Three-Phase Melting Curves in the Binary System of Carbon Dioxide and Water

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Abstract. Invariant, three-phase melting curves, of ice VI in equilibrium with solid CO$_2$, of ice VII in equilibrium with solid CO$_2$, and of solid CO$_2$ in simultaneous equilibrium with a majority aqueous and a majority CO$_2$ fluid, were explored in the binary system of carbon dioxide and water. Diamond-anvil cells were used to develop pressures of 5 GPa. Water exhibits a large melting temperature depression (73°C less than its pure melting temperature of 253°C at 5 GPa) indicative of large concentrations of CO$_2$ in the aqueous solution. The melting point of water-saturated CO$_2$ does not show a measurable departure from that of the pure system at temperatures lower than ~200°C and only 10°C at 5 GPa (from 327°C).

The binary system of carbon dioxide and water, despite its importance to planetary sciences, has received little attention at high pressures and temperatures. A recent paper [1] follows the melting curve of ice VI under conditions of CO$_2$ saturation up to 2.3 GPa, while the extent of fluid/fluid miscibility has been reported to a maximum pressure of only 0.35 GPa [2]. Preliminary to studying the fluid/fluid solubility surface we explored its boundaries given by the invariant three-phase melting curves of ice VI in equilibrium with solid CO$_2$, ice VII in equilibrium with solid CO$_2$, and solid CO$_2$ in simultaneous equilibrium with a majority aqueous and a majority CO$_2$ fluid.

Diamond-anvil cells of a modified Merrill-Bassett [3] design were first loaded with water and a bubble of air. They were subsequently immersed in liquid CO$_2$ at ~10°C and 58 bar and re-opened, allowing liquid CO$_2$ to displace the air, then re-sealed. Gaskets of Inconel 718 were found to corrode above ~300°C in the mixed fluid and were used only for temperatures less than 200°C. For most of the loads, and all brought above 200°C, rhenium was used. The two gasket materials yielded comparable data at the lower temperatures.

The cells were placed in an oven with optical access, heated, and the contents observed in transmitted light. Temperature was determined by way of thermocouples situated adjacent to the diamonds. The system was calibrated at the melting point of Pb and is believed to be accurate to 0.1°C at room temperature and better than 1°C at the highest temperatures. Pressures were determined with either ruby fluorescence [4] or Raman scattering from cubic boron nitride (cBN), each load containing one or the other of the markers. Ruby fluorescence was used only below 200°C and pressure was measured by the difference in the R1 line positions of a marker contained within the cell and another in contact with the outer surface of one of the diamonds and thus at a similar temperature; any temperature drift occurring between acquisitions of the two spectra was compensated by an added shift [5] of 0.02 GPa/°C.
cBN was purchased from Diamond Innovations (Ohio, U.S.A) as commercial grinding grit (BMP-400 30-40). The crystals produced a tolerable amount of fluorescence, the power per wavenumber being roughly comparable to that of the Raman signal. The crystals were used without annealing and, among those used, the center frequencies of their signals were offset by as much as 1 cm\(^{-1}\) (equivalent to 0.3 GPa); the offsets were found to be independent of pressure and temperature, and once measured could be subtracted out. Raman shifts were measured for both the marker in the cell and a reference crystal held at room temperature and 1 bar.

Variations of the Raman frequencies, \(\nu\), of cBN with pressure, \(P\), and absolute temperature, \(T\), have been reported [6]. In order to use cBN as a pressure marker the data of reference 6 were fit to a polynomial:

\[
\nu = c_1 P + c_2 PT + c_3 P^2 + c_4 T + c_5 T^2 + c_6
\]

with \(c_1 = 3.303\) cm\(^{-1}\)/GPa, \(c_2 = 1.85 \times 10^{-4}\) cm\(^{-1}\)/GPa/K, \(c_3 = -9.72 \times 10^{-3}\) cm\(^{-1}\)/GPa\(^2\), \(c_4 = 5.28 \times 10^{-3}\) cm\(^{-1}\)/K, \(c_5 = -2.94 \times 10^{-5}\) cm\(^{-1}\)/K\(^2\), and \(c_6 = 1054.96\) cm\(^{-1}\). The resulting fit gives a root-mean-square deviation from the data of 0.06 GPa and shows no systematic deviations, either in pressure or temperature. In use, the nominal Raman frequency at the pressure and temperature of the reference crystal (0 GPa, \(\sim 294\) K) is calculated from equation (1) and then added to the measured difference between the high pressure and reference crystals; this corrected frequency is used in equation (1) to solve for pressure.

During the melting of water it is difficult to determine visually whether both water and CO\(_2\) solids are present. We therefore monitor the (approximately) isochoric pressure changes as temperature is increased; melting on the three-phase line is signaled by a rapidly rising pressure, along a path which is independent of starting pressure (figure 1). The melting of CO\(_2\) can be observed by the same method but also, often, visually.

Data are shown in figure 2. Up to pressures of \(\sim 5\) GPa the water ices exhibit significant and increasing melting point depression indicative of increasing concentrations of CO\(_2\) in the aqueous phase. In contrast, the melting point of water-saturated CO\(_2\) does not show a measurable departure.
from that of the pure system at temperatures lower than ~200°C, indicating that up to these temperatures the solubility of water in fluid CO₂ remains small.

Figure 3 shows an enlarged section of figure 2. Both water ices can be seen to melt from the field of stability of the other. The current data for ice VI agree nicely with those of reference 1. The current data agree nicely with those of Bollengier et al. [1] (black "x").

Figure 3. An enlarged section of figure 2. Symbols have the same meanings, however those representing data taken along the ice VI melt are now distinguished by being filled. The current data agree nicely with those of Bollengier et al. [1] (black "x").
invariant, four-phase point at which ice VI, ice VII, CO\textsubscript{2}(s), and aqueous solution co-exist at equilibrium is found to be at 69.9°C and 2.19 GPa.

Curves in the figures are fits of the data to the Simon-Glatzel relation, equation 2, with parameters given in table 1. The melting curves of ices VI and VII were fit only to points for which (the more precise) ruby served as the pressure marker. A combination of the current data and those of reference 1 were used to define the ice VI curve. Rms misfits of the current (ruby-derived) pressures were 0.02 and 0.03 GPa, for ices VI and VII, respectively. In order to better determine the small departure of the melting curve of water-saturated CO\textsubscript{2} from that of the pure compound, the latter was also measured; uncertainties in the calibration of the cBN standard should thus be negligible for this purpose. Pressures determined with cBN had a rms misfit of 0.05 GPa.

\[ P = P_0 + a((T/T_0)^b - 1) \tag{2} \]

|                          | \(P_0\) (GPa) | \(T_0\) (K) | \(a\) (GPa) | \(b\)   |
|--------------------------|---------------|-------------|-------------|--------|
| ice VI, CO\textsubscript{2}(s) saturated | 0.77          | 279         | 0.412       | 7.201  |
| ice VII, CO\textsubscript{2}(s) saturated | 2.21          | 345         | 0.875       | 5.277  |
| pure CO\textsubscript{2}                | 0.00          | 216.59      | 0.451       | 2.444  |
| CO\textsubscript{2}, water saturated    | 0.00          | 216.59      | 0.404       | 2.588  |

In conclusion, the melting curves of both water (saturated in carbon dioxide) and of carbon dioxide (saturated in water) have been measured to a pressure of 5 GPa. Simon-Glatzel expressions have been fit to the data and the parameters given. The four-phase point at which ice VI, ice VII, solid carbon dioxide and fluid are in joint equilibrium has been determined. A commercial grinding grit of cubic boron nitride has proven to provide an adequate, and easily obtainable, pressure standard.

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