Stability of dense liquid carbon dioxide

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We present ab initio calculations of the phase diagram of liquid CO2 and its melting curve over a wide range of pressure and temperature conditions, including those relevant to the Earth. Several distinct liquid phases are predicted up to 200 GPa and 10,000 K based on their structural and electronic characteristics. We provide evidence for a first-order liquid–liquid phase transition with a critical point near 48 GPa and 3,200 K that intersects the mantle geotherm; a liquid–liquid–solid triple point is predicted near 45 GPa and 1,850 K. Unlike known first-order transitions between thermodynamically stable liquids, the coexistence of molecular and polymeric CO2 phases predicted here is not accompanied by metallization. The absence of an electrical anomaly would be unique among known liquid–liquid transitions. Furthermore, the previously suggested phase separation of CO2 into its constituent elements at lower mantle conditions is examined by evaluating their Gibbs free energies. We find that liquid CO2 does not decompose into carbon and oxygen up to at least 200 GPa and 10,000 K.

At ambient conditions, the sp2-valent second-row elements C, N, and O form simple volatile molecules characterized by double and triple bonds. These materials often undergo dramatic transformations at high pressures into extended single-bonded covalent phases with novel optical, energetic, and mechanical properties (1, 2). The polymerization of solid carbon dioxide has been studied extensively as a prototype for the evolution of a chemical bond under compression (2–7). CO2 also plays a fundamental role in the physics and chemistry of the Earth interior and its climate (8–14). However, the thermodynamic, chemical, and physical properties of CO2 at the high temperature (above 2,000 K) and pressure conditions relevant to planetary interiors remain largely unknown.

A critical factor for the Earth’s climate is the concentration of CO2 in the atmosphere, which is controlled by a complicated dynamical cycle involving terrestrial reservoirs and fluxes (8). The vast majority of CO2 is stored in the mantle primarily in the form of Ca and Mg carbonates (8–13). Experimental (11) and theoretical (13) works suggest that CO2 is produced at high pressure (P) and temperature (T) during decarbonating reactions with silica in subducted basalts and is subsequently released into the ocean and atmosphere during volcanic activity (8). Moreover, reactions between silica and free CO2 may also take place under such conditions, leading to the formation of silicon carbonates (15). Whether free CO2 is stable or decomposes into oxygen and diamond in the mantle is currently unclear (11, 12, 16, 17). Therefore, understanding the stability of CO2 is a major challenge in establishing the more general issue of terrestrial cycles of C and CO2. Furthermore, the presence of CO2 fluid is believed to be responsible for partial melting and rheological weakening of the mantle (9, 10) and even earthquake aftershocks (14). However, the range within the mantle where CO2 remains fluid is hitherto unknown.

The difficulties in determining the CO2 phase diagram for P < 10 GPa and T > 600 K arise mainly due to the rich polymorphism and metastability of its solid phases. The structure of high-temperature phases and the existence of intermediate bonding phases between molecular and polymeric CO2 are still highly debated. The melting curve has only been measured up to 30 GPa (17–19) and has not yet been computed. By focusing on liquid CO2 we avoid the problems of metastability associated with solid phases. Nevertheless, the evolution of liquid CO2 bonding with pressure sheds light on the high-T solid phases as well. Importantly, the work presented here answers questions about the stability of CO2 at thermodynamic conditions relevant to geochemical processes.

Results and Discussion

Phase Diagram and Liquid Structure. The phase diagram of liquid CO2 is mapped by a series of first-principles molecular dynamics (FPMD) simulations in the NVT ensemble (where N and V are the number of particles and volume, respectively). The statistical data generated from these calculations is subsequently analyzed to obtain thermodynamic, electronic, and structural properties. The predicted new features in carbon dioxide’s high-pressure phase diagram are summarized in Fig. 1 and are discussed in detail below.

The stability regimes for molecular and polymeric liquid CO2 are determined based on an evaluation of the coordination number of carbon atoms with respect to oxygen. Fig. 2 shows the fractions of 2- and 3-coordinated carbon over the entire liquid P-T range considered. The region of high 2-coordination in Fig. 2 at lower P and T clearly represents the liquid regime dominated by molecular CO2 and corresponds to the molecular boundaries drawn in Fig. 1. Similarly, the region showing high 3-coordination in Fig. 2B represents the region of stability for an emergent polymeric liquid and corresponds to the polymeric phase boundaries shown in Fig. 1. Another regime arises at high T and low P where we see a surge in the fraction (above 33%, see Fig. S1) of 1-coordinated carbon (short-lived CO units). The region classified as a dissociated metallic liquid refers to P-T conditions where all covalent bonding is highly unstable (20); it is the presence of C–C chemistry that promotes metallization in this regime (see Figs. S2 and S3). The range of pressures over which the polymerization takes place progressively decreases as the temperature is lowered, indicating a possible first-order liquid–liquid phase transition (LLPT) at lower temperatures. To substantiate such a claim, we have carried out a detailed evaluation of thermodynamic and structural properties across the transition.

First-Order Liquid–Liquid Phase Transition. The P(V) equation of state (EOS) for several isothersms is shown in Fig. 3A. A clear plateau exists in the EOS for T ≤ 3,000 K, indicating the coexistence of two distinct liquid phases with different densities at the transition pressure; the volume change at 3,000 K is ΔV ~ 5%. Calculations on a 200 K grid bracketed the critical point at Tc = 3,200 K and P = 48 GPa. Previous calculations of the molecular fluid (21) found short-lived CO2 dimers, which are likely precursors to the gradual dissociation found above Tc. Fig. 3A, Inset

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shows the isothermal compressibility \( \kappa_T = -V^{-1}(\partial V/\partial P)_T \), computed from polynomial fits of \( P(V) \). Below \( T_c \), the compressibility diverges with a maximum at the transition pressure—the expected behavior of thermodynamic response functions just above a critical point. The determination of \( \kappa_T \) maxima at other temperatures above \( T_c \) allows one to construct a Widom line (locus of response function maxima)—a natural extension of a first-order phase boundary above its critical point (shown in Fig. 1).

Similar to Fig. 2, the fractions of 2-, 3-, and 4-coordinated carbon are shown for temperatures below and above \( T_c \) in Fig. 3B and C, respectively. At 3,000 K, the 2-coordinated (molecular) fraction drops discontinuously at the transition pressure, accompanied by a sharp rise in 3-coordinated (polymeric) carbon. Immediately following the LLPT, carbon atoms are predominantly 3-coordinated, while a smaller fraction is either 4-coordinated or forming unstable CO\(_2\) molecules. The liquid character shifts continuously with pressure from 3- to 4-coordination before freezing into tetrahedral-like amorphous solids, consistent with the local structure of the proposed underlying crystalline phases (3, 6, 22, 23). The mixture of 3- and 4-coordinated carbon in the new liquid phase bears analogy to the low-\( T \) amorphous solid (5, 7); a similar analogy also exists between polymeric liquid and low-\( T \) amorphous nitrogen (24). Fig. 3C shows the gradual progression of the atomic coordination as CO\(_2\) dissociates well above the critical point. The presence of an LLPT gives a clear picture of the evolution of the CO\(_2\) bonding with pressure. For pressures below the sharp transition near 45 GPa, there are no changes in the nature of the CO\(_2\) molecules (no intermediate bonding regime was found). Based on this, it is reasonable to expect that the highly contested (25–27) intermediate bonding suggested (6) for high-\( T \) solid phases (largely elongated and nonlinear molecules) does not exist as a thermodynamically stable phase. Indeed, the transition pressure for the LLPT coincides with that of the solid phase polymerization.

The subject of LLPTs is fundamental in the theory of liquids. First-order transitions in thermodynamically stable (not supercooled) liquids are known for only a few systems (28–30) where they coincide with or are driven by metallization. Even in cases where they are sharp, but not necessarily first-order, liquid transitions are accompanied by electrical anomalies (31), which can drive a rapid change in volume. In this regard, the LLPT in CO\(_2\) is unique as it takes place between two insulating phases. In the absence of C–C bonding, the computed density functional theory (DFT)-generalized gradient approximation (GGA) band gap remains relatively unchanged across the transition at approximately 1.5 eV. The volume reduction due to the formation of 3-coordinated sp\(^2\) bonded networks is apparently sufficient to establish coexistence. However, it is not as large as in the case
of nitrogen (29) (ΔV ∼ 14%) where the LLPT is accompanied by metallization.

The high-pressure melting curve is calculated here using a single-phase simulation method where liquids are gradually compressed along isotherms. This technique can lead to supercooling and the melting curve presented in Fig. 1 should be interpreted as a lower bound to the true melting temperatures. Comparison with experimental measurements at low P gives an estimate for the error, which is relatively small and close to the uncertainty in our calculations. Importantly, a lower bound for the melting curve is sufficient to determine that free CO₂ in the lower mantle (above 60 GPa) would exist in the form of a covalently bonded polymeric solid. Unless melting can be induced by interaction with minerals, CO₂ would not play a role in the rheological weakening and partial melting of mantle rocks at these depths.

Free Energies and Phase Separation. Previous studies (16, 17) have reported that recovery of CO₂ from high P (30–80 GPa) and T (1,500–3,000 K) at room temperature yields diamond and ϵ-oxygen. From this, it was inferred that molecules in the high-T state are unstable and that CO₂ may even undergo a phase separation transition at those conditions. To address this issue, we have computed the finite-temperature Gibbs free energies of the relevant CO₂, C, and O phases over a wide range of P-T conditions.

Fig. 3. P-V equation of state along several isotherms near the liquid-liquid phase transition. (Inset) Corresponding isothermal compressibilities of carbon dioxide with pressure. (B) and (C) Fraction of 2-, 3-, and 4-coordinated carbon atoms as functions of pressure along the 3,000 and 5,000 K isotherms, respectively.

Fig. 4. Gibbs free energies of mixing of liquid CO₂ along several isotherms; negative values indicate the mixed phase is favored. (B) Corresponding enthalpies ΔH, and (C) entropies ΔS of mixing of liquid CO₂. Arrows and diamonds indicate the shift in the result when thermodynamic integration is used to evaluate liquid entropies.
Enthalpies are obtained directly from FPMD using time averages of the energy and pressure. In order to cover the wide $P$-$T$ range of interest, liquid entropies are first calculated from the FPMD vibrational density of states using an approximate but efficient approach, the accuracy of this method has been examined in previous work (32). The results for the Gibbs free energy of mixing $\Delta G_{\text{mix}}$ are shown in Fig. 4; $\Delta G_{\text{mix}} < 0$ indicates that the CO$_2$ + liquid system is thermodynamically stable. For the lower temperatures and pressures, the absolute values of $\Delta G_{\text{mix}}$ are well beyond the uncertainty of the method. For the highest temperature (10,000 K and about 200 GPa), where the energetic contributions are most significant, we have carried out rigorous thermodynamic integration. The entropy of mixing increases slightly by approximately 0.25 kcal/mol when computed with thermodynamic integration (Fig. 4C), leading to an even more negative $\Delta G_{\text{mix}}$.

Our results show that for all $P$-$T$ conditions considered, including along the geotherm, carbon dioxide does not phase separate ($\Delta G_{\text{mix}} < 0$), consistent with experiments (11) on the reduction of carbonates at high pressures (28–62 GPa) and temperatures (1,490–2,000 K) where free CO$_2$ was produced with no traces of diamond in the samples. Other measurements on the decomposition of carbonates (12) and vibrational frequencies of quenched CO$_2$ (16, 17) may also be explained by the presence of the LLPT; indeed, their pressure and temperature conditions compare well with our LLPT. We propose that the observed destabilization of molecular CO$_2$ at these conditions could be the result of liquid polymerization rather than phase separation and that the quenched reactive polymeric fluid may very well crystallize into its constituent elements. Furthermore, an analysis of the dense fluid’s vibrational frequencies is provided as supplemental material.

The presence of 1-coordinated carbon at low $P$ and high $T$ led us to consider the possible phase separation of CO$_2$ into CO and O under these conditions. However, the calculated free energy of mixing lies within our uncertainty in $T$-$S$ at these temperatures. Therefore, more accurate calculations must be performed before any conclusions can be drawn.

The results presented here establish the phase diagram of liquid carbon dioxide at high pressure and temperature. Given the important role that CO$_2$ plays in geochemical processes, a useful extension of our work would be to investigate how the mineral environment in the Earth’s interior will perturb the properties of pure CO$_2$ predicted here. Variations in the C–O stoichiometric ratio may also yield interesting results, with additional relevance to diamond-anvil cell experiments. The computed free energies of mixing of CO$_2$ lie outside the uncertainties of the computational method. Therefore, the evidence for lack of demixing that we have presented is rather conclusive. Considerations beyond idealized thermodynamic conditions and/or pure CO$_2$ may be required in order to interpret some of the previous experimental measurements.

Materials

FPMD simulations were performed using finite-temperature DFT (33, 34) within the Perdew-Burke-Erzerhöf (35) generalized gradient approximation using the Vienna ab initio Simulation Package (36, 37). We used Born–Oppenheimer dynamics, a Nosé-Hoover thermostat, and 32- and 64-molecule supercells. Simulations were equilibrated for 1 to 2 ps and run for an additional 10 ps using a 0.75 fs time-step (convergence verified with 0.30 fs). For the carbon (oxygen) atoms, we employed a four-electron (six-electron) projector augmented wave (PAW) pseudopotential (PP) with a 1.50 (1.52) Bohr core radius and 500 eV plane-wave cutoff. Convergence was verified with C and O PAW PPs with a 1.10 Bohr core radii and 875 eV cutoff, as well as an all-electron oxygen PP.

Atomic coordination is defined here as the number of oxygen atoms surrounding a given carbon atom within a given cut-off distance. The first minimum of the C–O pair correlation function is chosen as this distance; justification is provided in ref. (20).

The Gibbs free energies of mixing are calculated as $\Delta G_{\text{mix}} = G_{\text{CO}_2} - 1/3G_{\text{g}} - 2/3G_{\text{O}}$, where $G_{\text{g}}$ is the free energy of CO + liquid C. The internal energy, pressure, and temperature are FPMD ensemble (time) averages. The vibrational contributions to $G$ of liquid C, O, and CO$_2$ were computed as described in ref. 32, where the method was successfully used to predict mixing-demixing behavior in Na-I and Ca-I liquid alcohols.

Thermodynamic integration (TI) is a method for computing differences in the Helmholtz free energies of two systems related with a potential energy function of the form $U(\beta) = U_0 - \lambda (U_1 - U_0)$. Here $U_0$ is the potential energy of a reference system with known free energy and $U_1$ is the potential energy of the system under investigation. We have carried out TI in two steps: (i) from an ideal gas ($U_0 = 0$) to a classical system with pair interactions fit to DFT forces ($U_1 = U_{\text{cl}}(0)$), and (ii) from the classical ($U_1 = U_{\text{cl}}$) to the actual DFT system ($U_1 = U_{\text{DFT}}$).

Moreover, the free energies in this work have been checked using (FPMD configurations) with the successful Heyd-Scuseria-Ernzerhof (HSE) hybrid functional (38) as some phases considered are metallic. The maximum HSE correction to $\Delta G_{\text{mix}}$ is approximately 0.5 eV/atom when a metallic phase of liquid oxygen is present. These corrections do not affect any conclusions drawn here; in fact, they further support them. In all other cases, the corrections are negligible (<10 meV/atom).

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