which is 8.1 $kJ \cdot mol^{-1}$ more negative than that found by oxide-melt solution calorimetry at 986 K (Navrotsky et al., 1979), when the latter is corrected to 298.15 K.

The $Co_2SiO_4 + Co + SiO_2$ equilibrium has been studied a number of times before. The difference between these previous studies and the present results is illustrated in Figure 5. The agreement with the work of Lebedev et al. (1962) is very good, which is most encouraging as Lebedev et al. used a completely independent method involving equilibration with CO-CO_2 mixtures. The emf data of Rog et al. (1974) and Kozlowska-Rog and Rog (1979) are rather more oxidized, which may be due to polarization of the sample, an ever-present problem in emf measurements. They are also not in good agreement with the calorimetric data.

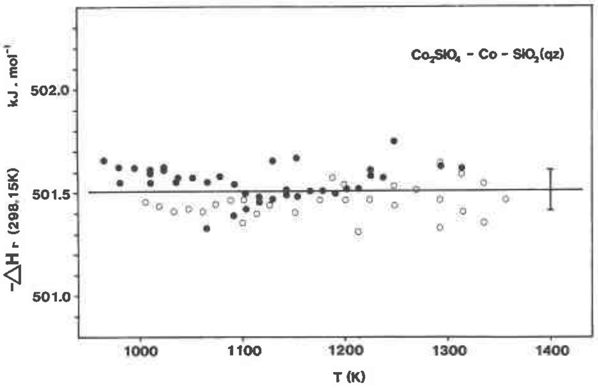

Fig. 4. Standard enthalpy, $\Delta H^0_{r,298.15}$, for the reaction $2Co + SiO_{2(qz)} + O_2 = Co_2SiO_{4(olivine)}$ calculated for each datum using the calorimetric data listed in Table 5 and plotted against the temperature of the datum. If the calorimetric data are correct, such a plot should yield a horizontal line. ●, obtained with the Fe + "FeO" reference electrode; ○, with Ni + NiO.

$Ni_2SiO_4 + Ni + SiO_2$

Three types of cell, as for the Co system, were studied:

$$\text{Pt, } Ni_2SiO_4 + Ni + SiO_{2(qz)}|\text{CSZ}|\text{Fe} + \text{"FeO," Pt} \quad \text{(IX)}$$

$$\text{Pt, } Ni_2SiO_4 + Ni + SiO_{2(crs)}|\text{CSZ}|\text{Fe} + \text{"FeO," Pt} \quad \text{(X)}$$

$$\text{Pt, } Ni_2SiO_4 + Ni + SiO_{2(qz)}|\text{CSZ}|\text{Ni} + \text{NiO, Pt.} \quad \text{(XI)}$$

The results are given in Table 5, and those involving SiO_2 in the form of quartz were analyzed by the "third-law" method, using the calorimetric data in Table 4, to obtain $\Delta_r H^0_{m,298.15}$ for each datum. These have been plotted against temperature in Figure 6, where it will be seen that, unlike for the Co system, there is a considerable temperature dependence to the calculated $\Delta_r H^0_{m,298.15}$.

In order to try to get some insight into why this might be so, some further investigations were undertaken. First, Ni_2SiO_4 has been reported to disproportionate to the oxides $NiO + SiO_{2(crs)}$ at 1818 K (Phillips et al., 1963). This observation was confirmed by a pair of reversal experiments. Ni_2SiO_4, NiO, and $SiO_{2(crs)}$ were mixed together in the molar proportions 1:2:1 and pressed into dense pellets with the aid of about 25% additional Ni metal, which not only serves to hold the pellet together, but should help to provide good grain-to-grain contact. Since the

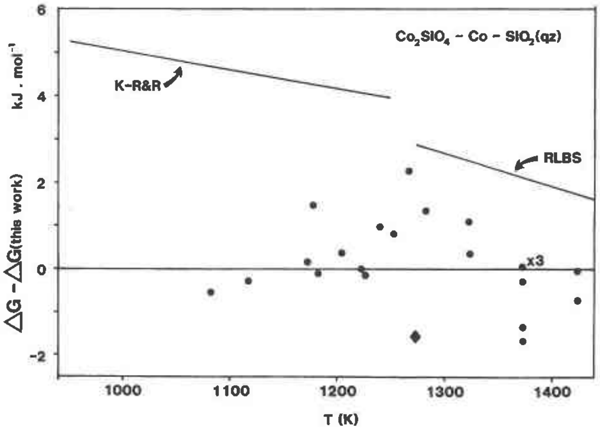

Fig. 5. Comparison showing the difference between various experimental determinations of the free energy of the reaction $2Co + SiO_2 + O_2 = 2Co_2SiO_4$ and that of this work. K-R&R: Kozlowska-Rog and Rog (1979); RLBS: Rog et al. (1974); ●, Lebedev et al. (1962); ◆, Aukrust and Muan (1963).

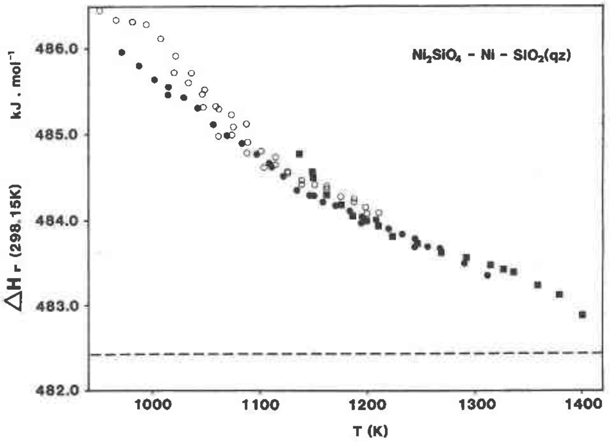

Fig. 6. Standard enthalpy, $\Delta H^0_{r,298.15}$, for the reaction $2Ni + SiO_{2(qz)} + O_2 = Ni_2SiO_{4(olivine)}$ calculated for each datum using the calorimetric data of Table 5. ■, run Ni-OL 1; ●, Ni-OL 2 (both vs. Ni + NiO); ○, Ni-OL 4 (vs. Fe + "FeO"). The dashed line is the result obtained using the heat-capacity data of Robie et al. (1984) together with the observed decomposition temperature of Ni_2SiO_4 (1820 K).

temperature range of interest is above the melting point of Ni, the Ni rapidly oxidizes to NiO during the run, which is therefore present in excess. The pellets were suspended with Pt wire in one of the furnaces used for the emf experiments, with a thermocouple that was calibrated against the melting point of Au positioned directly over the pellet. Only two runs, each of 16-h duration, were necessary to bracket the equilibrium: the first, at 1816 K, produced Ni_2SiO_4 + NiO only (determined by X-ray diffraction); the second, at 1821 K, produced NiO + $SiO_{2(crs)}$, with a faint trace of Ni_2SiO_4. The relative accuracy of the temperature measurements (there was no observable drift in temperature during the runs) is estimated to be within ±2 K, not including any error in extrapolating the calibration of the thermocouple from the melting point of Au. The breakdown temperature of Ni_2SiO_4 may therefore be given as 1820 ± 5 K. This is in perfect agreement with Phillips et al. (1963), although it should be mentioned that the IPTS-68 temperature scale was used in this study, whereas Phillips et al. must have used an earlier scale.

The decomposition point provides a datum on the thermodynamic properties of Ni_2SiO_4 that is not only derived from a method completely independent of the emf measurements, but also at a temperature well removed from the range these measurements cover. Using the results obtained for the Ni + NiO equilibrium and the calorimetric data in Table 5, plus the data given in Holmes et al. (1986) for NiO, all extrapolated to 1820 K, together with a reasonable assumption about the thermodynamics of the cristobalite-to-quartz transition (which will be explained in detail below), produces a value of the enthalpy of reaction, $\Delta_r H^0_m$, of -482.42 kJ·mol^{-1}, which has been drawn in Figure 7 as a straight line independent of the temperature. The emf data may be seen to tend toward intersecting this line near the correct temperature (~1820 K) and are therefore not inconsistent with the observed breakdown temperature. Although the heat capacity of Ni_2SiO_4 has only been measured to 1000 K, the extrapolation to 1820 K is not likely to produce much of an error; to illustrate this, a theoretical curve for the heat capacity of Ni_2SiO_4 at high temperatures was calculated by generating values from the relationship

$$C_P = C_V + \alpha^2 VT/\beta \qquad (7)$$

using $C_V = 3nR$, and data listed in Watanabe (1982) for α, β, and V, and joining these so as to meet smoothly with the measured values given by Robie et al. (1984). Using this curve gave a difference in the calculated $\Delta_r H^0_{m,298.15}$ of only 0.15 kJ·mol^{-1}.

Secondly, an investigation was made into whether the Ni_2SiO_4 used in either the calorimetric experiments or in this work might show large enough deviations from stoichiometry, particularly in the Ni to Si ratio, to account for the discrepancy. Robie et al. (1984) used Ni_2SiO_4 produced by slowly cooling a mixture of NiO and SiO_2 dissolved in a melt of Na_2WO_4. To investigate any possible nonstoichiometry in this material, three experiments were performed on mixtures of NiO, SiO_2, and Na_2WO_4 in suitable proportions. The results are summarized as follows: (1) SiO_2 in excess, 1323 K, 2 d, products—large (~150 μm), very euhedral crystals of Ni_2SiO_4 and long blades (500 × 50 μm) of SiO_2 (tridymite); (2) SiO_2 in excess, 1200 K, 7 d, products—Ni_2SiO_4 (~20 μm) and SiO_2 (~10 μm); (3) NiO in excess, 1200 K, 7 d, products—Ni_2SiO_4 (~20 μm) and NiO.

The Ni_2SiO_4 from all three runs was analyzed on a CAMECA electron microprobe in the wavelength-dispersive mode using Ni metal and natural quartz as standards. Although some of the Ni_2SiO_4 crystals contained an occasional minute inclusion of NiO, these could easily be avoided by using the back-scattered-electron image.

The results showed that there was no detectable Na or W in the Ni_2SiO_4 and that the ratio of Ni to Si was identical in the SiO_2-excess and NiO-excess experiments, and indistinguishable from the stoichiometric ideal of 2:1, within the analytical error. The product of the Ni_2SiO_4 breakdown run at 1816 K showed similar results. The two types of Ni_2SiO_4 used for the emf experiments were both too small in grain size for microprobe analysis, but X-ray diffraction experiments for all samples, including those grown in Na_2WO_4 and some emf run products, gave identical unit-cell lengths that were in excellent agreement with those reported in Brown (1980). There is thus no reason to suspect significant nonstoichiometry in Ni_2SiO_4. Incidentally, analogous pairs of experiments for Co_2SiO_4 and Mg_2SiO_4 ($MgSiO_3$ in excess rather than SiO_2) at 1200 K in Na_2WO_4 also showed no evidence of any nonstoichiometry.

The emf results plus the datum obtained from the breakdown of Ni_2SiO_4 were used to obtain the following expression for the Ni_2SiO_4 + Ni + $SiO_{2(qz)}$ equilibrium (in $J \cdot mol^{-1}$):

$$\mu_{O_2}\,(\pm 180) = -516\,690 + 362.97T - 22.297T \ln T.$$

The results from previous work are compared to this equation in Figure 7, together with that obtained using the calorimetric data of Robie et al. (1984) and the enthalpy of reaction determined from the breakdown point. The emf data of Levitskii et al. (1975) are in fairly good agreement with the present work, but show rather more scatter; those of Taylor and Schmalzried (1964) and Rog and Borchardt (1984) are intermediate between the present work and the calorimetrically derived curve; less weight should be given to the latter work as it employed (Ni,Mg)-substituted β''-alumina as the electrolyte, the suitability of which for accurate thermodynamic measurements is not well established. The data of Campbell and Roeder (1968) are at too high a temperature to discriminate between the emf and calorimetric curves. The data of Lebedev and Levitskii (1961), obtained from equilibration with circulating CO-CO_2 mixtures, are obviously highly anomalous and have not been shown. Thus none of the previous work supports the calorimetric data over the present emf results, and therefore the discrepancy between the two remains unresolved. Having said all this, it should be noted that the difference between the two methods, although large compared to the apparent precision of either, is nevertheless less than 0.2 log f_{O_2} at 950 K and becomes less at higher temperatures.

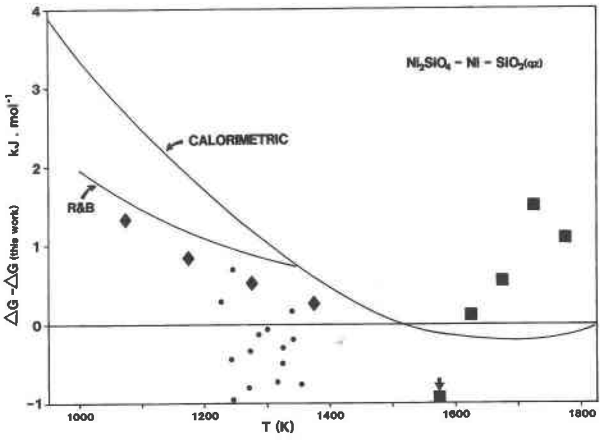

Fig. 7. Comparison showing the difference between various experimental determinations of the free energy of the reaction 2Ni + SiO_2 + O_2 = Ni_2SiO_4 and that of this work. The free energy of the reaction determined from the heat-capacity data of Robie et al. (1984) coupled with the observed decomposition temperature of Ni_2SiO_4 (1820 K) is labeled "calorimetric." R&B: Rog and Borchardt (1984); ●, Levitskii et al. (1975); ◆, Taylor and Schmalzried (1964). For these three studies, the values for the Ni + NiO equilibrium found in this work were used to recalculate the results. ■, Campbell and Roeder (1968) (the datum at 1573 K, indicated by the arrow, actually plots at −2.36 $kJ \cdot mol^{-1}$).

Combination of the results for the Ni_2SiO_4 + Ni + $SiO_{2(qz)}$ equilibrium with those for Ni + NiO gives the free energy of formation of Ni_2SiO_4 from the oxides (in $J \cdot mol^{-1}$):

$$\Delta_f G^0_{m,Ni_2SiO_4,oxides}\,(\pm 180) = -36\,560 + 118.10T - 13.108T \ln T \quad (960 < T < 1820).$$

TABLE 5. Calorimetric data used in calculating $\Delta H_{r,298.15}$ for 2Ni + SiO_2 + O_2 = Ni_2SiO_4 and 2Co + SiO_2 + O_2 = Co_2SiO_4

Substance	T range (K)	Ref. T (K)	$S_{(T)}$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$H_{(T)} - H_{(298)}$ $J \cdot mol^{-1}$	$C_P = A + BT + CT^{-2} + DT^{-1/2}$			
					A	B (×10^3)	(×10^{-6})	D
Ni*	700–1728	700	55.578	12342	20.668	9.9716	1.5223	—
Co*	700–1200	700	54.265	11718	−3.524	36.354	4.2758	—
	1200–1394	1200	73.421	29769	−141.419	118.022	61.940	—
$SiO_{2(qz)}$**	847–1676	900	109.045	38731	65.277	5.5288	1.8463	—
$SiO_{2(crs)}$**	532–1834	900	110.929	37989	66.930	4.8429	2.5419	—
Ni_2SiO_4†	298–1300‡	900	297.78	95239	289.73	−24.015	0.131045	−2779
Co_2SiO_4†	298–1300‡	900	321.75	100182	305.83	−31.952	0.269254	−2865.2
O_2*	700–1800	700	231.463	12498	34.2909	1.8865	−1.3027	—

* JANAF, Holmes et al. (1986).

** Richet et al. (1982).

† Robie et al. (1984).

‡ The measurements on which these data are based extend only to 1000 K, but owing to the nature of the third-law equation (Eq. 6 in the text), any errors from extrapolation to higher temperatures are expected to be small.

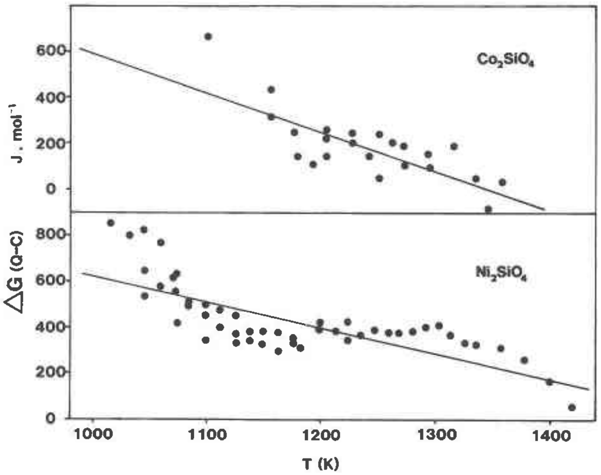

Fig. 8. The free energy of the reaction $SiO_{2(qz)} = SiO_{2(crs)}$ obtained by subtracting the data for the reactions $2Co + SiO_{2(crs)} + O_2 = Co_2SiO_4$ (run Co-OL 2) and $2Ni + SiO_{2(crs)} + O_2 = Ni_2SiO_4$ (run Ni-OL 3) from the results already obtained for the analogous reactions involving quartz.

QUARTZ-TO-CRISTOBALITE TRANSITION

Three polymorphs of SiO_2 are known at 1 atm: quartz, tridymite, and cristobalite. The rates of transformation between the three are too sluggish to be observed for pure SiO_2; consequently some kind of fluxing agent is necessary as a catalyst. For his classic investigation, Fenner (1913) used Na_2WO_4 and found that quartz transformed to tridymite at ~1143 K, and tridymite to cristobalite at ~1743 K. However, Holmquist (1961) showed that the precise temperature of the quartz-to-tridymite transition varied according to the flux used and also summarized other evidence showing that the properties of tridymite vary with the method of preparation. He therefore concluded that tridymite was not stable in the pure SiO_2 system and that in the absence of foreign ions, quartz transforms directly to cristobalite at a temperature he tentatively put at 1300 ± 25 K. That cristobalite formed as a metastable intermediate phase at temperatures as low as ~ 1160 K was thought to be due to the stabilizing effect of alkali ions on this phase too. Flörke (1956) investigated the problem using electrolysis experiments, which removed alkali ions to the cathode, where tridymite was formed; at the anode, quartz only was produced at 1323 K, cristobalite only at 1373 K. Therefore, the transition temperature between quartz and cristobalite is probably best given as 1350 ± 50 K.

In the present work, two runs, one each on the $Co_2SiO_4 + Co + SiO_2$ and $Ni_2SiO_4 + Ni + SiO_2$ equilibria, were done with SiO_2 in the form of cristobalite rather than quartz. The form of SiO_2 present after the run was confirmed by X-ray diffraction. The results are shown as the difference from the results of the runs with quartz in Figure 8 as a function of temperature. This difference is the free energy (in J·mol⁻¹) of the quartz-to-cristobalite reaction, which, by linear regression of the data from the Co system, is found to be

$$\Delta G^0_{\text{Q-C}}\ (\pm 98) = 2292 - 1.705T$$

and from the Ni system

$$\Delta G^0_{\text{Q-C}}\ (\pm 150) = 1724 - 1.103T.$$

These two equations give apparent equilibrium temperatures of the transition from quartz to cristobalite of 1344 and 1563 K, respectively.

Richet et al. (1982) have reviewed the available calorimetric data on quartz and cristobalite. From their selected values, the free energy (in J·mol⁻¹; T in kelvins) of the transition is given by

$$\Delta G^0_{\text{Q-C}} = \Delta H^0_{\text{Q-C},298} - 637 - 1.988T. \quad (800 < T < 1600).$$

Thus for the Co system, the present results are in good agreement not only with the preferred value of the transition temperature, but also with the selected calorimetric data pertaining to the free energy vs. temperature slope of the reaction and have therefore been adopted. For the Ni system, agreement is not quite so good, but nevertheless still adequate. Richet et al. (1982) used $\Delta H^0_{\text{Q-C},298} =$ 2836 J·mol⁻¹, giving a temperature of transition of 1106 K, which, being below the observed quartz-to-tridymite transition temperature, is obviously too low.

It should be mentioned that at the time these experiments were done, the intention was not so much to obtain data on the quartz-to-cristobalite transition, but to see whether using cristobalite, which might possibly be more reactive than quartz, would enable measurements to be obtained in the Co system at higher temperatures (although no difference was in fact observed in this regard); hence the data are concentrated at these higher temperatures and not within the optimum range of the method. Similarly, because of the discrepancy between the present results and the calorimetric data for the Ni_2SiO_4-Ni-SiO_2 system, the primary aim of using cristobalite rather than quartz was to provide another variable so as to try to check that the discrepancy was not caused by some artifact of the experimental method.

CONCLUSIONS

The apparent precision achieved in this study is on the order of ±100 J·mol⁻¹ of O_2, which is approximately equivalent to ±0.005 log f_{O_2} at 1000 K. This is superior to any previous study of which the author is aware on any of the equilibria considered here. Furthermore, this precision compares very favorably to that obtainable from calorimetric data. Free energies of reaction are normally determined calorimetrically from three types of measurements: low-temperature heat capacities for the standard entropy, high-temperature heat capacities or heat contents, and an enthalpy of reaction at one temperature. Of these, the standard entropies are usually the most precisely known, but nevertheless using modern methods, an error of ±0.2 J·K⁻¹·mol⁻¹ may be expected (e.g., Robie et al., 1982, 1984), which translates to ±200 J·mol⁻¹

at 1000 K. This is of course the contribution from just one substance in the reaction! Generally the enthalpy of reaction is the quantity least well known and provides most of the uncertainty in any determination of the free energy of a reaction, based solely on calorimetric data. However, the standard entropy and high-temperature heat capacities do provide a fairly rigorous constraint on the temperature dependence of the free energy, which in this study is satisfied by three of the four reactions. The exception is that involving Ni_2SiO_4, and the cause of this discrepancy remains unknown.

Finally, with this study and those of Holmes et al. (1986) and O'Neill (in prep.), there now exists a body of highly precise data with proven internal consistency on the four metal–metal oxide oxygen buffers Cu + Cu_2O, Ni + NiO, Co + CoO, and Fe + "FeO," which is also in good agreement with the best available calorimetric data. These buffers may therefore be used with some confidence.

ACKNOWLEDGMENTS

I would like to thank Professor A. E. Ringwood for providing the experimental facilities, Herb Niesler for help with the electronics, Paul Willis and Bill Hibberson for machining various parts, and Richard Arculus and Richard Holmes for helpful discussions on the techniques of solid electrolyte measurements during the early stages of this work. Richard Arculus and John L. Haas, Jr., contributed helpful reviews.

REFERENCES

Aukrust, E., and Muan, A. (1963) The stabilities of $CoO \cdot Al_2O_3$, $CoO \cdot Cr_2O_3$ and $2CoO \cdot SiO_2$. American Ceramic Society Journal, 46, 358.

Bergman, B., and Ågren, J. (1985) Thermodynamic assessment of the system MnO-NiO. American Ceramic Society Journal, 68, 444–450.

Boyle, B.J., King, E.G., and Conway, K.C. (1954) Heats of formation of nickel and cobalt oxides (NiO and CoO) of combustion calorimetry. American Chemical Society Journal, 76, 3835–3837.

Brown, G.E. (1980) Olivines and silicate spinels. Mineralogical Society of America Reviews in Mineralogy, 5, 275–381.

Campbell, F.E., and Roeder, P. (1968) The stability of olivine and pyroxene in the Ni-Mg-Si-O system. American Mineralogist, 53, 257–268.

Chase, M.W., Curnutt, J.L., Hu, A.T., Prophet, H., Syverud, A.N., and Walker, L.C. (1974) JANAF thermochemical tables, 1974 supplement. Journal of Physical and Chemical Reference Data, 3, 311–480.

Comert, H., and Pratt, J.N. (1984) The standard molar Gibbs free energy of formation of NiO from high temperature e.m.f. measurements. Journal of Chemical Thermodynamics, 16, 1145–1148.

Fenner, C.N. (1913) The stability relations of the silica minerals. American Journal of Science, 36, 331–384.

Flörke, O.W. (1956) Über das Einstoffsystem SiO_2. Naturwissenschaften, 43, 419–420.

Eugster, H.P. (1957) Heterogeneous reactions involving oxidation and reduction at high pressure and temperatures. Journal of Chemical Physics, 26, 1760.

Holmes, R.D., O'Neill, H.St.C., and Arculus, R.J. (1986) Standard Gibbs free energy of formation for Cu_2O, NiO, CoO, and Fe_xO: High resolution electrochemical measurements using zirconia solid electrolytes from 900–1400 K. Geochimica et Cosmochimica Acta, 50, 2439–2453.

Holmquist, S.B. (1961) Conversion of quartz to tridymite. American Ceramic Society Journal, 44, 82–86.

Huebner, J.S., and Sato, M. (1970) The oxygen fugacity–temperature relationships of manganese oxide and nickel oxide buffers. American Mineralogist, 55, 934–952.

Iwase, M., Kanazawa, T., and Mori, T. (1981) Kinetics of oxygen transfer at a solid oxide electrolyte—Mo, MoO_2 electrode interface. Solid State Ionics, 2, 331–336.

King, E.G. (1957) Heat capacities at low temperatures and entropies at 298.15° K of nickelous oxide, cobaltous oxide and cobalt spinel. American Chemical Society Journal, 79, 2399–2400.

King, E.G., and Christensen, A.U. (1958) Heat contents above 298.15° K of oxides of cobalt and nickel. American Chemical Society Journal, 80, 1800–1801.

Kozlowska-Rog, A., and Rog, G. (1979) Thermodynamics of zinc and cobalt silicates. Polish Journal of Chemistry, 53, 2083–2086.

Lebedev, B.G., and Levitskii, V.A. (1961) The nickel orthosilicate-carbon monoxide equilibrium at high temperatures. Russian Journal of Physical Chemistry, 35, 1380–1382.

Lebedev, B.G., Levitskii, V.A., and Burtstev, V.A. (1962) Equilibrium in reduction of cobalt orthosilicate by carbon monoxide. Russian Journal of Physical Chemistry, 36, 460–461.

Levitskii, V.A., Golovanova, Yu.G., Popov, S.G., and Chentsov, V.N. (1975) Thermodynamics of binary oxide systems. Thermodynamic properties of nickel orthosilicate. Russian Journal of Physical Chemistry, 49, 971–974.

Navrotsky, A., Pintchovski, F.S., and Akimoto, S. (1979) Calorimetric study of the stability of high pressure phases in the systems $CoO\text{-}SiO_2$ and "Fe-O"-SiO_2 systems. Physics of the Earth and Planetary Interiors, 19, 275–292.

O'Neill, H.St.C. (1985) Thermodynamics of Co_3O_4: A possible electron spin unpairing transition in Co^{3+}. Physics and Chemistry of Minerals, 12, 149–154.

——— (1987) Quartz-fayalite-iron and quartz-fayalite-magnetite equilibria and the free energy of formation of fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). American Mineralogist, 72, 67–75.

Pankratz, L.B. (1982) Thermodynamic properties of elements and oxides. U.S. Bureau of Mines Bulletin 672.

Phillips, B., Butta, J.J., and Warshaw, I. (1963) Phase equilibria in the system $NiO\text{-}Al_2O_3\text{-}SiO_2$. American Ceramic Society Journal, 46, 579–583.

Richet, P., Bottinga, Y., Denielou, L., Petitet, J.P., and Tequi, C. (1982) Thermodynamic properties of quartz, cristobalite and amorphous SiO_2: Drop calorimetry measurements between 1000 and 1800 K and a review from 0 to 2000 K. Geochimica et Cosmochimica Acta, 46, 2639–2658.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452.

Robie, R.A., Hemingway, B.S., and Takei, H. (1982) Heat capacities and entropies of Mg_2SiO_4, Mn_2SiO_4 and Co_2SiO_4 between 5 and 380 K. American Mineralogist, 67, 470–482.

Robie, R.A., Hemingway, B.S., Ito, J., and Krupka, K.M. (1984) Heat capacity and entropy of Ni_2SiO_4-olivine from 5 to 1000 K and heat capacity of Co_2SiO_4 from 360 to 1000 K. American Mineralogist, 69, 1096–1101.

Rog, G., and Borchardt, G. (1984) Thermodynamics of nickel orthosilicate. Journal of Chemical Thermodynamics, 16, 1103–1105.

Rog, G., Langanke, B., Borchardt, G., and Schmalzried, H. (1974) Determination of the standard Gibbs free energies of formation of the silicates of cobalt, magnesium and strontium by e.m.f. measurements. Journal of Chemical Thermodynamics, 6, 1113–1119.

Taylor, R.W., and Schmalzried, H. (1964) The free energy of formation of some titanates, silicates and magnesium aluminate from measurements made with galvanic cells involving solid electrolytes. Journal of Physical Chemistry, 68, 2444–2449.

Watanabe, H. (1982) Thermochemical properties of synthetic high-pressure compounds relevant to the earth's mantle. In S. Akimoto and M.H. Manghani, Eds. High-pressure research in geophysics, p. 441–464. Reidel, Dordrecht.

Worrell, W.L., and Iskoe, J.L. (1973) Kinetics of oxygen transfer at the interface between a zirconia-based electrolyte and a metal-metal oxide electrode. In W. van Gool, Ed. Fast ion transport in solids, p. 513–521. North-Holland, Amsterdam.

MANUSCRIPT RECEIVED APRIL 23, 1986
MANUSCRIPT ACCEPTED NOVEMBER 7, 1986