REDOX EQUILIBRIA IN DIOPSIDIC MELT. Krystna W. Semkow and Larry A. Haskin, Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130.

An understanding of the reduction-oxidation equilibria in silicate melts is of great importance to geology and glass technology. If an element M is oxidized in a silicate melt, the oxidation-reduction equilibrium may be represented by an equation such as the following:

\[ \text{MO} + 1/2 \text{O}_2 = \text{M}^2+ + \text{O}^2- \]  

(1)

The reversible cell representing this composition is the following:

\[ \text{O}_2 / \text{O}^2- , \text{M} / \text{M}^2+ \]  

(2)

In this work, M=Fe, Ni, Co or Zn, all in diopside melt. The cell reaction was investigated at various temperatures in the range of 1425-1575°C. Charges were suspended in a loop of Pt wire which acted as the reference electrode with a constant potential determined by \( \text{pO}_2 \) [1,2]. In addition, two Pt wires were immersed in the diopside melt. One served as the counter electrode. The second was used as the working electrode in voltammetric reduction of \( \text{M}^2+ \) ions. The cell potential was measured between the reference and working electrodes. The dependence of the cell potential on temperature was obtained at \( E = E^* \), where \( E^* \) is the standard reduction potential of \( \text{M}^2+ \) ion against the reference potential of \( \text{O}_2 \) in diopside in equilibrium with air (Semkow et al., 1982). At this potential, the activity ratio of \( \text{M}/\text{M}^2+ \) at the electrode surface is unity. The resulting values of \( E^* \) and their temperature dependence allowed us to calculate the change in free energy and entropy of the cell. All experiments were done in air atmosphere at \( dp/dT=0 \) and in diopside, where the activity of oxide ions is known to be \( 5.4 \pm 0.4 \times 10^{-5} \) mole/l [2]. The standard cell potential, \( E^0 \), the equilibrium constant, \( K \), the standard free energy, \( \Delta G^0 \), enthalpy, \( \Delta H^0 \) and entropy, \( \Delta S^0 \), of reaction (1) were calculated at 1450°C (Table 1). Also, the standard reduction potential, \( E^* \), of the following reaction was determined:

\[ \text{O}_2 + 4e = 2\text{O}^2- \] 

(diop)

(3)

The value is -0.73±0.02V (vs. the oxygen reference electrode equilibrated with oxygen at 1 atm., 1450°C).

Results show that the reaction (1) gives similar standard entropy values for all four elements. All four reactions are exothermic. It is interest-
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In order to see that $\Delta G^0$ values are all positive, suggesting that there would be no spontaneous reaction between $M$ in diopside and oxygen gas to produce $M^{2+}$ and $O_2^-$, both in diopside. It must be noticed, however, that $\Delta G^0$ refers to an unstable situation in which diopside would contain 1 mole/l of oxide ions. The reactions do occur spontaneously as long as oxide ion concentration is kept low by melt depolymerization (see companion abstract).

An electromotive force series can be formed using the standard cell potentials as: $E^0_{Zn} >> E^0_{Co} >> E^0_{Fe} >> E^0_{Ni}$ in which Ni is the easiest and Zn is the hardest ion to reduce.

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References:

Table 1. Thermodynamic Parameters for the Reaction:

\[ M^0_{(diop)} + \frac{1}{2} O_2(g) = M^{2+}_{(diop)} + O^{2-}_{(diop)} \]

<table>
<thead>
<tr>
<th>M</th>
<th>$E^0(V)^\dagger$</th>
<th>K[mole/l.atm]</th>
<th>$\Delta G^0$[kcal/mole]</th>
<th>$\Delta H^0$[kcal/mole]</th>
<th>$\Delta S^0$[e.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>-0.218±0.014</td>
<td>0.054±0.010</td>
<td>10.0±0.7</td>
<td>-56.0±4.1</td>
<td>-38.3±2.0</td>
</tr>
<tr>
<td>Co</td>
<td>-0.208±0.014</td>
<td>0.062±0.012</td>
<td>9.6±0.7</td>
<td>-57.5±7.4</td>
<td>-38.9±3.9</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.330±0.004</td>
<td>0.012±0.001</td>
<td>15.2±0.2</td>
<td>-47.9±3.6</td>
<td>-36.6±2.0</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.128±0.004</td>
<td>0.180±0.011</td>
<td>5.9±0.2</td>
<td>-61.2±3.8</td>
<td>-38.9±2.1</td>
</tr>
</tbody>
</table>

$E^0$ is the standard cell potential for the overall reaction, independent of the choice of reference electrode used in obtaining $E^*$ values.