High-Pressure Compounds in Methane-Hydrogen Mixtures

M. S. Somayazulu, L. W. Finger, R. J. Hemley, H. K. Mao

The effect of pressure on chemical interactions in molecular mixtures is important for problems spanning fundamental chemistry, planetary science, and materials science. Diamond-anvil cell studies reveal pressure-induced chemistry in the CH₄-H₂ system. The system, which has no known compounds at ambient conditions, formed four molecular compounds, CH₃H₂₆, CH₂H₆₂, CH₁H₆₂, and CH₂H₅₂, at pressures up to 10 gigapascals. These have been characterized by synchrotron single-crystal x-ray diffraction, polycrystalline x-ray diffraction, Raman spectroscopy, and optical observation. Although CH₁H₆₂ crystallizes in the MgZn₂-type, hexagonal Laves phase structure, (CH₄)H₂ has a body-centered tetragonal structure that is similar to that of Al₃Cu. The 1:1 and 1:2 mixtures are stable at least to 30 gigapascals.

Chemical interactions in dense materials are important in a broad range of problems in physical science, and the nature of such interactions in mixtures of simple molecular systems has become the focus of attention recently (1). Fundamentally, the study of such systems under pressure is important for theories of bonding in highly condensed states, for example, the evolution of bonding states (such as van der Waals, covalent, and metallic) with compression (2). Technologically, investigation of such systems, particularly those containing hydrogen, is important for the design of energetic compounds and hydrogen storage materials (3).

A wide range of pressures (up to several hundred giga-pascals) can be concentrated with a diamond anvil cell. High-pressure studies have been conducted to explain how simple gases and liquids mix under pressure, and some early observations showed that mixtures of helium and nitrogen formed an unusual compound with the formula He(N₂)₉ under pressures of approximately 8 GPa. Chemical compounds that are stable only at high pressure were discovered (4) and termed van der Waals compounds (5–7). In addition, high-pressure H₂-H₂O (8) and He-H₂O (9) clathrate have been discovered. Here we present a detailed study of methane-hydrogen mixtures under pressure. The study revealed four new solid compounds having H₂CH₄ molar ratios of 1:2, 2:1, 4:1, and 1:1.

A total of 17 different compositions in the CH₄-H₂ system were studied. The initial concentration of the mixture was fixed from the partial pressures of the gases, corrected with the virial coefficients. Each mixture was loaded in the diamond anvil cell after sufficient time for homogenization had been allowed (typically a week), with a ruby chip for pressure calibration. To minimize reaction of hydrogen, Be-Cu was used as the gasket material. For all our compositions, it was found that the
relative intensities of the C-H stretch and the H-H stretch (10) reproduced the ratio of CH₄ and H₂ within 3% in the gas and the fluid phases. It was thus possible to determine the composition of the liquid in the two-phase solid-plus-liquid region of the phase diagram, and to determine the pressure (P) - composition (X) relation of the liquidus. In a typical run, P was raised in small steps until the liquidus boundary was crossed. While within the two-phase region, the temperature (T) of the cell was then raised to revert back into the fluid field, and the solid was recrystallized by cooling so that a part of the sample chamber was free from the solid and consisted of only the liquid. These isochoric P-T scans also enabled a reproducible determination of the liquidus boundary for each composition. The laser line from an Ar⁺ ion laser was focused to about 10 μm, and a spatial filter assured that the Raman signals from the two coexisting phases could be separated. The H-H peak became more intense and narrower in the solid phases; typically the line width decreased from about 20 cm⁻¹ to 7 cm⁻¹. This allowed us to determine the P of the eutectic point (Fig. 1). Two eutectic points at 10 and 30% CH₄ were observed, as well as peritectic points at 60 and 15% CH₄.

A single solid phase was observed to form at 5.4 GPa for a starting composition of 20% CH₄. The minimum in the liquidus at this composition has been confirmed from the observed increase in freezing pressures of neighboring compositions (Fig. 1). The stoichiometry of this phase was determined to be CH₄(H₂)₄ (Fig. 2A shows this phase grown from a starting composition of 24% CH₄). The x-ray diffraction pattern of this phase indicated a body-centered tetragonal (bct) structure; however, we believe this phase is due to the methane substructure. It is possible that the diffusion from the H₂ molecules could yield a primitive unit cell, but such intensities are below our detection limit. Incongruent melting of this phase was observed at 6.1 GPa and 298 K, at which pressure the solid changes stoichiometry through the reaction CH₄(H₂)₆ (S) → CH₄(H₂)₂ (S) + L (S, solid; L, liquid). At high temperatures, this transition was also accompanied by a change in dP/dT in the isochoric P-T scans. X-ray intensity data for this phase were collected at 6.2 GPa and indicated a hexagonal unit cell with a = 5.414 (2), c = 8.855 (8) Å, and volume V = 224.8 (3) Å³, for a coordination number Z = 4. The space group was identified to be P6₃/mmc. If the equation of state of H₂ (5) and CH₄ (6) is used, the volume is occupied by about 4 CH₄ and 8 H₂, with a 1% excess volume of mixing. The structure is that of a MgZn₂ (Laves phase) structure (7). Figure 3A shows where the H₂ molecules occupy the Zn sites and the CH₄ molecules occupy the Mg sites. Above 6.7 GPa, another solid with the composition CH₄H₂ was formed (Fig. 2B). It has a hexagonal crystal structure similar to that of CH₄(H₂)₂, with a smaller c/a.

Fig. 1. The P-X phase diagram of the binary molecular system H₂-CH₄ at 298 K. The solid symbols denote the freezing pressures (liquidus boundary) and the pressures at which complete solidification (eutectic pressures) is observed. The open symbols represent the composition determined from the liquid in the two-phase solid-plus-liquid regions.

Fig. 2. Photomicrographs of phases in the sample chamber, about 150 μm in diameter, corresponding Raman spectra of the H-H stretching mode shown for each phase. The spectra are plotted relative to the frequency of the Q₁ (J) vibron of pure hydrogen at that pressure (vertical dashed line). (A) CH₄(H₂)₄ at 5.4 GPa. The doublet indicates the spectrum was collected from a two-phase mixture: solid CH₄ and hydrogen-rich liquid. (B) CH₄H₂ at 5.1 GPa in a solid H₂ medium. The Raman spectra were collected from a 50-50 starting composition. The mode from (CH₄)₂H₂ is shown by a dashed line, and the mode from CH₄H₂ is shown by a solid line. (C) (CH₄)₂H₂ at 5.4 GPa. The hydrogen Q₁(J) mode occurs at a higher frequency in this compound compared with that in pure hydrogen at this pressure. (D) Pure methane at 5.6 GPa in the solid medium (CH₄)₂H₂. The horizontal dashed line is the spectrum collected from the pure methane region.

Fig. 3. (A) Crystal structure of the compound CH₄(H₂)₂. The H₂ and CH₄ molecules are represented as spheres because they appear to be orientationally disordered at these pressures. This phase is stable between 5.8 and 7 GPa, above which it continues to be hexagonal but changes stoichiometry. (B) Crystal structure of the compound (CH₄)₂H₂. Raman measurements on this solid indicate that it is stable up to at least 30 GPa.
Comparison of Radiative and Physiological Effects of Doubled Atmospheric \textit{CO}_2 on Climate


The physiological response of terrestrial vegetation when directly exposed to an increase in atmospheric carbon dioxide (\textit{CO}_2) concentration could result in warming over the continents in addition to that due to the conventional \textit{CO}_2 "greenhouse effect." Results from a coupled biosphere-atmosphere model (SiB2-GCM) indicate that, for doubled \textit{CO}_2 conditions, evaporative transport will drop and air temperature will increase over the tropical continents, amplifying the changes resulting from atmospheric radiative effects. The range of responses in surface air temperature and terrestrial carbon uptake due to increased \textit{CO}_2 are projected to be inversely related in the tropics year-round and inversely related during the growing season elsewhere.

A number of simulation studies have investigated the impact of increasing atmospheric \textit{CO}_2 concentration on the energy balance, precipitation, and surface air temperature of the Earth. A recent assessment of the results produced by different atmospheric general circulation models (AGCMs) indicates that the globally averaged surface air temperature increase by 1.5° to 4.5°C in response to a doubling of atmospheric \textit{CO}_2 (J). In almost all cases, the impacts of increasing \textit{CO}_2 are conventionally associated with changes in the radiation and energy balances; physiologically induced effects on climate are ignored. In this report we investigate the potential for additional warming over the continents as a result of the physiological response of terrestrial vegetation when exposed to an equilibrium doubling in atmospheric \textit{CO}_2 concentration.

Terrestrial vegetation takes up \textit{CO}_2 for photosynthesis through small pores in the leaf surfaces called stomates. At the same time, water vapor from the leaf interior diffuses out through the stomates to the atmosphere (transpiration). Plants continuously adjust the widths of their stomatal apertures, apparently to enhance \textit{CO}_2 uptake for a given evaporative loss of leaf water (2). Leaf stomatal conductance to water vapor transfer appears to be sensitive to variations in net photosynthetic rate, and hence to light intensity, temperature, soil moisture, and atmospheric \textit{CO}_2 concentration, as well as to changes in humidity and \textit{CO}_2 concentration at the leaf surface. Leaf-scale models of net photosynthetic assimilation, \textit{A}, and stomatal conductivity, \textit{g}_s, have been formulated to describe these relations [see, for example, (3)].

The physiological effects on climate caused by increasing atmospheric \textit{CO}_2 result from the dependence of photosynthesis and stomatal conductance on \textit{CO}_2 partial pressure (Fig. 1). Short-term exposure of \textit{C}_3 plants to 2 × \textit{CO}_2 (a doubling of the \textit{CO}_2

10. Normalized with respect to the gas phase scattering strengths of the H-N(\textit{A}_1) mode at 2914 cm\(^{-1}\) and the H-H(\textit{A}_1) mode at 4156 cm\(^{-1}\).

12 October 1995; accepted 16 January 1996