GENERAL RESEARCH

CO₂ Hydrates in Refrigeration Processes

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Global warming concerns have led the refrigeration industry to seek and develop new refrigeration systems with a reduced impact on the environment. The use of two-phase secondary refrigerants generated by a primary closed refrigeration circuit is a promising solution. Solid–fluid secondary refrigerants are known for their higher energy efficiency compared to single-phase fluids, because of the additional latent heat of the solid phase. The objective of the present work is to investigate experimentally the latent heat of CO_2 hydrate–ice mixture systems in comparison to that of ice slurry systems. By using a new DTA apparatus, the CO_2 hydrate–ice mixture was shown to offer a dissociation enthalpy of 507 kJ/kg that is higher than that of ice (333 kJ/kg). Artificial tuned CO_2 hydrate–fluid systems appear to be an environment-friendly alternative for refrigeration and air-conditioning systems that can be used in a wide range of applications.

Introduction

Environmental issues related to the depletion of the ozone layer and the emission of greenhouse gases pose a great concern for the refrigeration industry. Primary refrigerants such as CFCs and HCFCs are gradually being phased out in compliance with the Montreal Protocol (1987). Two main research directions have been proposed to reduce the emissions of greenhouse gases: one approach is to reduce the quantities of fluids involved, and another is to optimize the energy efficiency of Heating, Ventilation and Air Conditioning (HVAC) and refrigeration equipment. The first approach involves the use of secondary refrigerants to reduce the load of primary refrigerants. The secondary refrigerant is first cooled in a reduced-load primary refrigeration circuit and then distributed to places for use. However, the use of a secondary refrigerant at intermediate refrigerant temperatures reduces the exergy of the system because a circulating pump is required. This can be overcome by using two-phase secondary refrigerant fluids, which offer a higher energy efficiency than traditional single-phase secondary refrigerants because of the latent heat of fusion of the phase-change material.

Two-phase secondary refrigerants cover a wide range of phase-change fluids and are divided into four subgroups: (a) phase-change materials that are encapsulated and protected from the carrying medium. Some examples that enter into this subgroup include emulsions, fine suspensions of water droplets in a carrying hydrophobic medium (e.g., oil), and suspensions of oil droplets (e.g., paraffin) in water; (b) stabilized slurries[1]

for which the phase-change material (generally water) is retained inside porous particles of suspensions in a non-water-miscible carrying liquid; (c) ice slurries[2] in which the carrying fluid and the phase-change material are identical (e.g., water–ice system); and (d) hydrate slurries[3] in which the carrying fluid is an aqueous solution and the phase-change material is a clathrate hydrate.[4]

Presently, two-phase secondary refrigerant slurries are not extensively used in industry. Actually, the development of two-phase slurries is limited by the weak feedback on recent research advances in the ice slurry technology, the lack of "trouble-free" slurry generators, and the absence of reliable devices to control the ice concentration of slurry.

A nonmechanical generator was developed in a previous work[5] to produce two-phase secondary refrigerants by the displacement of the thermodynamic equilibrium of an aqueous mixture toward a solid–liquid mixture and the addition of a third agent (e.g., CO_2). Using this approach, one can benefit from the formation of CO_2 hydrate–water mixtures, whose latent heat can be used in a wide range of temperature conditions that are suitable for secondary fluids. Moreover, according to Sloan,[4] some of the hydrates have a latent heat similar to that of ice. Unlike oil companies, which for a long time have sought means to inhibit the formation of these hydrates,[4,6,7] particularly in pipelines, the present study makes use of the optimal dissociation enthalpy of CO_2 hydrates. Although the use of other hydrates (e.g., CFC, HCFC hydrates)[4,8–12] as phase-change materials in refrigeration applications has been known for many years, their function is currently forbidden because of the high global warming potential (GWP) of CFC and HCFC molecules. Starting from the thermal studies on

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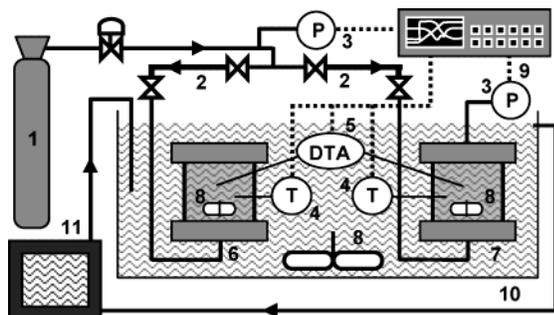
Figure 1. Experimental device: (1) CO_2 bottle, (2) injection tube, (3) pressure gauge, (4) thermocouples, (5) differential thermal analyzer, (6) reference cell, (7) measuring cell, (8) stirrer, (9) acquisition interface, (10) temperature-controlled bath, (11) cooling/heating unit.

hydrates produced with harmless CO_2, the objective of this article is to show that these environmentally friendly solid compounds have thermophysical characteristics that are well-suited for refrigeration applications, especially in the field of air conditioning.

Materials and Methods

A temperature (250−290 K) and pressure (0−4 MPa) experimental apparatus was developed to characterize the thermal behavior of binary and ternary mixtures, establish the phase diagram of CO_2 hydrate mixtures and measure the heat transfer. The experimental device (Figure 1) consisted of a differential thermal analysis (DTA) apparatus and two symmetric transparent glass cells. Each glass cell had an inner diameter of 30 mm and a volume of 46 cm[3]. One of the cells contained the mixture to be studied, and the other cell contained an inert solution that was used as a reference. The setup was immersed in a temperature-controlled bath. A calibrated injection system was used to determine the total quantity of gas injected into the cell.[5] A T-type thermocouple was placed inside each cell, and two pressure gauges were used to measure the "in situ" fluid pressure (as shown in Figure 1). Another eight T-type thermocouples were connected in series to measure the temperature difference between the two cells and perform the DTA measurements. The cells were subjected to cyclic decreasing/increasing temperature changes to monitor the cooling and heating rates of both a ternary (CO_2−water−ethanol) and binary (CO_2−water) mixture. Various methods can be used to determine the solid formation/dissociation equilibrium conditions. For example, the equilibrium conditions can be determined at constant pressure by increasing the temperature[13−15] or at constant-temperature conditions by reducing the pressure.[16] The approach at constant-pressure conditions was adopted here, which relies on the use of the DTA signal to detect the end of the melting process.

Results and Discussion

Phase Diagrams. Figure 2 shows the CO_2−water and CO_2−water−ethanol mixture equilibrium relationships for which the first two-phase zone (indicated by I) resulting from an antisolvent[17] effect was studied. In zone I, the ice and liquid in the mixture coexist only within a limited range of pressure and temperature conditions, restricting the application of such an antisolvent concept for only ice slurry generation. A second two-phase solid−liquid zone (zone II) attributed to the
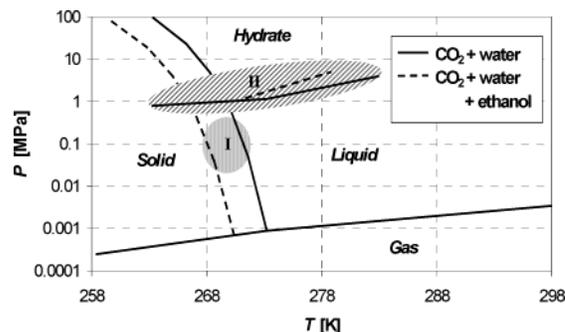
Figure 2. CO_2−water and CO_2−water−ethanol mixture equilibrium relationship.
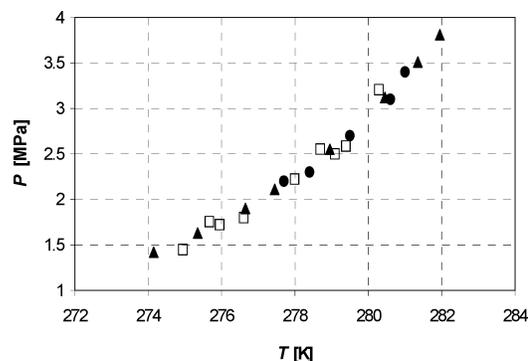
Figure 3. Pressure vs temperature of formation of CO_2 hydrate. Results from the literature: ▲ Adisasmito et al.,[13] Adisasmito and Sloan;[14] ● Yang et al.[15] Our results: □ DTA signal.
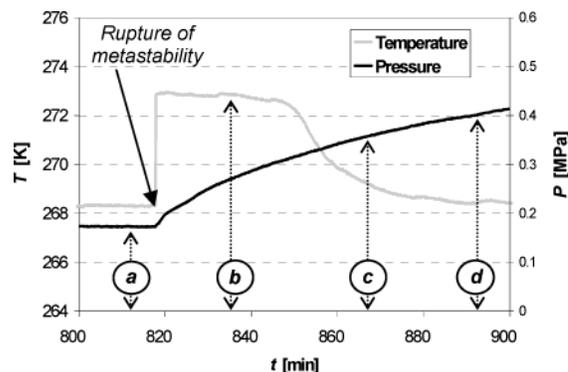
Figure 4. CO_2 hydrate−ice mixture crystallization.

presence of clathrate hydrates is shown in Figure 2. The clathrate hydrates are solid inclusion compounds, whose formation is based on the physical enclosure of a guest molecule by a set of host molecules. The host molecules here are water molecules held together by hydrogen bonds. Three types of structures are known, namely, cubic I,[18] cubic II,[19] and hexagonal H.[20] These structures correspond to various arrangements of the water molecules but also depend on the nature and size of the guest molecule.

The exothermic process of gas hydrate formation is expressed as follows

$$G + nH_2O \leftrightarrow G \cdot nH_2O \qquad \text{(hydrate)} \qquad (1)$$

where G represents 1 mol of gas and n is the hydrate number, i.e., the average number of water moles per mole of gas. However, gas hydrates are nonstoichiometric compounds that are formed at the gas−liquid interface as well as within the liquid phase.[21]
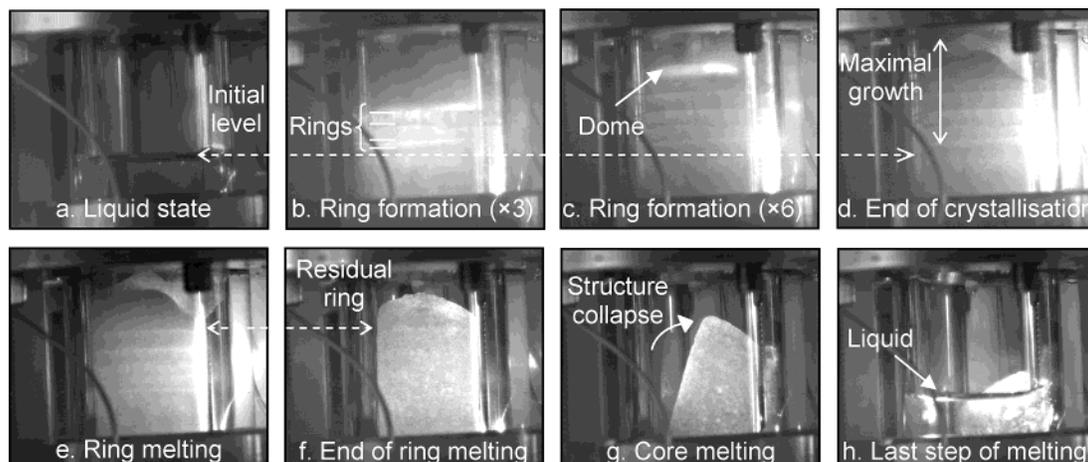
Figure 5. Crystallization and dissociation mechanisms for the CO_2 hydrate−ice mixture.

Figure 3 shows the experimental results of CO_2 hydrate formation compared with literature data. Good agreement was observed between the literature and the results obtained by the DTA method. Unlike the ice formation caused by an antisolvent effect (zone I of Figure 2), the CO_2 hydrate formation zone (zone II of Figure 2) covers a much wider range of conditions. Therefore the following results would only deal with the behavior of CO_2−water compounds.

CO_2−Water Mixture Cooling. The cooling process of a supercooled CO_2-saturated aqueous solution down to 268.3 K was studied at the equilibrium pressure of 0.17 MPa. The crystallization of the CO_2−water mixture was initiated by a rupture of metastability caused by a short period of stirring action (Figure 4). Following this metastability, the temperature of the mixture was increased to 272.9 K, which is 0.25 K below the theoretical freezing temperature of water at atmospheric pressure. The crystallization mechanism is illustrated in Figure 5. The formation of a solid phase (defined as "ring") approximately 3 mm in thickness was observed along the cell wall while the central zone remained in its liquid state. Afterward, a domelike structure was formed above the central part of the cell, which was attributed to a centripetal motion of the ring's interface. After a few minutes, the dome broke apart and the liquid was spread outside the solid block forming a new crystalloid ring. The same process was repeated to generate a set of successive rings (Figure 5b−c). At the end of this crystallization process, the sample occupied approximately 30 cm^3 of the cell (Figure 5d), whereas in its liquid state, it occupied a volume of only 20 cm^3 (Figure 5a), which corresponds to a swelling of approximately 50%.

CO_2−Water Mixture Heating. A positive temperature gradient of 0.1 K/min was applied to melt the formed solid. As shown in Figure 6, an initial plateau in the temperature data appeared at 272.1 K. The rings of the peripheral part of the solid started to melt, as shown in Figure 5e. After the first plateau was reached, a temperature rise from 272.4 to 274.3 K was observed that was followed by a sudden temperature drop (Figure 6) and a second temperature plateau. The sudden temperature drop could be attributed to the endothermic melting process of the CO_2 hydrates in the mixture, which would cause freezing of the previously produced liquid water. This refreezing phenomenon has already been observed by various other authors[6,22] for the depressurization of a hydrate−ice mixture. As shown
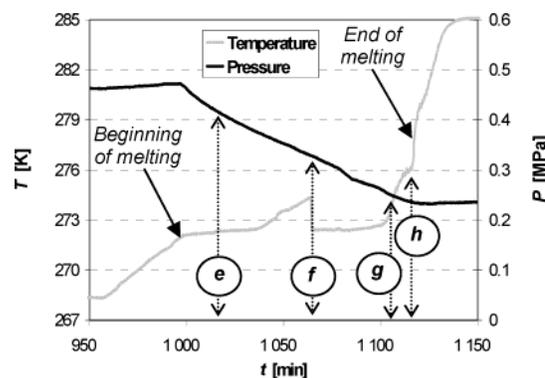
Figure 6. Heating process of the CO_2 hydrate−ice mixture at a rate of 0.1 K/min.
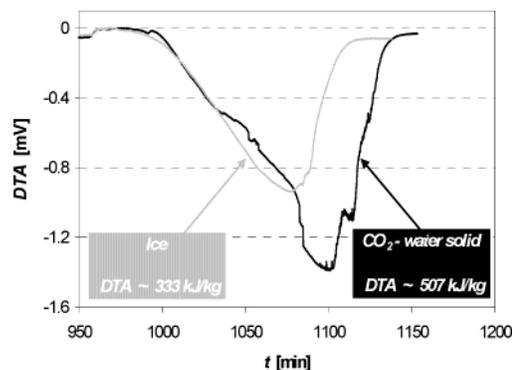
Figure 7. DTA signal for the dissociation of the CO_2 hydrate−ice mixture at a rate of 0.1 K/min.

in Figures 5f and 6, the beginning of the second plateau corresponds to the disappearance of the external rings. The melting of the homogeneous central solid was accelerated (Figure 5h) when the temperature reached the final pseudo-plateau from 274.8 to 276.2 K (Figure 6). It was reasonable to conclude that this pseudo-plateau was caused by the residual hydrate melting, as revealed by the peak in the DTA graph between 66 500 and 67 000 s (Figure 7).

Dissociation Enthalpy of the CO_2 Hydrate−Ice Mixture. The system of the CO_2 hydrate−ice mixture was compared with that of pure ice to estimate the latent heat of the hydrate−ice mixture. First, a substantial swelling difference was noted between the homogeneous formation of pure ice, which typically causes a volume expansion of approximately 10%, and

Table 1. CO$_2$ Hydrate Dissociation Enthalpy and x' Results[a]

T (K)	P (MPa)	n (mol/mol)	$\Delta H_{\text{H–CC}}$ (kJ/mol)	$\Delta H_{\text{H–Yoo}}$ (kJ/mol)	$\Delta H_{\text{H–And}}$ (kJ/mol)	$\Delta H_{\text{H–Yoo}}$ (kJ/kg)	x' (kg/kg)
277.15	1.99	6	66.9	61.1	60.0	566.1	0.254
278.15	2.25	5.9	66.6	60.6	59.3	570.2	0.266
279.15	2.55	5.9	67.3	60.7	59.2	571.6	0.271
280.15	2.91	5.9	68.6	61.3	59.5	577.2	0.287
281.15	3.34	5.9	69.6	61.5	59.4	579.5	0.294

[a] $\Delta H_{\text{Tot}} = 507$ kJ/kg for x' calculation.

the formation of crystal rings for the CO_2–water mixture, which had a corresponding expansion volume of 50%. In addition, an obvious difference was observed in the level of the DTA signal that characterizes the phase change of the mixture. As shown in Figure 7, the DTA signal revealed that the dissociation enthalpy of the solid formed from the CO_2–water mixture is significantly higher than the melting enthalpy of ice. The integral under the DTA curve of the ice-melting process was considered to be equivalent to 333 kJ/kg of water. It was therefore deduced that the total dissociation enthalpy of the solid formed from the CO_2–water mixture was 507 kJ/kg of water.

Proportion of Ice and CO$_2$ Hydrate in the Mixture. Given the total dissociation enthalpy of the solid formed from the CO_2–water mixture, it was possible to estimate the amount of ice and CO_2 hydrates in the mixture. Assuming that all water present in the cell is exclusively converted to ice or hydrate, then the following enthalpy balance related to an additive mixture law can be written without taking into account the enthalpy of mixing

$$\Delta H_{\text{Tot}} = x'\Delta H_{\text{I}} + (1 - x')\Delta H_{\text{H}} \qquad (2)$$

where ΔH_{Tot}, ΔH_{H}, and ΔH_{I} are respectively the total dissociation enthalpy of the solid formed from the CO_2–water mixture (hydrate–ice), the dissociation enthalpy of pure hydrate, and the latent heat of pure ice. In eq 2, x' is the mass fraction of ice, i.e., the mass of formed ice divided by the initial mass of water, and $(1 - x')$ represents the mass of water contained in the hydrate divided by the initial mass of water. Given ΔH_{Tot} (507 kJ/kg) and ΔH_{I} (333 kJ/kg), the only missing parameter for the determination of x' is the dissociation enthalpy of pure hydrate. A Clausius–Clapeyron model[23] was used to calculate ΔH_{H}

$$\frac{\text{d} \ln P}{\text{d}\left(\dfrac{1}{T}\right)} = -\frac{\Delta H_{\text{H}}}{zR} \qquad (3)$$

An improved expression[24] of the Clausius–Clapeyron model for dissolved gases, such as carbon dioxide in water, is

$$\frac{\text{d} \ln P}{\text{d}\left(\dfrac{1}{T}\right)} = -\frac{\Delta H_{\text{H}} + nx\Delta H_{\text{s}}}{\dfrac{R}{y}\left(1 - \dfrac{nx}{1 - x}\right)z - n\dfrac{P\Delta v}{T}} \qquad (4)$$

The above expression takes into account the dissolution enthalpy (ΔH_{s}), which can be described by the following polynomial expression[25]

$$\Delta H_{\text{s}} = 106.56 - 6.2634 \times 10^4 T^{-1} + 7.475 \times 10^6 T^{-2} \qquad (5)$$

The improved model of Clausius–Clapeyron described

by eq 4 also takes into account the molar volume change, Δv, between hydrate and liquid water, which is a parameter that depends only on the hydrate structure type and can be readily found in the literature.[26] The molar fraction of gas dissolved in water, x, was calculated by the generalized Henry's law. The hydrate number n was estimated from literature data.[27,28]

The determination of the hydrate dissociation enthalpy (ΔH_{H}) consists of converting (T, P) pairs from the equilibrium phase diagram into $(1/T, \ln P)$ pairs. The dissociation enthalpy results from eq 3 ($\Delta H_{\text{H–CC}}$), eq 4 ($\Delta H_{\text{H–Yoo}}$), and Anderson[27] ($\Delta H_{\text{H–And}}$) are given in Table 1. Good agreement is observed between $\Delta H_{\text{H–Yoo}}$ and $\Delta H_{\text{H–And}}$ for all pressure and temperature conditions investigated. The data obtained using eq 3 ($\Delta H_{\text{H–CC}}$) are 10% higher under similar conditions, probably because this model does not take into account the dissolution enthalpy of CO_2 in water.

As shown in Table 1, the CO_2 hydrate dissociation enthalpy is about 60 kJ per mole of hydrate. Given that the hydrate number is approximately 6 (that is 1 mol of hydrate for every 6 mol of water), the dissociation enthalpy is roughly 60/6 or 10 kJ/mol of water. By dividing this dissociation enthalpy by the molar mass of water (0.018 kg/mol), a hydrate dissociation enthalpy higher than 560 kJ/kg of water is achieved. Table 1 also presents values of the mass fraction of ice, x', contained in the CO_2 hydrate–ice mixture calculated using the total dissociation enthalpy of 507 kJ/kg of water. The dissociation enthalpy of pure hydrates used here was obtained by the improved model of Clausius–Clapeyron (eq 4), $\Delta H_{\text{d,Yoo}}$ (expressed in kilojoules per kilogram of water contained in the hydrate).

The uncertainty of the ice mass fractions given in Table 1 depends on the pressure and temperature conditions used to calculate $\Delta H_{\text{d,Yoo}}$; however, these conditions were higher than those set in our experimental runs. Moreover, hydrate formation also involves other measurement uncertainties, as the ice-hydrate mixture formation mechanism is still not clear. Nevertheless, this approach enables us to estimate that the amount of ice contained in the solid mixture is between 25 and 30 wt %, or a corresponding hydrate proportion ranging from 70 to 75 wt %. This percentage of hydrate seems rather surprising given that a larger amount of ice would be expected as described earlier (see Figure 6).

Discussion of Ice–Hydrate Mixture Formation Conditions. Experiments showed that the pressure and temperature conditions during the formation of the mixture are different from the hydrate formation conditions frequently encountered in the literature. Nevertheless, the CO_2 hydrate–ice mixture studied in this paper shows characteristics that are peculiar to the behavior of an ice-hydrate mixture. The differences in formation conditions between the present data and others might be due to the fact that liquefied CO_2 was not used in this study as is often the case in the literature.[29,30] The studies that examined hydrate for-

mation from gaseous CO_2 show higher pressure ranges at ambient temperature[31,32] and at low temperatures based on the injection of gaseous CO_2 on ice crystals.[33] The present method is different from those employed in these studies, because the crystallization of the ice−hydrate mixture is initiated by a short stirring period of a supercooled CO_2-saturated solution at low temperatures. Moreover, depending on whether the production is static or dynamic, the hydrate type formed can be different.[21] Finally, the rupture of the supercooled state reduces the residual liquid phase, which would increase the dissolved CO_2 concentration and make hydrate formation more favorable.

Conclusion

The experimental study presented in this paper enabled us to estimate the latent heat of a solid formed from a supercooled CO_2-saturated aqueous solution model. Despite the fact that the formation conditions were different from those frequently encountered in the literature, the present results revealed that this system is a mixture of ice and CO_2 hydrate. The novelty of this work is that the CO_2 hydrate−ice mixture would be suitable for use as a phase-change material in two-phase secondary refrigerant applications, given that its dissociation enthalpy is higher than that of pure ice. The swelling phenomenon that was observed during the solidification process and the dissociation kinetics leading to an unusual temperature behavior could confirm the existence of a hydrate phase. The hydrate would stabilize the solid medium and could therefore promote its use as a secondary refrigerant, as a constant temperature is normally required. A simple calculation indicated that a smaller quantity of ice existed than expected from the experiments. The dissociation enthalpy of the mixture will be further checked in another work using the traditional calorimetry principle. Future work on the selection of homemade hydrates with high latent heat is being carried out for other pressure and temperature conditions used in refrigeration applications. Last, the overall energy efficiency of the system is currently being studied by taking into account various factors involved in this process, such as the upstream gas production or the dynamic aspect of the application.

The results from this work confirm a novel nonmechanical concept for CO_2 hydrate slurry formation by displacing the phase equilibrium of an aqueous solution and adding CO_2 gas. Possibilities for improving the available enthalpy of the mixture by a careful selection of the guest molecules would be of future interest. However, two main points have to be evaluated for the use of these two-phase solid−fluid secondary refrigerants, namely, (1) the effect of transient conditions on hydrate slurry formation and (2) the effect of aging on the aqueous solution.

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Note Added after ASAP Posting. HVAC was incorrectly identified. This article was released ASAP on August 27, 2004. The correct version was posted on August 31, 2004.

Nomenclature

H = enthalpy (kJ/kg of water, kJ/mol of hydrate, or kJ/mol of dissolved CO_2)
n = hydrate number (mol/mol)
P = pressure (MPa)
R = universal gas constant (J/mol·K)
t = time (min)
T = temperature (K)
v = molar volume (m³/mol of water)
x' = mass fraction of ice contained in the CO_2 hydrate−ice mixture (kg of ice/kg of water)
x = molar fraction of gas dissolved in water (mol/mol)
y = molar fraction of gas in the vapor phase (mol/mol)
z = compressibility factor

Greek Letter

Δ = change

Subscripts

And = based on Anderson[27]
CC = based on the Clausius−Clapeyron equation[23]
H = CO_2 hydrate
I = ice
s = dissolution
Tot = total (solid mixture)
Yoo = based on Yoon et al.[24]

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