DATA ON THE FUGACITY OF CO₂*
IN MIXTURES OF CO₂ AND H₂O

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ABSTRACT. Data on the P-T stability of magnesite in equilibrium with vapors containing carbon dioxide and water are utilized to obtain values for the fugacity of CO₂ in these vapors. The ratio of the fugacity of CO₂ in the mixture to that of pure CO₂ at the same T and P is found to be considerably greater than the mole fraction of CO₂.

INTRODUCTION

In an earlier paper (Walter, Wyllie, and Tuttle, 1962), data were presented concerning the stability of magnesite at high temperatures in equilibrium with a vapor consisting of H₂O and CO₂. These data can be utilized to obtain approximations of the fugacity of CO₂ in such a vapor phase. Values of the fugacity are required for evaluating the chemical effects of mixtures of these two important components of petrologic systems on mineral equilibria.

DETERMINATIONS

Fugacities were determined by the following method:
1. An isobaric section (P₁ = 1000 bars) along the join Mg(OH)₂-MgCO₃ is shown here in figure 1. At temperature T₁, the vapor in equilibrium with MgO and MgCO₃ is a mixture of CO₂ and H₂O (plus the small amount of MgO that is soluble in the vapor phase). The temperatures at which MgO, MgCO₃, and vapor of various compositions coexist are shown in table 1. The ratio of CO₂ to H₂O listed in the second column of this table is that in the mixture of Mg(OH)₂ and MgCO₃ at composition X₁ and can be computed or determined graphically.

2. These data are applied to the univariant P-T curve for the dissociation of magnesite (fig. 2) as determined by Harker and Tuttle (1955). In the

**Table 1**

Original data and determined fugacities

<table>
<thead>
<tr>
<th>X</th>
<th>Wt % MgCO₃</th>
<th>Vapor Comp. Mole % of CO₂</th>
<th>T (°C)</th>
<th>Pₑ CO₂(bars) at Pₛ = 1000 bars</th>
<th>Fugacity of CO₂ in the vapor mixture (bars)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7.1</td>
<td>641</td>
<td>236</td>
<td>325 ± 30</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>18.7</td>
<td>682</td>
<td>421</td>
<td>490 ± 40</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>40.8</td>
<td>738</td>
<td>715</td>
<td>918 ± 70</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>67.5</td>
<td>766</td>
<td>918</td>
<td>1245 ± 70</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>775</td>
<td>1000</td>
<td>1388 ± 10</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7.1</td>
<td>722</td>
<td>1040</td>
<td>1421 ± 70</td>
<td></td>
</tr>
</tbody>
</table>

* Contribution No. 61-10, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

** Presently with Theoretical Division, Goddard Space Flight Center, National Aeronautics and Space Administration, Greenbelt, Maryland, as National Academy of Sciences-National Research Council Research Associate.
binary system MgO–CO₂, the pressure at which magnesite and periclase coexist at T₁ is Pe. Pe cannot be considered the “effective” pressure of CO₂ in the ternary system because the total pressure on the solid phases, Pₑ, causes the equilibrium to be displaced. Thompson (1955) has presented the following equation, here given in the terminology of Greenwood (1961), which relates the change in the pressure on the solid phases (∂Pₑ) to the variation in the temperature of equilibrium (∂T) at constant equilibrium pressure (PₑCO₂):

\[
\left( \frac{\partial Pₑ}{\partial T} \right)_{PₑCO₂} = \frac{\Delta S_{\text{total}}}{\Delta Vₑ}
\]

PₑCO₂ is defined by Greenwood (1961) as the pressure of pure CO₂ at the same temperature and exhibiting the same chemical potential as in the gas mixture. The change of volume of the solid phases, \( \Delta Vₑ = V_{\text{MgO}} - V_{\text{MgCO₂}} \) = 11.23 – 28.11 = -16.88 cm³/g mole and is assumed to be independent of temperature and pressure (see Thompson, 1955). The change in entropy, \( \Delta S_{\text{total}} \), may be determined by the Clapeyron equation:

\[
\Delta S_{\text{total}} = \left( \frac{dP}{dT} \right) \Delta V_{\text{total}}
\]

utilizing the slope (dP/dT) of the univariant curve for the dissociation of magnesite and the volume change of the solid phases mentioned above, as well as the CO₂ P-V-T data of Kennedy (1954). These calculations appear in table 2.

Values for \( \left( \frac{\partial Pₑ}{\partial T} \right)_{PₑCO₂} \) obtained in this manner appear in table 2. These values represent only the slopes of the Pₑ-T projections of curves of constant PₑCO₂ at the point of intersection with Harker and Tuttle’s curve for the dissociation of magnesite where PₑCO₂ = Pₑ. Barnes and Ernst (1963) have derived the following equation, which expresses the rate of change of the slope of the PₑCO₂ contours with temperature at constant Pₑ:

\[
\left( \frac{\partial^2 Pₑ}{\partial T^2} \right)_{PₑCO₂, Pₑ} = \frac{1}{\Delta Vₑ} \left( \frac{\Delta C_p}{T} \right)
\]

in which \( \Delta C_p = (C_p)_{\text{MgO}} + (C_p)_{\text{CO₂}} - (C_p)_{\text{MgCO₂}} \). Expressions for the

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P (bars)</th>
<th>dP/dT (bars/°C)</th>
<th>Molar V_{CO₂} (cm³/mole)</th>
<th>( \Delta V_{\text{total}} = \frac{V_{\text{CO₂-16.88}}}{°C \text{ mole}} )</th>
<th>( \Delta S_{\text{total}} ) (bar cm³/°C mole)</th>
<th>( \left( \frac{\partial Pₑ}{\partial T} \right)_{PₑCO₂} ) (bars/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>272</td>
<td>3.13</td>
<td>296</td>
<td>279</td>
<td>874</td>
<td>-52 ± 5</td>
</tr>
<tr>
<td>700</td>
<td>456</td>
<td>4.70</td>
<td>197</td>
<td>180</td>
<td>846</td>
<td>-50 ± 5</td>
</tr>
<tr>
<td>750</td>
<td>748</td>
<td>7.82</td>
<td>137</td>
<td>120</td>
<td>939</td>
<td>-56 ± 5</td>
</tr>
<tr>
<td>800</td>
<td>1264</td>
<td>12.19</td>
<td>96.5</td>
<td>79.6</td>
<td>970</td>
<td>-57 ± 5</td>
</tr>
</tbody>
</table>
values of \((C_p)_{MgO}\) and \((C_p)_{MgCO_3}\) were obtained from Kelley (1949). The differences between these quantities become less with increasing temperature (Thompson. 1955). \((C_p)_{CO_2}\) has been determined for the \(P-T\) region up to \(450^0\)K and 1500 bars by Price (1955). At elevated temperatures and at 1000 bars pressure, this quantity approaches 14 cal/mole degree. Using this data the expression:

\[ \Delta C_p = 5.56 - 12.06 \times 10^{-3}T + 2.68 \times 10^3T^{-2} \]

is obtained and evaluated at \(T = 1000^0\)K and the result. \(\Delta C_p = -6.23\) cal/mole degree. With \(V_s = -16.88 \text{ cm}^3/\text{mole}\), \((\partial^2 P/\partial T^2)_{P_{ECO_2}, v_s}\) is determined to be \(1.53 \times 10^{-2}\) bars/degrees\(^2\) or 3.06 bars/degree over a 200° temperature interval. This quantity is negligible compared to the slope of the \(P_{ECO_2}\) contours, which is in the range of -50 to -60 bars/degree. Consequently, variations in the slope of the contours at constant \(P_s\) may, in the case of the present system, be neglected. As plotted in figure 2, the projections of these contours have only a slight curvature.

The point at \(T_1\) and \(P_1\) falls at some value of \(P_{ECO_2}\) which is read off at the intersection of this contour with the experimentally determined decarbonation curve where \(P_{ECO_2} = P_s\). This is point \(o\) in figure 2.

3. According to the definition of \(P_{ECO_2}\), the chemical potential of \(CO_2\)

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![Diagram](image.png)

**Fig. 1.** Isobaric (1000 bars) section of the system \(MgO-H_2O-CO_2\) along the join \(Mg(OH)_2\)-\(MgCO_3\). At this pressure, \(P_1\), and at temperature \(T_1\), composition \(X_1\) consists of the phases \(MgO, MgCO_3,\) and vapor. The ratio \(CO_2/H_2O\) in the vapor is computed from \(X_1\).
Fig. 2. Unvariant P-T curve for the dissociation of magnesite in the system MgO-CO$_2$ (after Harker and Tuttle, 1955). Curves with negative slopes are projections, representing the variation of temperature of this dissociation with change in total, inert, pressure on the solid phases while the equilibrium vapor pressure, $P_{E_{CO_2}}$, remains constant.

The $P_{E_{CO_2}}$ in the case of a reaction taking place at $T_1$ and $P_1$ is determined by following the $P_{E_{CO_2}}$ contour from $P_1$, $T_1$ to point o which is at $P_{E_{CO_2}}$.

in mixture $X_1$ at $T_1$ and $P_1$ is the same as that at $P_{E_{CO_2}}$ and $T_1$. By the definition of fugacity ($\mu = \mu^0 + RT \ln f$, where $\mu$ is the chemical potential, $\mu^0$ is the standard chemical potential and $f$ is the fugacity) the fugacities under both conditions are also equal. The values of $P_{E_{CO_2}}$ and $T$ can be converted to fugacities by reference to the data of Majumdar and Roy (1956). These fugacities are listed in table 1.

For a more detailed discussion of the relations of $P_E$, $P_s$, and $T$, and an analysis of the errors involved in the determination of the fugacities, the reader is referred to Greenwood (1961).

DISCUSSION

These data, which are shown graphically in figure 3, are offered as approximations. More precise and complete data will be useful and will test the validity of the assumptions concerning entropy and volume change that are made in the present approach.
Data on the Fugacity of CO$_2$ in Mixtures of CO$_2$ and H$_2$O

Comparison of fugacity of CO$_2$ in vapor mixtures to fugacity of pure CO$_2$ at $P_s = 1000$ bars

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>641</th>
<th>682</th>
<th>738</th>
<th>766</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole Fraction of CO$_2$</td>
<td>0.0714</td>
<td>0.1863</td>
<td>0.498</td>
<td>0.675</td>
</tr>
<tr>
<td>*Fugacity of pure CO$_2$ (bars)</td>
<td>1372.</td>
<td>1380.</td>
<td>1388.</td>
<td>1388.</td>
</tr>
<tr>
<td>Fug. CO$_2$ in vapor/Fug. CO$_2$</td>
<td>0.24±.025</td>
<td>0.35±.04</td>
<td>0.66±.06</td>
<td>0.90±.06</td>
</tr>
</tbody>
</table>

* From Majumdar and Roy, 1956

It is interesting to note that, in the P-T range investigated, the fugacity of CO$_2$ in H$_2$O-CO$_2$ mixtures is considerably higher than might be expected. That is, the ratio of the fugacity of CO$_2$ in the binary vapor to the fugacity of

Fig. 3. Partially schematic P-T-X box showing, in heavy line, surfaces of equal fugacity of CO$_2$. Data for the five points on the 1000 bar isobar and the one on the 4000 bar isobar appear in table 1.
pure CO$_2$ at the same temperature and pressure is greater than the mole fraction of CO$_2$ in the vapor. These data are summarized in table 3.

As shown in figure 3, the fugacity of CO$_2$ is lowered only slightly by the addition of small amounts of H$_2$O. The equilibrium temperatures of decarbonation reactions (see Bowen, 1940) are, to a large extent, directly dependent upon the fugacity of CO$_2$. These temperatures, therefore, are not greatly diminished by the presence of a small amount of water in the CO$_2$.

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REFERENCES

Walter, L. S., Wyllie, P. J., and Tuttle, O. F., 1962, Phase relations in the system MgO-H$_2$O-CO$_2$: Jour. Petrology, v. 3, p. 49-64.