Free energies of formation of NiO, CoO, Ni$_2$SiO$_4$, and Co$_2$SiO$_4$

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

\[ 2\text{Ni} + \text{O}_2 = 2\text{NiO} \]
\[ 2\text{Co} + \text{O}_2 = 2\text{CoO} \]
\[ 2\text{Ni} + \text{SiO}_2 + \text{O}_2 = \text{Ni}_2\text{SiO}_4^{(\text{dixinite})} \]
\[ 2\text{Co} + \text{SiO}_2 + \text{O}_2 = \text{Co}_2\text{SiO}_4^{(\text{dixinite})} \]

have been measured using an electrochemical technique. The results are (\(\mu_\text{O}_2\) in J mol\(^{-1}\), T in kelvins)

for Ni + NiO,
\[ \mu_\text{O}_2 (\pm 120) = -480104 + 244.700T - 9.167T \ln T \quad (800 < T < 1420), \]

for Co + CoO,
\[ \mu_\text{O}_2 (\pm 120) = -491649 + 508.527T - 53.284T \ln T + 0.025T^2 \quad (800 < T < 1397), \]

for Co$_2$SiO$_4$ + Co + SiO$_2^{(qs)}$,
\[ \mu_\text{O}_2 (\pm 130) = -491141 + 122.815T + 3.5527T \ln T \quad (960 < T < 1397), \]

for Ni$_2$SiO$_4$ + Ni + SiO$_2^{(qs)}$,
\[ \mu_\text{O}_2 (\pm 180) = -516690 + 362.977T - 22.297T \ln T \quad (960 < T < 1820), \]

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

For all the equilibria except Ni$_2$SiO$_4$ + Ni + SiO$_2$, the results are in excellent agreement with the calorimetric data. Ni$_2$SiO$_4$ breaks down to NiO + SiO$_2$ (cristobalite = crs) at 1820 ± 5 K. Since for the two equilibria involving SiO$_2$ both quartz (qs) and cristobalite were used, some information is also given for the reaction

\[ \text{SiO}_2^{(qs)} = \text{SiO}_2^{(crs)}. \]

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$^{2+}$)$_{3}$$\text{SiO}_4$, as the components Ni$_2$SiO$_4$ and Co$_2$SiO$_4$, which are the only binary phases found in the systems NiO-SiO$_2$ and CoO-SiO$_2$ at atmospheric pressure.

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

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

\[ 2\text{Ni} + \text{O}_2 = 2\text{NiO} \quad (1) \]
\[ 2\text{Co} + \text{O}_2 = 2\text{CoO} \quad (2) \]
\[ 2\text{Ni} + \text{SiO}_2 + \text{O}_2 = \text{Ni}_2\text{SiO}_4 \quad (3) \]
\[ 2\text{Co} + \text{SiO}_2 + \text{O}_2 = \text{Co}_2\text{SiO}_4 \quad (4) \]

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

With the recent measurements on the heat capacities of Ni$_2$SiO$_4$ and Co$_2$SiO$_4$ 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
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 H₂-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, \( r \text{O}_2 \) and \( p \text{O}_2 \), 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 \( \mu \text{O}_2 \) between the two electrodes by

\[
4FE = \mu \text{O}_2^A - \mu \text{O}_2^B
\]

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 \( \mu \text{O}_2 \), 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 \( \mu \text{O}_2 \), 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 \( \mu \text{O}_2 \), and another with a lower. In this study, Fe + “FeO” mixtures were used for the lower \( \mu \text{O}_2 \), reference electrode; for the determination of the Ni + NiO equilibrium, Cu + CuO was used as the higher \( \mu \text{O}_2 \) reference electrode. The \( \mu \text{O}_2 \) values defined by the Fe + “FeO” and the Cu + CuO equilibria have been recently redetermined to a high degree of accuracy in this laboratory (O'Neill, in prep.) using air (the \( \mu \text{O}_2 \) of which is determined from the nitrogen content) and for Fe + “FeO” (+90)

\[
-605 812 + 1366.7187T - 182.79557 \ln T + 0.103 \ln T^2
\]

(833 < \( T < 1042 \))

\[
-519 357 + 59.427T + 8.9276T \ln T
\]

(1042 < \( T < 1184 \))

\[
-551 159 + 259.4047 - 2.9053T \ln T
\]

(1184 < \( T < 1450 \))

and for Cu + CuO (±40)

\[
-347 705 + 246.096T - 12.90537 \ln T
\]

(750 < \( T < 1330 \))

The reference pressure for oxygen is 1 bar (10⁵ 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 + CuO 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 \( \mu \text{O}_2 \) 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 overvoltage produced by passing a small current through a symmetrical cell of the type

\[
M + MO/CSZ/M + MO
\]

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 + MoO₂ 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 + CuO and Fe + “FeO”) for the primary experiments against air, this problem may be minimized.

2. The \( \mu \text{O}_2 \) 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 \( \mu \text{O}_2 \) of the unknown than if air were the reference.

Although the Cu + CuO 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 + CuO 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 \( \mu \text{O}_2 \) values. Hence, after determining the \( \mu \text{O}_2 \) of the Ni + NiO equilibrium against both Fe + “FeO” and Cu + CuO, Ni + NiO was thereafter used as the higher- \( \mu \text{O}_2 \) reference electrode for the other reactions. Also Cu + CuO invariably sticks to the electrolyte tube, and although there is no evidence of any chemical reaction (the Cu + CuO 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 CuO, Fe and “FeO”, Ni and NiO, and Co and CoO in the molar ratio 3:1. Cu₂O was prepared from Cu and CuO.
and “FeO” from Fe and Fe₂O₃, 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 Co₂O₃ 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 SiO₂ were used: quartz from a large natural crystal of gem quality, with no inclusions visible under the optical microscope; and cristobalite from amorphous SiO₂·2H₂O, sintered in air at 1550°C for 3 d.

Co₃SiO₄ olivine was synthesized from CoO and amorphous SiO₂, 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 SiO₂ detectable either by X-ray diffraction or optical examination. This material was used for all the runs (with both quartz and cristobalite) using Fe and “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 Co₃SiO₄ 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.

Ni₃SiO₄ olivine proved rather difficult to synthesize. Attempts using NiO and dried amorphous SiO₂ never reacted completely, even at 1500°C for 1 week with one intermediate grinding. However, a gel method using Ni(NO₃)₂·6H₂O 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 SiO₂ in the form of cristobalite. This material was used for run Ni-OL 1. For all the other runs, Ni₃SiO₄ 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. Subsequently, 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 Co₃SiO₄ + Co + SiO₂ equilibrium behaved similarly, except that rather longer was needed to reach equilibrium initially, and stable emfs could not be achieved below ~950 K. For the run with Ni + NiO as the reference electrode, in which the Co₃SiO₄ 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 Ni₃SiO₄-containing cells differed markedly according to the provenance of the Ni₃SiO₄. The cells using Ni₃SiO₄ commercially supplied by Tem-Pres achieved equilibrium quite rapidly and generally performed similarly to those with Co₃SiO₄. Those with Ni₃SiO₄ made from a gel approached equilibrium very slowly, and reasonable results could not be obtained below 1150 K, the apparent μₜ being anomalously low, i.e., more reducing at lower temperatures. Attempts using Ni₃SiO₄ made from NiO and amorphous SiO₂ (which was known to be incompletely reacted) also gave anomalously low μₜ values, which is opposite to the extent that might be expected if the μₜ was buffered by NiO + Ni. The emfs 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 + H₂O, 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-Pt₀.₉Rh₀.₁ 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 emfs 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 Pt, M + MO₂ |CSZ|M + MO₂, 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 + Cu₂O; these latter showed small (~1.0 mV), reproducible emfs 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 emfs are expected to be independent of the composition of the sample electrode, they were subtracted from the final readings obtained with the Cu + Cu₂O 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 emfs have therefore been reported without ±ve or vve 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:

Pt, Ni + NiO |CSZ|Cu + Cu₂O, Pt (I)
Pt, Ni + NiO |CSZ|Fe + “FeO”, Pt (II)
Pt, Fe + “FeO” |CSZ|Ni + NiO, Pt. (III)
### TABLE 1. Results from the cells used to measure the free energy of formation of NiO

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<th>T (K)</th>
<th>emf (mV)</th>
<th>T (K)</th>
<th>emf (mV)</th>
<th>T (K)</th>
<th>emf (mV)</th>
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<td>261.8</td>
<td>1007</td>
<td>258.8</td>
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<td>1006</td>
<td>258.7</td>
<td>1024</td>
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<td>1098</td>
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<tr>
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<tr>
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<td>1124</td>
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<td>1187</td>
<td>277.5</td>
<td>1248</td>
<td>271.1</td>
</tr>
</tbody>
</table>

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

O’NEILL: $\Delta G^\circ$ OF NiO, CoO, Ni, SiO, AND Co, SiO

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 $\mu_{O_{2}}$ that is slightly lower than that of Holmes et al. (1986). For the runs vs. Cu + Cu, O linear regression analysis of this difference ($\Delta \mu_{O_{2}}$) as a function of temperature gives (in J·mol⁻¹)

$$\Delta \mu_{O_{2}} (± 85) = -424 (± 62) + 0.084 (± 0.059) T$$

and for the runs vs. Fe + “FeO”

$$\Delta \mu_{O_{2}} (± 97) = -52 (± 101) - 0.2505 (± 0.094) T.$$
Fig. 2. Comparison of the present results for the free energy of the reactions $2\text{Ni} + \text{O}_2 = 2\text{NiO}$ and $2\text{Co} + \text{O}_2 = 2\text{CoO}$ with that derived from calorimetric data as assessed in Pankratz (1982; Pz), Robie et al. (1978; RHF), and Chase et al. (1974; JANA$). The curves are smoothed representations of values tabulated at 100-K intervals.

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 $\mu_{\text{Fe}}^\circ$ 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
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),

\[ \Delta \mu_{\text{O}_2} \pm 75 = +1157 \pm 63 - 1.200 \pm 0.053 T, \]

and for the runs with Ni + NiO,

\[ \Delta \mu_{\text{O}_2} \pm 64 = +1000 \pm 57 - 1.065 \pm 0.055 T. \]

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

\[ \Delta \mu_{\text{O}_2} \pm 71 = +1075 \pm 40 - 1.133 \pm 0.036 T, \]

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

\[ \mu_{\text{O}_2} \pm 120 = -491.649 + 508.527T - 53.284T \ln T + 0.025T^2 \quad (800 < T < 1397). \]

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 \( \Delta H \) of approximately 0.7 J·K⁻¹·mol⁻¹ (assuming the entropies of Co and O₂ 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

\[ 3\text{CoO} + 1/2\text{O}_2 = \text{Co}_3\text{O}_4, \]

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 Co₃O₄ between the emf results and the calorimetrically determined \( \mu_\text{O}_2 \) vs. \( T \) slope of the reaction. If the data given in O’Neill (1985) are re-examined using the new values for the Cu + CuO 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 CorO₂ 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):

\[
\Delta H_{\text{f298.15}} = -236.86 \text{ kJ mol}^{-1}.
\]

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 CorO₂ and CorSiO₂ 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).

Co₆SiO₄ + Co + SiO₂

Three types of cell were examined:

\[
\begin{align*}
\text{Pt, Co₆SiO₄ + Co + SiO₂} & \text{ vs. Fe + “FeO” Pt (VI)} \\
\text{Pt, Co₆SiO₄ + Co + SiO₂} & \text{ vs. FeO“Pt (VII)} \\
\text{Pt, Co₆SiO₄ + Co + SiO₂} & \text{ vs. Ni + NiO, Pt (VIII)}
\end{align*}
\]

The results are given in Table 3. Those involving SiO₂ 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:

\[
\Delta H_{\text{f298.15}} = \Delta G_{\text{f298.15}} - \int_{298.15}^{T} \Delta C_{p,m} dT
\]

\[+ T \left( \Delta S_{298.15} + \int_{298.15}^{T} (\Delta C_{p,m}/T) dT \right)\]

using the calorimetric data listed in Table 4. The calculated values of \( \Delta H_{\text{f298.15}} \) have been plotted against the temperature of the datum in Figure 4. Such a plot should give a horizontal line (i.e., \( \Delta H_{\text{f298.15}} \) 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 \( \Delta H_{\text{f298.15}} \) gives (in J mol⁻¹)

\[
-501.579 (±179) + 0.025 (±0.160) T (±89)
\]

or, independent of \( T \),

\[
-501.551 ± 88,
\]

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

\[
-501.232 (±157) - 0.185 (±0.132) T
\]

or

\[
-501.452 (±76).
\]

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

\[
-501.621 (±130) + 0.100 (±0.113) T (±97)
\]

or, independent of temperature,

\[
-501.507 (±96).
\]

(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
for $\Delta H_{m,298,15}^0$ 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 $\text{Co}_2\text{SiO}_4 + \text{Co} + \text{SiO}_2$:

$$\mu_{\text{O}_2}(\pm 130) = -491141 + 122.815T + 3.5527T \ln T.$$  

This, when combined with the data for the Co + CoO equilibrium, gives the following values for the free energy of formation of $\text{Co}_2\text{SiO}_4$ from the oxides (in J mol$^{-1}$):

$$\Delta G_{m,\text{Co}_2\text{SiO}_4,\text{oxides}}^0(\pm 120) = -31224 + 134.475T$$  

for $900 < T < 1400$ K.

The standard enthalpy of formation of $\text{Co}_2\text{SiO}_4$ from the oxides is then calculated to be

$$\Delta H_{m,\text{Co}_2\text{SiO}_4,\text{oxides}}^0 = -27.79 \text{ kJ mol}^{-1},$$

which is 8.1 kJ 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 $\text{Co}_2\text{SiO}_4 + \text{Co} + \text{SiO}_2$ 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 enthalpy 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.

$\text{Ni}_3\text{SiO}_4 + \text{Ni} + \text{SiO}_2$

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

$$\text{Pt, } \text{Ni}_3\text{SiO}_4 + \text{Ni} + \text{SiO}_2(\text{ox}) | \text{CSZ} | \text{Fe} + \text{“FeO”}, \text{Pt}$$

(IX)

$$\text{Pt, } \text{Ni}_3\text{SiO}_4 + \text{Ni} + \text{SiO}_2(\text{ox}) | \text{CSZ} | \text{Fe} + \text{“FeO”}, \text{Pt}$$

(X)

$$\text{Pt, } \text{Ni}_3\text{SiO}_4 + \text{Ni} + \text{SiO}_2(\text{ox}) | \text{CSZ} | \text{Ni} + \text{NiO}, \text{Pt}$$

(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 $\Delta H_{m,298,15}^0$ 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 $\Delta H_{m,298,15}^0$.

In order to try to get some insight into why this might be so, some further investigations were undertaken. First, $\text{Ni}_3\text{SiO}_4$ has been reported to disproportionate to the oxides NiO + SiO$_2$ at 1818 K (Phillips et al., 1963). This observation was confirmed by a pair of reversal experiments, $\text{Ni}_3\text{SiO}_4$, NiO, and SiO$_2$ 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

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**Table 4.** Results for the reaction $\text{Ni}_3\text{SiO}_4 = 2\text{Ni} + \text{SiO}_2 + \text{O}_2$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\text{emf (mV)}$</th>
<th>Temperature (K)</th>
<th>$\text{emf (mV)}$</th>
<th>Temperature (K)</th>
<th>$\text{emf (mV)}$</th>
<th>Temperature (K)</th>
<th>$\text{emf (mV)}$</th>
</tr>
</thead>
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<tr>
<td>1020</td>
<td>9.6</td>
<td>1030</td>
<td>9.6</td>
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<td>9.6</td>
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<td>9.6</td>
<td>1080</td>
<td>9.6</td>
<td>1090</td>
<td>9.6</td>
</tr>
<tr>
<td>1100</td>
<td>9.6</td>
<td>1110</td>
<td>9.6</td>
<td>1120</td>
<td>9.6</td>
<td>1130</td>
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<td>9.6</td>
<td>1160</td>
<td>9.6</td>
<td>1170</td>
<td>9.6</td>
</tr>
</tbody>
</table>

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**Fig. 4.** Standard enthalpy, $\Delta H_{m,298,15}^0$, for the reaction $2\text{Co} + \text{SiO}_2(\text{ox}) + \text{O}_2 = \text{Co}_2\text{SiO}_4$ 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. O, obtained with the Fe + “FeO” reference electrode; O, with Ni + NiO.
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$_3$SiO$_4$ + NiO only (determined by X-ray diffraction); the second, at 1821 K, produced NiO + SiO$_2$ with a faint trace of Ni$_3$SiO$_4$. 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$_3$SiO$_4$ 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$_3$SiO$_4$ that is not only derived from a method completely independent of the emf experiments, 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, Δ\text{H}'$_{m,298,15}$, 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$_3$SiO$_4$ 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$_3$SiO$_4$ at high temperatures was calculated by generating values from the relationship

\[ C_p = C_v + \alpha^2 VT/\beta \]  

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 Δ\text{H}'$_{m,298,15}$ of only 0.15 kJ·mol$^{-1}$.

Secondly, an investigation was made into whether the Ni$_3$SiO$_4$ 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$_3$SiO$_4$ produced by slowly cooling a mixture of NiO and SiO$_2$ dissolved in a melt of Na$_2$WO$_4$. To investigate any possible nonstoichiometry in this material, three experiments were performed on mixtures of NiO, SiO$_2$, and Na$_2$WO$_4$ 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$_3$SiO$_4$ and long blades (500 × 50 μm) of SiO$_2$ (tridymite); (2) SiO$_2$ in excess, 1200 K, 7 d, products—Ni$_3$SiO$_4$ (∼20 μm) and SiO$_2$ (∼10 μm); (3) NiO in excess, 1200 K, 7 d, products—Ni$_3$SiO$_4$ (∼20 μm) and NiO.

The Ni$_3$SiO$_4$ 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$_3$SiO$_4$ 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 \( \text{Ni}_2\text{Si}_3\text{O}_8 \) and that the ratio of Ni to Si was identical in the SiO, excess and NiO-excess experiments, and indistinguishable from the stoichiometric ideal of 2:1, within the analytical error. The product of the \( \text{Ni}_2\text{Si}_3\text{O}_8 \) breakdown run at 1816 K showed similar results. The two types of \( \text{Ni}_2\text{Si}_3\text{O}_8 \) 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,WO, 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 \( \text{Ni}_2\text{Si}_3\text{O}_8 \).

Incidentally, analogous pairs of experiments for \( \text{Co}_2\text{Si}_3\text{O}_8 \) and \( \text{Mg}_2\text{Si}_3\text{O}_8 \) (MgSiO, in excess rather than SiO, at 1200 K in Na,WO, also showed no evidence of any nonstoichiometry.

The emf results plus the datum obtained from the breakdown of \( \text{Ni}_2\text{Si}_3\text{O}_8 \) were used to obtain the following expression for the \( \text{Ni}_2\text{Si}_3\text{O}_8 + \text{Ni} + \text{SiO}_2(\text{g}) \) equilibrium (in J mol\(^{-1}\)):

\[
\mu_{\text{O}_2} (\pm 180) = -516.690 + 362.977 - 22.297 T \ln T.
\]

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) 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 \( \beta' \)-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, 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 \( \log f_{\text{O}_2} \) at 950 K and becomes less at higher temperatures.

Combination of the results for the \( \text{Ni}_2\text{Si}_3\text{O}_8 + \text{Ni} + \text{SiO}_2(\text{g}) \) equilibrium with those for \( \text{Ni} + \text{NiO} \) gives the free energy of formation of \( \text{Ni}_2\text{Si}_3\text{O}_8 \) from the oxides (in J mol\(^{-1}\)):

\[
\Delta G^\circ_{\text{f, Ni}_2\text{Si}_3\text{O}_8, \text{oxides}} (\pm 180) = -36560 + 118.107 T

- 13.1087 \ln T

(960 < T < 1820).

**Table 5.** Calorimetric data used in calculating \( \Delta H^\circ_{\text{f, Ni}_2\text{Si}_3\text{O}_8, \text{oxides}} \) for \( 2\text{Ni} + \text{SiO}_2 + \text{O}_2 = \text{Ni}_2\text{Si}_3\text{O}_8 \) and \( 2\text{Co} + \text{SiO}_2 + \text{O}_2 = \text{Co}_2\text{Si}_3\text{O}_8 \)

<table>
<thead>
<tr>
<th>Substance</th>
<th>( T ) range (K)</th>
<th>Ref. ( T ) (K)</th>
<th>( S_{\text{f}} ) (J/K mol(^{-1}))</th>
<th>( H_N ) (J mol(^{-1}))</th>
<th>( \Delta G^\circ_{\text{f, Ni}_2\text{Si}_3\text{O}_8, \text{oxides}} ) (J mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni}^* )</td>
<td>700 - 1728</td>
<td>700</td>
<td>55.578</td>
<td>12342</td>
<td>20.668</td>
</tr>
<tr>
<td>( \text{Co}^* )</td>
<td>700 - 1200</td>
<td>700</td>
<td>54.265</td>
<td>11178</td>
<td>-3.524</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>1200 - 1394</td>
<td>1200</td>
<td>73.421</td>
<td>29769</td>
<td>-141.419</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>847 - 1676</td>
<td>900</td>
<td>109.045</td>
<td>38731</td>
<td>65.277</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>652 - 1834</td>
<td>900</td>
<td>110.929</td>
<td>37989</td>
<td>66.930</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>298 - 1300 ( \dagger )</td>
<td>900</td>
<td>297.78</td>
<td>95239</td>
<td>289.73</td>
</tr>
<tr>
<td>( \text{Co}_2\text{Si}_3\text{O}_8 )</td>
<td>298 - 1300 ( \dagger )</td>
<td>900</td>
<td>321.75</td>
<td>100182</td>
<td>305.83</td>
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<tr>
<td>( \text{O}_2 )</td>
<td>700 - 1800</td>
<td>700</td>
<td>231.463</td>
<td>12498</td>
<td>34.2909</td>
</tr>
</tbody>
</table>

\( \text{Ni}^* \): JANAF, Holmes et al. (1986).
\( \text{Co}^* \): Richet et al. (1982).
\( \text{SiO}_2 \): Robie et al. (1984).
\( \dagger \): 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.
O'NEILL: $\Delta G^0$ OF NiO, CoO, Ni$_2$SiO$_4$, AND Co$_2$SiO$_4$

Fig. 8. The free energy of the reaction $\text{SiO}_2 \rightarrow \text{SiO}_2$ obtained by subtracting the data for the reactions $2\text{Co} + \text{SiO}_2 \rightarrow \text{CoSi}_2$ (run Co-OL 2) and $2\text{Ni} + \text{SiO}_2 \rightarrow \text{NiSi}_2$ (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$_2$WO$_4$, and found that quartz transformed to tridymite at $\approx 1143$ K, and tridymite to cristobalite at $\approx 1743$ 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 $1300 \pm 25$ K. That cristobalite formed as a metastable intermediate phase at temperatures as low as $\sim 1160$ 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 $1350 \pm 50$ K.

In the present work, two runs, one each on the Co$_2$SiO$_4$, Co + SiO$_2$, and Ni$_2$SiO$_4$, 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

$$\Delta G^0_{\text{Q-c}} = \Delta H^0_{298} - 637 - 1.988T.$$  

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 $\Delta H^0_{298} = 2836$ 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$_2$SiO$_4$-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 $\pm 100$ J·mol$^{-1}$ of O$_2$, which is approximately equivalent to $\pm 0.005 \log f_o$ 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 $\pm 0.2$ J·K$^{-1}$·mol$^{-1}$ may be expected (e.g., Robie et al., 1982, 1984), which translates to $\pm 200$ 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$_3$SiO$_4$, 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 + CuO, 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.

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References


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


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