Studies of CO₂ Hydrate Formation and Dissolution

W H E E L E R   J .   N O R T H , *
V E R O N I C A   R .   B L A C K W E L L ,   A N D
J A M E S   J .   M O R G A N

W. M. Keck Engineering Laboratories, California Institute of Technology, Pasadena, California 91125

Sequestering waste CO₂ in the deep ocean as a gas, liquid, or hydrate has been variously proposed (*1−3*). We describe experiments producing CO₂ hydrate that may eventually assist in developing methodology for large-scale creation of this ice-like substance. We produced a simple and inexpensive system for conducting high-pressure experimentation. We established the minimum ratio of CO₂ to water (both deionized water and seawater) needed to produce stable traces of hydrate. We suggested an explanation for the differences observed in forming hydrate from the two media. We demonstrated that hydrate decomposed when exposed to an intermittent flow of water. We proposed a model of pathways involved in forming CO₂ hydrate. Previous reports on hydrate formation have emphasized pressure−temperature relationships and effects thereon. Our experimentation focused on the amount of CO₂ in all phases inside the pressure chamber (designated as Y-CO₂). The minimum Y-CO₂ needed for producing hydrate varied with pressure. Hydrate became unstable and decomposed in intermittently flowing water. Our approach has yielded new information regarding requirements for hydrate formation and the potential for dissolution in the deep ocean

FIGURE 1. Phase diagram for the CO₂−water system, modified after Miller (*18*).

Introduction

Hydrates of methane or CO₂ occur as natural deposits in many locations worldwide where high pressure and low temperature favor hydrate formation (Figure 1). Prior research has tended to emphasize hydrates of individual hydrocarbons as well as mixtures thereof, because this category of hydrates sometimes plugs oil and gas lines. Major findings include phase diagrams, structures of the hydrate lattices, theoretical models that predict conditions favoring hydrate formation (*4*), and rates of formation and inhibitors (*5, 6*). Several Japanese organizations have conducted laboratory and field studies to produce hydrate from waste CO₂, oceanic disposal, and natural occurrence on the sea floor (*3, 7, 8*) as a means of controlling CO₂ buildup in the atmosphere. Englezos (*9*) utilized his model (*5*) for computing incipient formation pressures for CO₂ hydrate in NaCl solutions at various concentrations and temperatures. Takenouchi and Kennedy (*10*) produced a phase diagram for CO₂ hydrate and calculated its density as 1.16, somewhat greater than the usual densities of seawater (ca. 1.035). Thus, CO₂ released into the ocean should sink.

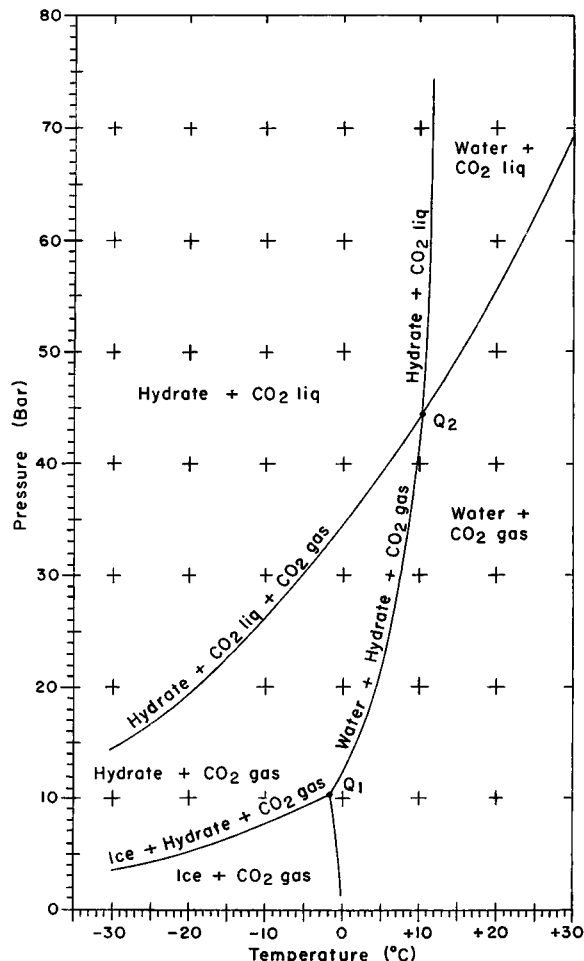Rose (*11*) discussed four principal alternatives for sequestering waste CO₂ and sizes of their reservoirs: deep subterranean aquifers, 87 Gton; exhausted gas and oil wells, 125 Gton; enhanced oil recovery, 4 Gton; the deep oceans 20 million Gton. CO₂ injected into ocean depths, however, would eventually return 13% to the atmosphere, equilibrating over several centuries. Another alternative, cultivating biomass, when used as an energy source would recycle CO₂. Spencer (*12*) estimated terrestrial and marine cultivation requirements at 1.6 million km²/Gton of carbon captured.

The Englezos hydrate model predicted that methane hydrate formed more readily in pure water than in seawater (i.e., hydrate in pure water vs seawater formed at a higher temperature for a given pressure or at a lower pressure for a given temperature) (*5*). A similar relationship was calculated for CO₂ hydrate (*9*). Experiments involving production of methane hydrate in various concentrations of electrolytes generally agreed with effects predicted by Englezos' model (*6, 13−15*). Similar results were obtained from forming hydrate in artificial seawater (*13*) and in actual seawater (*16*). The latter study demonstrated that the temperature depression for producing methane hydrate in a seawater medium was constant at −1.1 °C throughout the pressure range tested (27−100 bar). Sloan (*17*), Miller (*18*), and Englezos (*19*) have reviewed the extensive hydrate literature.

Materials and Methods

Pressure Chambers. We constructed several types of pressure chambers, but for the studies reported herein, we

* Present address: Kerckhoff Marine Laboratory, 101 Dahlia Ave., Corona del Mar, CA 92625; phone: 714-675-5804; fax: 714-675-1837.
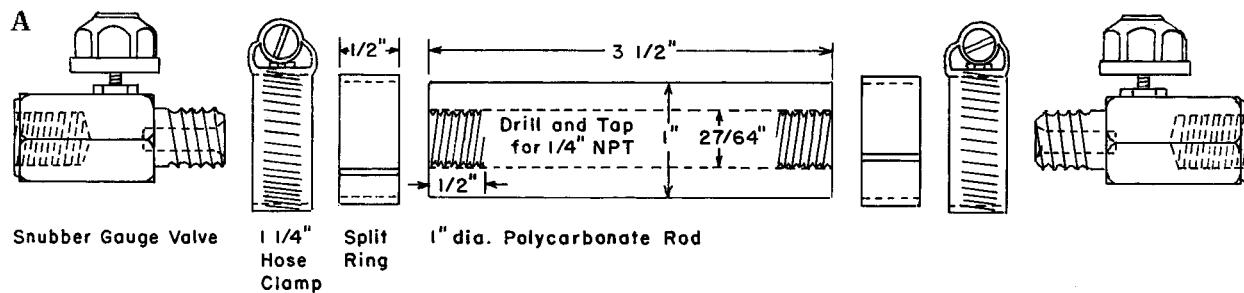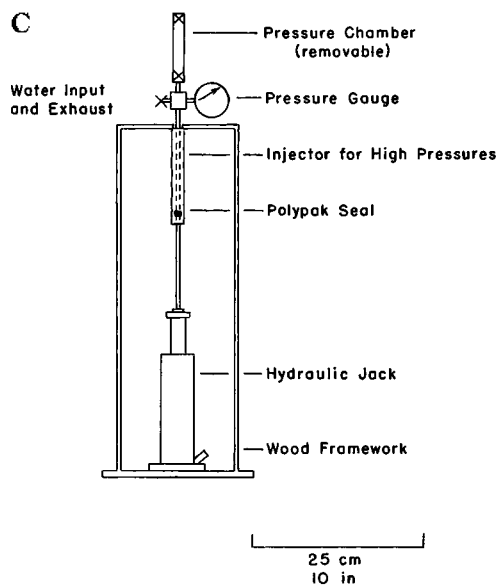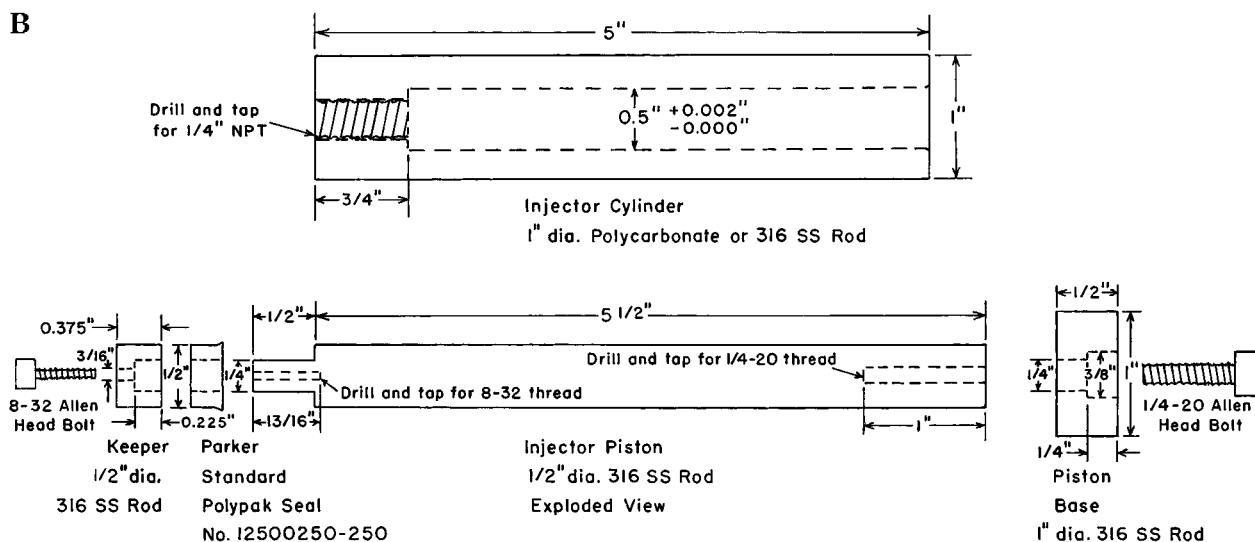
FIGURE 2. (A) Diagram of the polyearbonate pressure chamber. (B) High pressure water injector. (C) Assembled pressurizing apparatus.

utilized simple polycarbonate tubes produced by drilling a 27/64 in. diameter hole through a 1 in. diameter rod and threading each end to accommodate steel valves manufactured by Sun Hydraulics (Figure 2A). The chambers were pressure tested to approximately 200 bar and operated at pressures ranging from 55 to 145 bar. They had capacities from 6 to 8 mL, weighed about 250 g, and cost about $35 to produce.

Pressurizing Equipment. A piston–cylinder system, the injector, served to generate pressure and force deionized water into the chambers (Figure 2B). The piston was of stainless steel and equipped with a Polypak seal (Parker No. 12500250-250). Cylinders were fashioned either from polycarbonate or stainless steel. Small commercial cylinders supplied pressurized CO_2. Analysis by a local commercial laboratory indicated a purity greater than 99.9% for the CO_2 (He, H_2O, O_2, Ar + N_2, Ne, CO, and CH_4 were undetectable).

Pressure was applied to the injector by a 3-ton hydraulic jack held in a pressurizing stand fashioned of wood reinforced by threaded steel rods (Figure 2C). A pressure-relief valve (Nupro, Series R3A) was attached to the fitting for experiments requiring an intermittent water flow through the chamber.

TABLE 1. Physical Appearance of Chamber Contents for Various Values of Y-CO_2, for Experiments Using Deionized Water and Pressures of about 55 bar (a Pressure at Which CO_2 Was Always a Liquid) and Temperatures of about 5 °C

Y-CO_2	physical appearance
0.02	clear fluid
0.03	clear or temporary white turbidity
0.04	stable particles or small amounts of unstable floc; white turbidity
0.05	moderate amounts of granular or flocculent solids; gels and white turbidity
0.06	granular and flocculent masses loosely filling the chamber; gels and turbidity; rod moves freely
0.09	crystals and granules pack the chamber; rod moves slowly and may become trapped as hydrate matures
0.12	chamber packed with solid hydrate; rod is soon trapped by solid material
0.24	crystals pack the chamber; rod trapped; clear fluid (liquid CO_2) present
0.33	80% of chamber is packed crystals; 20% is clear fluid
0.52	30% of chamber is packed crystals; 70% is clear fluid

The amount of water needed to dissolve all the CO_2 hydrate required several refillings of the injector, which led to an "intermittent" flow.

Metal or glass rods (about 10 mm long × 6 mm diameter) were included in the chambers to enhance agitation of the system when shaken vigorously.

CO_2 Computation. Most of our experiments produced at least two and sometimes three phases in the chamber. Our interests usually were concerned with the entire amount of CO_2 contained in a chamber (not just the amount residing in any of the phases present), in relation to the amount of water also present. We will use the term Y-CO_2 as representing

$$\frac{\text{total mol of } CO_2}{\text{total mol of } CO_2 + \text{total mol of } H_2O}$$

CO_2 Uptake by Polycarbonate. CO_2 slowly dissolved in the polycarbonate walls of our chambers at the pressures involved during our experiments. We assessed this CO_2 uptake by several experiments and determined that it was modest for the time periods for most of our experiments, including those reported herein. For example, a polycarbonate chamber containing only CO_2, at about 5 °C and an initial pressure of 146 bar, yielded pressure losses of 6% in the first 10 min, 7% after 2 h, 10% after 4 h. Most of the loss occurred rapidly, soon saturating the chamber walls, so that subsequent uptake was slow.

Results and Discussion

Minimal Values of Y-CO_2 for Hydrate Formation. We undertook experimentation to establish the minimal Y-CO_2 value required to just produce traces of hydrate. One set of experiments involved observing conditions inside pressure chambers each containing different amounts of CO_2. Results taken immediately after agitation indicated that the minimal Y-CO_2 level occurred between 0.03 and 0.04 (Table 1). The Y-CO_2 value of 0.12, where water disappeared, corresponded well with the reported ratio of 1 CO_2:7 H_2O for experimentally produced CO_2 hydrate (20).

Another set of experiments involved a series of chambers containing various proportions of deionized water and CO_2, all within the same temperature range (4.3−5.7 °C) and initial pressure (55 bar). Results were classed into three categories: (A) no hydrate appeared; (B) hydrate appeared in small
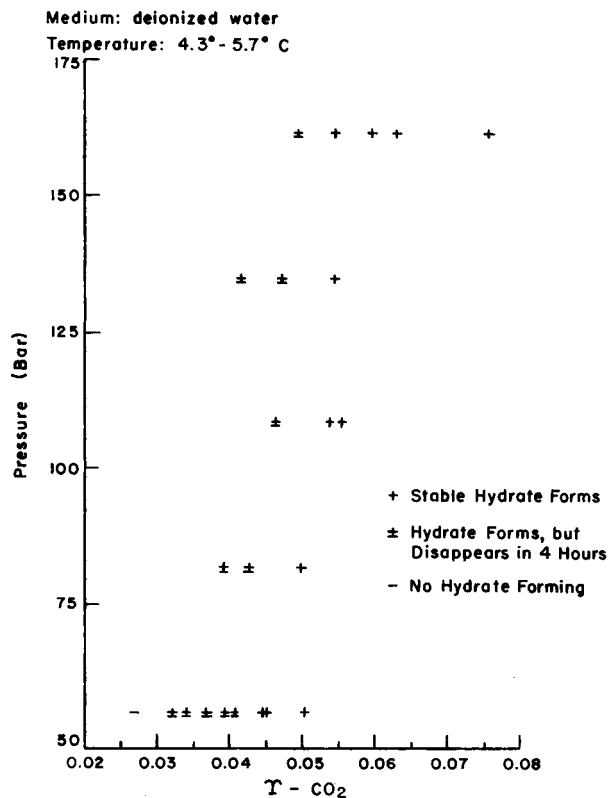

FIGURE 3. Results from an experimental series showing the minimal Y-CO_2 values required to produce CO_2 hydrate at the indicated pressures.

amounts but vanished within 4 h; (C) hydrate appeared in various amounts (usually related to Y-CO_2) but did not vanish during a period of 4 h. The minimal CO_2 loading was assumed to lie midway within the B category or at a Y-CO_2 value between 0.037 and 0.04 (Figure 3). The 4 h allowed for hydrate disappearance in category B would permit moderate losses of CO_2 from uptake by the chamber walls. Consequently, the minimal Y-CO_2 required for stable hydrate formation was probably about 0.036 or slightly less. This conclusion agreed with results presented in Table 1.

Minimal CO_2 loading values were also determined at three additional initial pressures of 83, 110, and 165 bar. Results indicated that a line connecting minimal Y-CO_2 values for the various pressures would slope somewhat to the right from a vertical configuration (Figures 3 and 4). Additional experimentation using a seawater medium also yielded a sloping line for Y-CO_2 vs pressure, lying to the left of the line for deionized water (Figure 4).

The experiments clearly showed that hydrate did not appear until the Y-CO_2 exceeded a critical value. We hypothesize that CO_2 in the liquid phase exists in two categories: dissolved CO_2 and CO_2 combined with structured water (i.e., possible hydrate precursors). If we regard the two categories as reservoirs that must be filled to saturation before the hydrate can form, then the dissolved CO_2 reservoir should accommodate additional CO_2 as pressure increases. This would explain the positive slopes of the two lines shown in Figure 4.

The slopes of the lines in Figure 4 are very steep, implying that CO_2 solubility is enhanced only slightly by large pressure increases for the range of pressures shown. Houghton et al. (21) showed that the relation between CO_2 solubility and pressure was nonlinear and did indeed steepen as pressure increased (Figure 5).

Dickens and Quinby-Hunt (16) ascribed the altered temperature−pressure requirement for methane formation
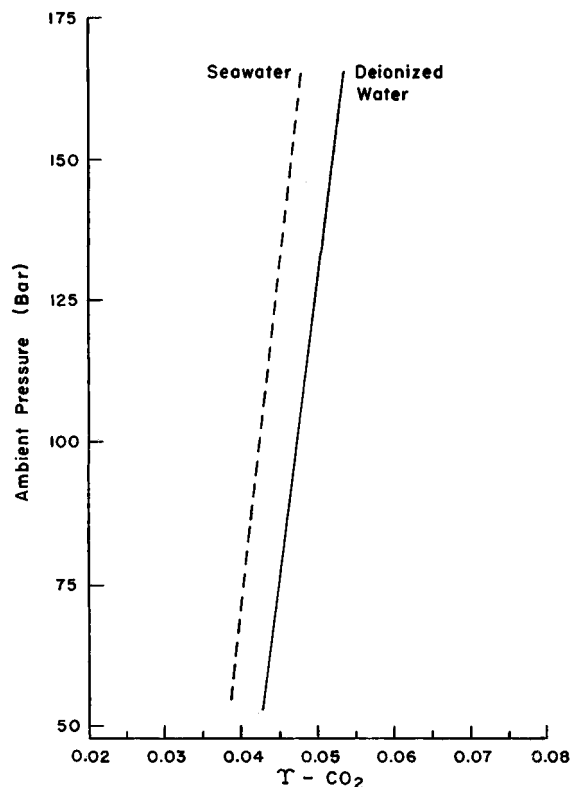
FIGURE 4. Comparisons of minimal Y-CO_2 values of CO_2 needed to produce stable hydrate for deionized water vs seawater. The lines represent the lowest values of Y-CO_2 as shown in Figure 3 and designated by a plus (+) symbol.
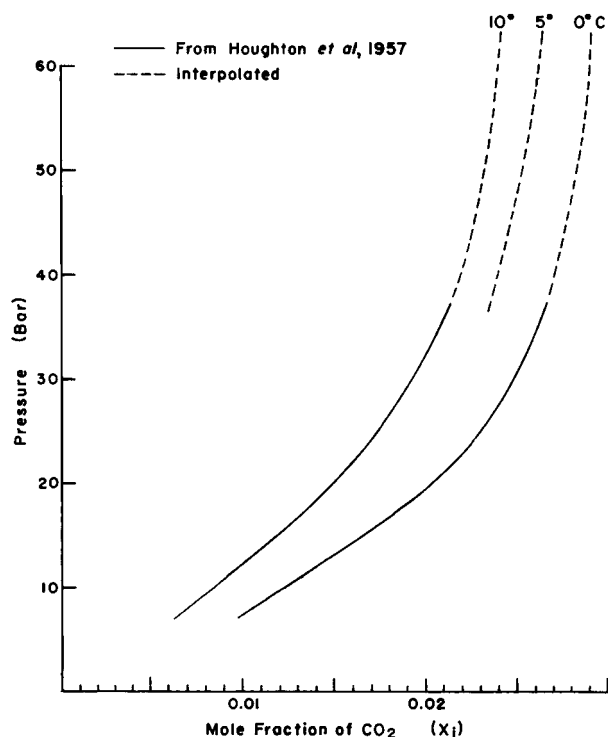

FIGURE 5. Solubility of CO_2 in water vs pressure for selected temperatures, according to Houghton et al. (21) with interpolations by us for 5 °C and extensions to 62 bar.

FIGURE 6. Plot of the amount of water needed to dissolve a mass of formed hydrate vs the Y-CO_2 of CO_2 existing in the chamber prior to injection of the intermittent water flow.

in seawater vs pure water to decreased entropy of the water molecules in seawater. Dissolved ions in seawater are, to some extent, considered to be surrounded by "bound" water molecules. This pheno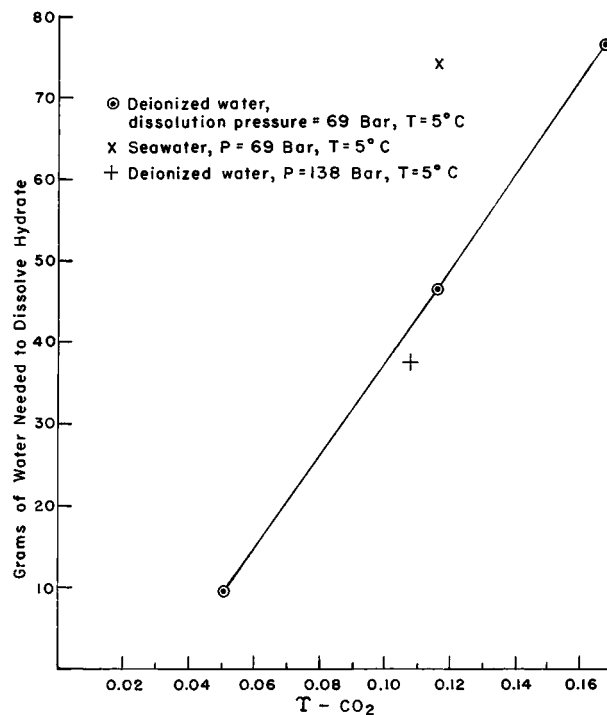menon presumably reduces the size of the reservoir of water available for dissolving CO_2. If so, a reduced water reservoir would explain why the seawater line lies to the left of the deionized water line in Figure 4.

Hydrate Dissolution in Intermittently Flowing Water. Hydrate deposited on the sea floor would presumably be exposed to water not saturated in CO_2. We explored the possibility that exposure to undersaturated water might decompose the hydrate.

We conducted 10 experiments in which the watery medium surrounding the hydrate was replaced by pulses of new water flowing slowly (0.8–2 g min^{-1}) through the chamber. Hydrate decomposed in all cases and eventually disappeared. All but one experiment was conducted at a pressure of about 69 bar (i.e., for both hydrate formation and dissolution).

Grams of deionized water required for complete dissolution were linearly related to Y-CO_2 of the initial system (Figure 6). A single experiment at 138 bar required slightly less water for complete dissolution vs requirement at half the pressure. Presumably more CO_2 could dissolve at the higher pressure, so the removal rate per gram of water exchanged was faster than at 69 bar. Conversely, the removal rate was less for seawater vs deionized water, so more seawater medium was required to dissolve a given mass of CO_2 hydrate. Again, this can be explained by presuming that some of the water was associated with dissolved ions, thus reducing the quantity of water available for dissolution of CO_2 hydrate.

The line shown for the 69 bar data in Figure 6 intercepted the horizontal axis at a Y-CO_2 of about 0.34. A non-zero intercept suggested that hydrate formation required a Y-CO_2 of at least 0.034. This value was moderately below the critical Y-CO_2 of about 0.039 indicated for 69 bar and deionized water in Figure 4, revealing a rather close agreement.

We can reasonably postulate from our data that the minimal amount of CO_2 required to form hydrate at 69 bar and 5 °C almost certainly lies within the Y-CO_2 range of 0.034–0.039. The mole fraction of dissolved CO_2 is estimated at approximately 0.030 under these conditions (Figure 5). The mole fraction of CO_2 contained in the "intermediates"
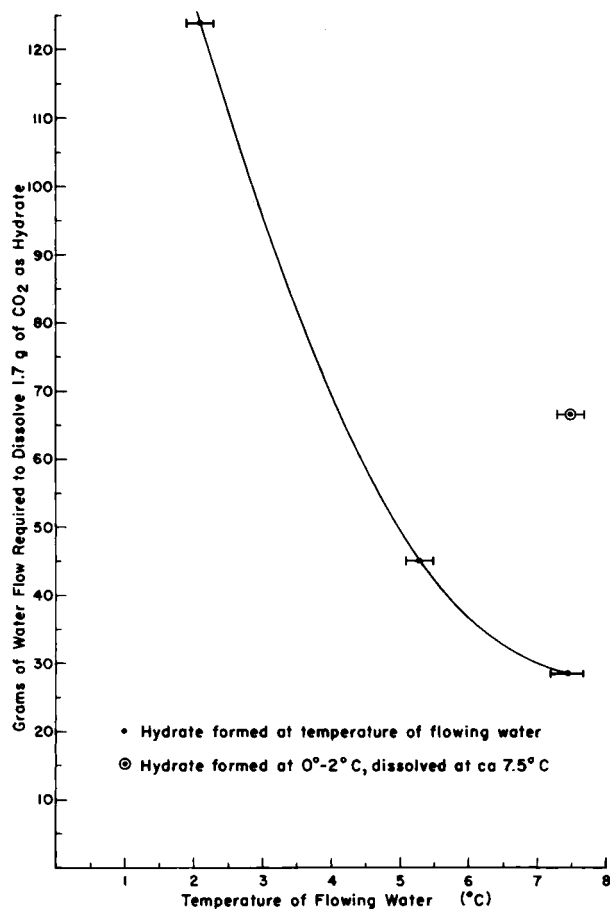
FIGURE 7. Amount of water needed to dissolve a mass of formed hydrate produced from 1.7 g of CO_2 vs temperature of the system. Forming hydrate at a low temperature seemed to help stabilize the mass when exposed to flowing water at about 6 °C higher than the temperature of formation.

(i.e., associations of water and CO_2) would then be 0.004–0.009 or 12–23% of all CO_2 residing in the water. This approach assumes that the water is not supersaturated in CO_2 and that two distinct reservoirs of CO_2 exist.

Temperature influenced the amount of water exchange needed to dissolve a given amount of hydrate. The required water flow rose rapidly as temperature declined (Figure 7).

All of the experiments wherein we exposed hydrate to water intermittently flowing through the chamber sooner or later resulted in hydrate dissolution and disappearance. These findings suggested that any solid hydrate sequestered in the oceanic depths would eventually dissolve in the surrounding water. This finding contradicts statements by Handa (22) and by Shindo et al. (7). CO_2 hydrate might serve as a suitable means of conveying CO_2 to a destination in the deep sea. It would not, however, serve as a mechanism for indefinite storage unless it were capped by a barrier separating hydrate from the overlying water.

Modeling Hydrate Formation. Sloan (17), referring to work by Englezos and co-workers, noted that methane concentration became supersaturated in the solution prior to hydrate formation. Our experimentation with CO_2 also suggested that this compound became supersaturated before hydrate formed. Interpolation of the data of Houghton et al. (21) to 55 bar and 5 °C suggested that, in the absence of hydrogen bonding between CO_2 and water, maximum CO_2 solubility would occur at a Y-CO_2 value of about 0.027 (Figure 5). A Y-CO_2 of about 0.034–0.037 was actually required at this temperature and pressure before the hydrate could be produced. We suggested that this supersaturated or solu-
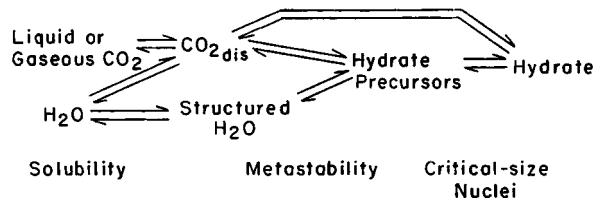

FIGURE 8. Hypothetical model showing various categories of components thought to exist when pure CO_2 and water combine to produce hydrate. The bottom line displays terminology used by Sloan (17) to characterize three stages in the process.

bilized CO_2 actually consisted of two categories: dissolved CO_2 and CO_2 combined with structured water, which we classified as intermediates. At least a portion of the intermediates may be hydrate precursors.

The intermediates are in equilibrium with dissolved CO_2 and are probably constantly forming and decomposing. A membrane of hydrate always formed at the interface between water and liquid CO_2, prior to agitation in our experiments. The membrane is undoubtedly situated in the region where concentration of dissolved CO_2 and intermediates are highest. High CO_2 concentration would favor formation, growth, and persistence of intermediates. Five CO_2 molecules are needed to fill all cavities in the hydrate unit cell, and the concentration of dissolved CO_2 must be maintained at saturation to stabilize the intermediate entity. The obvious location where CO_2 availability is greatest lies at the water–CO_2 interface. A steady supply of CO_2 seems necessary for maintaining a concentration of dissolved CO_2 and to allow for growth by intermediates to the point of hydrate formation. A model describing our concepts of hydrate formation visualizes the hydrate precursors as a central element within the process (Figure 8). The double set of arrows leading to hydrate symbolize the need for a large and continuing supply of CO_2 throughout the formation process.

Supporting Information Available
Four tables (5 pp) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for $15.00 for photocopy ($17.00 foreign) or $12.00 for microfiche ($13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL http://www.chemcenter.org. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To download the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202)872-6333.

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