THE EFFECT OF REDUCED H₂O FUGACITY ON THE BUFFERING OF OXYGEN FUGACITY IN HYDROTHERMAL EXPERIMENTS

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ABSTRACT

The effect of varying H₂O fugacity on the oxygen fugacity in hydrothermal experiments is analyzed for both the solid external buffer and the controlled hydrogen pressure methods. Lowering of H₂O fugacity in the experimental charge either by a second species in the vapor phase, or by the absence of a free vapor phase, lowers the oxygen fugacity in the charge.

INTRODUCTION

Within the last fifteen years, great strides have been made in the study of the geochemistry of elements with variable oxidation states by means of the solid buffer technique (Eugster, 1957) and by the use of gas mixtures (Shaw, 1967). One of the basic assumptions inherent in the use of these buffering techniques to control oxygen fugacity is that the charge contains abundant water. (Shaw, 1967; Eugster, 1957) Recently, experiments have been conducted in which the availability of water has been purposely limited (Whitney and
In such experiments involving iron bearing compositions, the concept of buffering oxygen fugacity must be modified. Although these modifications are quite simple, the author feels that they need to be outlined so that the limitations will be fully realized by experimenters starting vapor absent work on iron bearing systems.

OXYGEN FUGACITY IN A STELLITE PRESSURE VESSEL

Suppose that a charge containing iron or some other element of variable oxidation state has been loaded into a metal capsule permeable to hydrogen (e.g., Pd–Ag alloy, or Pt at high temperatures) which is to be held at pressure and temperature within a pressure vessel made of the commonly used Stellite 28, or some other high nickel alloy, with water as the pressure medium.

Classically it has been assumed that the hydrogen fugacity in the vessel is controlled by the oxidation of nickel to bunsenite, along with the decomposition of H₂O:

\[
\begin{align*}
\text{(1)} & \quad \text{Ni}^{(s)} + \frac{1}{2} \text{O}_2^{(g)} = \text{NiO}^{(s)} \quad K_{\text{Ni-NiO}} = f_{\text{O}_2}^{-1/2} \\
\text{(2)} & \quad \text{H}_2^{(g)} + \frac{1}{2} \text{O}_2^{(g)} = \text{H}_2\text{O}^{(g)} \quad K_w = \frac{f_{\text{H}_2\text{O}}}{f_{\text{H}_2}(f_{\text{O}_2})^{1/2}}
\end{align*}
\]

This yields the over all buffering reaction (3) which controls hydrogen fugacity within the pressure vessel.

\[
\begin{align*}
\text{(3)} & \quad \text{Ni}^{(s)} + \text{H}_2\text{O}^{(g)} = \text{NiO}^{(s)} + \text{H}_2^{(g)} \quad K_B = \frac{f_{\text{H}_2}^B}{f_{\text{NiO}}^B}
\end{align*}
\]

It must be remembered that buffering by the Ni–NiO oxidation can only be true for alloys like Stellite 25, which are dominantly composed of nickel. Even in this case, there is an aging effect, which causes the oxygen fugacity within the vessel to vary with its time in operation. As oxide forms within the vessel, the accessibility of the nickel to the pressure medium decreases, so that the buffering tendency is diminished. With time, the oxygen fugacity in the vessel tends to increase (Eugster and Wones, 1962). Thus, the hydrogen fugacity is only approximately controlled by equation (3), and the value will change with the alloy used, and the age of the vessel.

Since the sample capsule is supposedly permeable to hydrogen, the fugacity of hydrogen in the pressure vessel must be equal to the fugacity of hydrogen in the charge (4). This, combined with the dissociation of H₂O in the charge (5), controls the fugacity of oxygen in the charge (7).
(4) \[ f_{\text{H}_2}^B = f_{\text{H}_2}^C \]

(5) \[ \text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) \quad K_w = \frac{(f_{\text{H}_2\text{O}}^C)}{(f_{\text{H}_2}^C)(f_{\text{O}_2}^C)^{1/2}} \]

(6) \[ K_B f_{\text{H}_2\text{O}}^B = \frac{(f_{\text{H}_2\text{O}}^C)}{K_w(f_{\text{O}_2}^C)^{1/2}} \]

(7) \[ f_{\text{O}_2}^C = (K_w \cdot K_B)^{-2} \left( \frac{f_{\text{H}_2\text{O}}^C}{f_{\text{H}_2\text{O}}^B} \right)^2 \]

Since \( K_B = K_{\text{N}_1-\text{N}_10}/K_w \), equation (7) simplifies to:

(7') \[ f_{\text{O}_2}^C = (K_{\text{N}_1-\text{N}_10})^{-2} \left( \frac{f_{\text{H}_2\text{O}}^C}{f_{\text{H}_2\text{O}}^B} \right)^2 \]

When the fugacity of \( \text{H}_2\text{O} \) in the charge is equal to the fugacity of \( \text{H}_2\text{O} \) in the vessel, this equation does indeed reduce to:

(8) \[ f_{\text{O}_2}^C = (K_{\text{N}_1-\text{N}_10})^{-2} = f_{\text{O}_2}^B \]

which allows us to assume that the oxygen fugacity in the charge is the same as that in the buffering assemblage.

However, when these fugacities of \( \text{H}_2\text{O} \) are not equal, then the oxygen fugacity is no longer the same in both assemblages. Curve (A) of Figure 1 demonstrates the variation of \( f_{\text{O}_2}^C \) with changing \( f_{\text{H}_2\text{O}}^C \) for a system at 800°C and 2 kilobars pressure, externally buffered by nickel–bunshenite. If the fugacity of \( \text{H}_2\text{O} \) in the charge is decreased relative to that in the buffer, either by solution of other volatile species in the vapor phase, or by the absence of a hydrous vapor phase due to the presence of another hydrous phase, the oxygen fugacity will be lowered in the charge relative to the buffer.

The dissociation of water in the charge also needs further discussion. The dissociation equation used (5) is only rigorously correct when a free, aqueous vapor phase is present in the charge. If another species is present, then the gas mixture may be quite non–ideal, especially at high pressures. Data on the gas mixture is needed to determine the fugacity of \( \text{H}_2\text{O} \) in the charge, as well as the dissociation constant for \( \text{H}_2\text{O} \) in the mixture which will determine the fugacity of oxygen.

If no vapor phase is present in the system, the problems are magnified, as the nature of the dissociation reaction for \( \text{H}_2\text{O} \) will be dependent on the state of the \( \text{H}_2\text{O} \) dissolved in other hydrous phases. For example, in the case of a silicate melt in a vapor absent assemblage, the water originally in the charge may be present in many different forms, and the dissociation reaction may have a different
reaction constant depending on the species present and the nature of the bonding within the melt. The reaction of hydrogen with this dissolved water is similar to a gas dissociation problem where the dissociation constant is unknown, and presents a substantial problem in vapor absent experimentation.

**Oxygen Fugacity in Experiments Using an External Buffer**

Suppose now that the permeable capsule is surrounded by a solid buffer as described by Eugster (1957). If the buffer were composed of fayalite, quartz, and magnetite, saturated with water, the following would be the buffering equation (11).

\[
3 \text{Fe}_2\text{SiO}_5(s) + \text{O}_2(g) = 3 \text{SiO}_2(s) + 2 \text{Fe}_3\text{O}_4(s) \quad K_QF_M = (f_{O_2} B)^{-1}
\]

**Fig. 1.** Variation of \( f_{O_2} \) with \( f_{H_2O} \) for several different buffering techniques, at 800°C and 2000 bars total pressure.

Curves (A) and (B) have been constructed from Eugster and Skippen (1967), Table 1, and Figure 5. Curve (C) has been constructed using the method outlined in detail by Shaw (1967).
MINERALOGICAL NOTES

(10) \[ \text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) \quad K_w = \frac{(f_{\text{H}_2\text{O}}^\text{B})}{(f_{\text{H}_2}^\text{B})(f_{\text{O}_2}^\text{B})^{1/2}} \]

(11) \[ 3 \text{Fe}_2\text{SiO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{g}) = 3 \text{SiO}_2(\text{s}) + 2 \text{Fe}_3\text{O}_4(\text{s}) + 2 \text{H}_2(\text{g}) \]

\[ K_B = \frac{K_{\text{QFM}}}{K_w^2} = \frac{(f_{\text{H}_2}^\text{B})^2}{(f_{\text{H}_2\text{O}}^\text{B})^2} \]

Combined with hydrogen diffusion, and the dissociation of \text{H}_2\text{O} in the charge, this relationship yields the fugacity of oxygen in the charge (12).

\[ f_{\text{O}_2}^\text{C} = (K_{\text{QFM}})^{-1} \left( \frac{f_{\text{H}_2\text{O}}^\text{B}}{f_{\text{H}_2}^\text{B}} \right)^2 \]

Curve (B) of Figure 1 demonstrates the variation of \( f_{\text{O}_2}^\text{C} \) with changes in \( f_{\text{H}_2\text{O}}^\text{C} \) for a system at 800°C and 2 kilobars pressure, externally buffered by quartz-fayalite-magnetite. The trend is similar to that seen for nickel-bunsenite.

EXPERIMENTS USING CONTROLLED PARTIAL PRESSURE OF HYDROGEN

Suppose the permeable capsule is placed in a gas pressure medium containing a controlled partial pressure of hydrogen as described by Shaw (1967). Then, following his calculations for oxygen fugacity in the charge, we have:

\[ f_{\text{H}_2}^\text{B} = f_{\text{H}_2}^\text{C} = K_w^{-1} \left( \frac{f_{\text{H}_2\text{O}}^\text{C}}{f_{\text{O}_2}^\text{C}} \right)^{1/2} \]

\[ f_{\text{O}_2}^\text{C} = (K_w f_{\text{H}_2}^\text{B})^{-2} \left( f_{\text{H}_2\text{O}}^\text{C} \right)^2 \]

Curve (C) of Figure 1 shows the variation of oxygen fugacity with changes in \( f_{\text{H}_2\text{O}}^\text{C} \) for a system at 800°C and 2 kilobars pressure, for a partial pressure of hydrogen of 50 bars. The same decrease in oxygen fugacity with \( f_{\text{H}_2\text{O}}^\text{C} \) is seen, as in the previous solid buffer situations.

EXPERIMENTS IN AN ARGON ATMOSPHERE, WITH A MOLYBDENUM SAMPLE HOLDER

Suppose the permeable capsule were placed within a molybdenum sample holder, which was partially covered with molybdenum oxide, and both were then held at temperature and pressure in a dominantly argon atmosphere with a small partial pressure of hydrogen present. This model is an approximation to the conditions present at the beginning of an experiment at high pressures in an internally heated pressure vessel with a molybdenum sample holder.
MINERALOGICAL NOTES

\[ \text{(15)} \quad \text{Mo}_3 + 3/2 \text{O}_2 = \text{MoO}_3 \quad K_{\text{MoO}_3} = (f_{\text{O}_2})^{3/2} \]

\[ \text{(16)} \quad \text{Mo}_3 + 3 \text{H}_2 \text{O} = \text{MoO}_3 + 3 \text{H}_2 \text{(aq)} \quad K_B = K_{\text{MoO}_3} \cdot K_w^{-3} = \left(\frac{f_{\text{H}_2 \text{O}}}{f_{\text{H}_2 \text{O}}}\right)^3 \]

This results in the following expression for oxygen fugacity in the charge:

\[ \text{(17)} \quad f_{\text{O}_2}^c = (K_{\text{MoO}_3})^{-2/3} \left(\frac{f_{\text{H}_2 \text{O}}}{f_{\text{H}_2 \text{O}}}\right)^2 \]

In a dominantly argon pressure medium, the fugacity of H$_2$O will be very low relative to that in most charges. As a result, the oxygen fugacity in the charge will be considerably higher than that fixed by the oxidation-reduction of the sample holder.

**USE OF ACTIVITY IN PLACE OF FUGACITY**

The fugacity of H$_2$O may be rewritten in terms of the activity of water:

\[ \text{(18)} \quad f_{\text{H}_2 \text{O}} = a_{\text{H}_2 \text{O}} f_{\text{H}_2 \text{O}}^0. \]

In this equation, $f_{\text{H}_2 \text{O}}^0$ is the fugacity of H$_2$O at an arbitrary standard state. Substitution into the equation for oxygen fugacity in the charge in the solid buffer cases, yields the following equation:

\[ \text{(19)} \quad f_{\text{O}_2}^c = C \left(\frac{a_{\text{H}_2 \text{O}}}{a_{\text{H}_2 \text{O}}}\right)^2 \]

where $C$ is a function of the equilibrium constant of the original oxygen buffering equation, and is constant for constant temperature and pressure.

If the standard state for water is chosen to be pure H$_2$O at the pressure and temperature of the experiment, and if the vapor phase in the buffer is pure H$_2$O, then:

\[ \text{(20)} \quad a_{\text{H}_2 \text{O}} = 1 \]

and equation (19) simplifies to:

\[ \text{(21)} \quad f_{\text{O}_2}^c = C (a_{\text{H}_2 \text{O}}^0)^2 \]

In the direct control of hydrogen pressure by osmotic equilibrium, the equation involving the activity of water includes the fugacity of H$_2$O in the standard state, and is of the following form:

\[ \text{(22)} \quad f_{\text{O}_2}^c = (K_w \cdot f_{\text{H}_2 \text{O}}^0)^{-2} (f_{\text{H}_2 \text{O}}^0 \cdot a_{\text{H}_2 \text{O}}^0)^2 \]
DISCUSSION

It can be seen from this presentation that when the fugacity of \( \text{H}_2\text{O} \) in hydrothermal experiments is reduced either by solution of other species in the vapor phase, or by the absence of a vapor phase due to the presence of other water bearing phases, such as silicate liquids, the value of the oxygen fugacity also changes significantly. Therefore, it can be expected that in low \( \text{H}_2\text{O} \) fugacity experiments, the effective oxygen fugacity will be significantly lower than would be the case in high \( \text{H}_2\text{O} \) fugacity experiments at the same temperature and pressure.

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