Formation of Hydrates from Single-Phase Aqueous Solutions and Implications for Oceanic Sequestration of CO_2.

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Introduction[a]

Gas hydrates are crystalline solids formed from mixtures of water and low molecular weight compounds, referred to as hydrate formers, that typically are gases at ambient conditions (1). Generally, hydrates are formed in the laboratory from two-phase systems by contacting a hydrate former or formers in the gas or liquid phase with liquid water and increasing the pressure until crystalline hydrate forms. However, the formation of hydrate from a single-phase aqueous system using only the hydrate former dissolved in the aqueous phase has been demonstrated in prior work at the National Energy Technology Laboratory (NETL) (2) and more recently by others (3).

The prior work at NETL focused on the impact of CO_2 hydrate on oceanic sequestration of CO_2 and showed that the initial effective density of a hydrate cluster depends on the number of phases present when the hydrates form (2). If the hydrate was formed from a two-phase system of either gaseous or liquid CO_2 and water, the hydrate clusters were initially less dense than the water-rich phase because of the presence of free CO_2 that adheres to or is occluded in the hydrate clusters without actually being incorporated in the lattice of the hydrate. However, if the hydrate was formed from a single-phase system consisting of CO_2 dissolved in water or seawater, the hydrate that formed was initially more dense than the aqueous phase. This would have implications in some processes being considered to inject CO_2 into the deep ocean (>500 m) for the purposes of non-atmospheric sequestration. Forming a sinking hydrate particle could facilitate such a process by transporting the CO_2 to depths greater than that used for injection. On the other hand, a rising hydrate particle would have the opposite impact.

This preprint summarizes a general thermodynamic model and experimental results that demonstrate the formation of hydrates from single-phase aqueous systems. A complete description has been accepted for publication (4)

Results and Discussion

Models for Hydrate Equilibrium

For calculation of hydrate formation from a single-phase water-rich liquid containing dissolved hydrate former, the conditions where the hydrate phase is in equilibrium with the water-rich liquid are needed. At these conditions, the chemical potentials of the species in various phases must be equal. The following equations describe the chemical potential difference of water in the hydrate phase ($\Delta\mu_H$) and the chemical potential difference of water in the water phase ($\Delta\mu_L$) (4).

$$\Delta m_H = -RT \sum_{j,cavities} n_j \ln\left(1 - \sum_i q_{ji}\right) \qquad (1)$$

$$\frac{\Delta m_L}{RT} = \frac{\Delta m^0}{RT_o} - \int_{T_o}^{T_F} \frac{\Delta h}{RT^2} dT + \int_0^P \frac{\Delta v}{RT} dP - \ln X_w \qquad (2)$$

In these equations, $\Delta\mu_H$ is the difference in the chemical potential between an empty hydrate water lattice and one occupied by a guest molecule (5), $\Delta\mu_L$, Δh, and Δv are the chemical potential, enthalpy, and volumetric differences, respectively, between water in an empty hydrate lattice and pure water, and $\Delta\mu^0$ is a reference chemical potential treated as a constant whose value can change according to the gas species present. Also in these equations, $<_j$ is the ratio of j type cavities present to the number of water molecules present in the hydrate phase, 2_{ji} is the fraction of j-type cavities occupied by i-type guest molecules, and X_w is the mole fraction of water in the water-rich liquid phase. 2_{ji} is related to P^{sat} which is the pressure required to obtain a given solubility of hydrate former in the water phase (4). At pressures lower than P^{sat}, the hydrate former will come out of solution as a gas bubble or liquid drop.

Using these two equations with different saturation pressures, the possibility of hydrate formation from a single-phase, water-rich system containing dissolved CO_2 can be determined (4). This is illustrated graphically in Figure 1 for a temperature of 275 K.

In this figure, point A represents the pressure at which hydrate would form if excess CO_2 were present (VLH equilibria). Point B represents the pressure at which hydrates would form from a water-rich single-phase system containing 0.016 mole fraction CO_2. At point A, the water rich liquid would contain more CO_2 ($\cong 0.0188$) than at point B. At 275 K, all compositions less than that at Point A hydrates could form if the pressure was sufficiently high. This is shown in Figure 2, which gives the pressure required to form hydrates for various amounts of dissolved CO_2 at 275 K and at two other temperatures. As the mole fraction of CO_2 decreases, the pressure required to form hydrates will increase.

It is evident from Figure 1, that the formation of hydrates from a subsaturated water-rich liquid requires the slope of the chemical potential of liquid water vs. pressure from Equation 2 be less than the slope of the chemical potential of hydrate water vs. pressure from Equation 1. A similar analysis has been performed for other hydrate formers (4). Single-phase hydrate formation is predicted to be possible for methane and ethane; however, it may not be possible for propane. Experimental work is underway to verify these predictions.
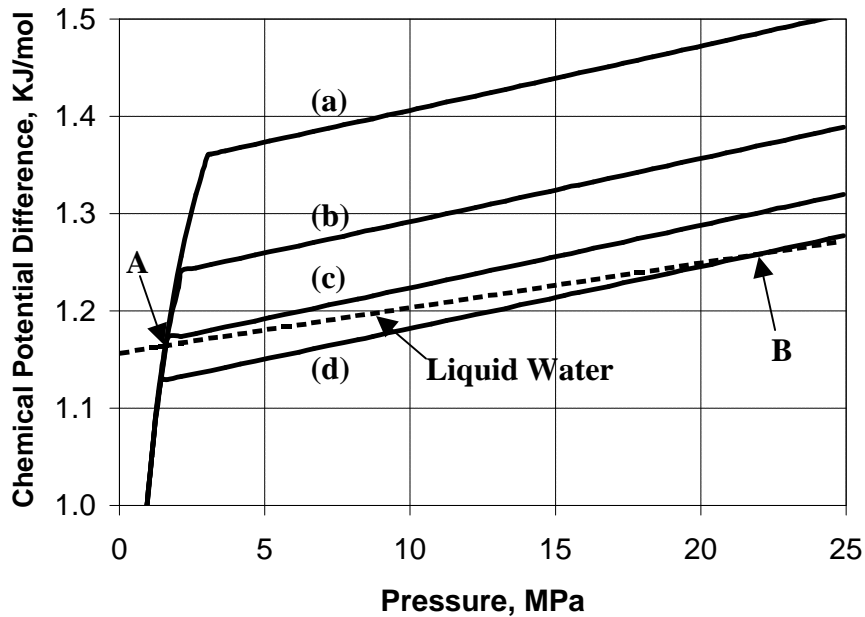
Figure 1. The chemical potential difference of water in the CO_2 hydrate and in the aqueous phases. Lines (a) through (d) represent calculations for water in the hydrate phase at a saturation pressure P^{sat} and mole fraction of dissolved CO_2, respectively, of: (a) 3.0 MPa, 0.026; (b) 2.0 MPa, 0.020; (c) 1.6 MPa, 0.019; (d) 1.4 MPa, 0.016. The points of intersection A and B are equilibrium points for VLH and LH equilibria respectively. T=275 K.
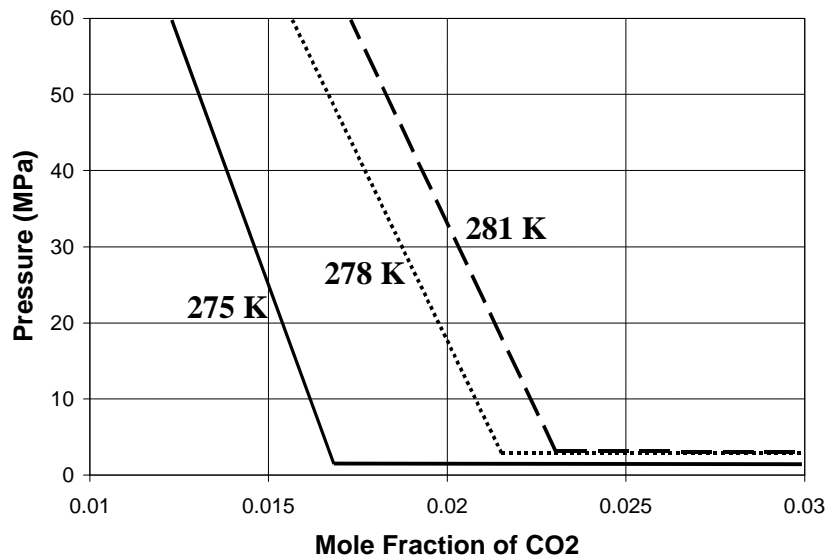

Figure 2. Pressure required to form hydrates as a function of the overall mole fraction of CO_2 in a CO_2 water system at three different temperatures. Hydrates are predicted to form in the region of the line.

Experimental Observations of Hydrate Formation from Dissolved CO_2
Experimental observations of hydrate formation have been made at NETL in a high-pressure, variable-volume viewcell that demonstrated the formation of CO_2 hydrate from single-phase aqueous systems (2, 4). As previously mentioned, formation under these conditions always resulted in a CO_2 hydrate that was more dense than the aqueous phase that it formed in.

Experiments are continuing at NETL to better understand and define the single-phase hydrate formation process. A new viewcell system is being used that permits improved control of the experimental parameters and better data collection capabilities. Figure 3 contains the pressure/temperature history of a recent experiment in which a single-phase solution of water (prepared by reverse osmosis and vacuum degassing) and CO_2 (0.018 mole fraction) was subjected to hydrate forming conditions. The rate of cooling and heating was 0.3 K/h. The pressure drop observed upon cooling at 276.7 K and 17.5 MPa indicates the formation of hydrate. As the system was warmed the hydrate gradually decomposed with complete decomposition occurring near 278.1 K and 18.3 MPa.
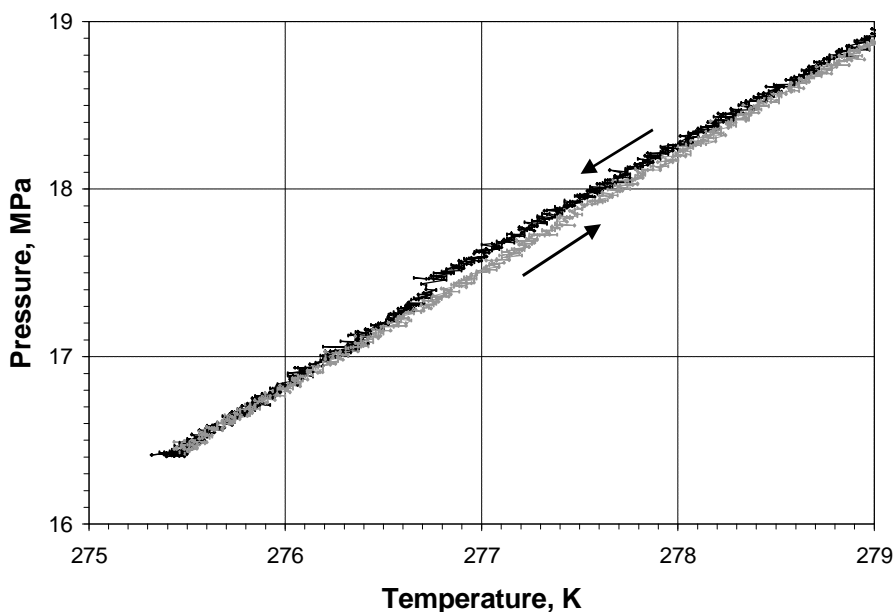

Figure 3. Experimental pressure and temperature data showing evidence for hydrate formation from a single phase solution containing CO_2 dissolved in water.

Conclusions

It is clear from both theoretical and experimental evidence that hydrates can form from dissolved gas in the absence of a free-gas phase. Experiments show that CO_2 hydrate will form when no gas phase is present when the solution contains dissolved CO_2. Conventional models can be modified to predict the hydrate formation pressure as a function of the amount of dissolved CO_2 allowing for the design of experiments or processes utilizing this phenomena.

References

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