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Phase behaviour of liquid CO₂ with an impurity of water: Influence of CO₂ hydrate.

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The solubility of water in liquid CO₂ coexisting with CO₂ hydrate or liquid water is evaluated in order to investigate the thermodynamic conditions to avoid the formation of CO₂ hydrate in transportation processes of liquid CO₂. To this end, theoretical calculations have been carried out to obtain the chemical potentials of water and CO₂ in all the phases involved in the coexistence. The solubility of water in liquid CO₂ coexisting with liquid water decreases with decreasing temperature over a wide range of temperature and pressure except for the vicinity of the critical point of CO₂. The decrease in the solubility is further enhanced by formation of hydrate. We estimate the Gibbs energy of



hydrate formation, which is an important property for sequestration of CO₂, for cases where the temperature or pressure of water-saturated liquid CO₂ decreases. We also estimate the amount of water precipitated as hydrate during these processes, which has a direct bearing on flow assurance in CO₂ transportation. The present study will contribute to the development of a low-energy, safe CO₂ transport network aiming at achieving large-scale carbon neutrality.

Introduction

Carbon dioxide (CO₂) is often used in industry as a non-toxic solvent to extract precious substances mostly under supercritical conditions.¹ Advantage is taken of the fact that its critical temperature, 304.2 K, is well within the room temperature range and supercritical CO₂ acts as a good solvent for a variety of substances. It is also utilised as a cooling agent owing to the large latent heat of sublimation of dry ice, 25 kJ mol⁻¹,² which is associated with its triple point pressure (0.517 MPa) being higher than the atmospheric pressure.³

One of the imperative concerns on CO₂ is how the emitted greenhouse gas is reduced by CO₂ capture and storage (CCS).⁴ Formation of clathrate hydrate (hereafter hydrate) at low temperatures and high pressures poses a potential risk of causing pipeline blockage during transportation of CO₂ containing water as an impurity in the CCS process.⁵ It is possible to suppress the hydrate formation by dosing kinetic inhibitors such as polyvinyl caprolactam or thermodynamic inhibitors such as methanol. Extensive efforts have been devoted to finding efficient inhibitors and explore possible mechanisms for the inhibitors to work.⁶⁻¹⁰ The other way is removal of water prior to transportation. To implement this strategy to exploit safe and feasible CCS, it is an urgent task to gain a comprehensive



understanding of various features of water dissolved in liquid CO₂.

A hydrate is a crystal composed of water molecules forming the host lattice structure in which small guest molecules are encapsulated.¹¹ It is a nonstoichiometric compound as to the guest composition, i.e., the number of guest molecules in the host lattice. Its thermodynamic stability and the composition of guest significantly depend on temperature and pressure. We have studied the thermodynamic stability of hydrates engaging various kinds of guest species based on atomistic models of intermolecular interactions.¹²⁻¹⁸ Our theory stems from the van der Waals and Platteeuw (vdWP) theory¹⁹⁻²¹ originally developed to predict the three-phase coexistence (water, hydrate, and guest fluid phases) but is different in ensemble to which the relevant partition function is linked. The free energy derived from our theory enables to evaluate the two two-phase coexistences, between the hydrate and aqueous phases and between the hydrate and guest fluid phases. We reveal that this approach, which requires only a few empirical parameters, plays a significant role in achieving this objective.

Hydrates have been utilised for storing various gases of small molecular size, desalination of seawater, and energy resource.¹¹ Natural CH₄ hydrate is expected to be an energy resource. Recovering CH₄ from hydrate is essential to mitigate the global warming, otherwise release of CH₄ into the atmosphere from the hydrate accelerates it because CH₄ has a stronger greenhouse effect than CO₂ does. Replacing CH₄ in hydrate with CO₂ may provide an efficient way to contribute to CCS. Hence, the phase behaviour of CH₄ hydrate would also be a key issue in CCS.

The solubility of water in liquid CO₂ is an important property for CCS. Although a fairly large number of measured solubility data have been accumulated^{22,23}, the solubility values depend on individual measurements, and the deviation among them is considerably



large. The solubility of water in liquid CO₂ is approximately an order of 10⁻³ in mole fraction at 280 K around a pressure of 10 MPa, which is one order lower than that of CO₂ in liquid water.^{24,25} One of the serious concerns that has not been fully addressed is the influence of hydrate formation on the solubility. Liquid CO₂ coexists with water in the high-temperature and low-pressure region while it coexists with CO₂ hydrate in the low-temperature and high-pressure region. We have developed a method to evaluate the solubility under the coexistence of hydrate taking account of the change in the chemical potential of water due to the formation of hydrate.¹⁷ We expect that an application of this method to an extended range of thermodynamic conditions could be useful for practical transportation and storage of liquid CO₂ containing water.

In the present study, we address the following three issues. First, the solubility of water in liquid CO₂ is calculated in the presence or absence of hydrate. Our calculations are performed in a temperature range between 220 and 325 K and at pressures of 5, 10, 20, 30, 50 and 100 MPa. In contrast to our previous study,¹⁷ this range includes temperatures and pressures above the critical point of CO₂. This extent of the coverage is essential since some operations in CO₂ transportation would be made under such conditions to avoid bubbling. Next, we examine various properties of CO₂ hydrate that affect the thermodynamic properties of the coexisting phases, and compare them with those of CH₄ hydrate obtained in our previous studies.¹⁴⁻¹⁶ Finally, we investigate the amount of CO₂ hydrate formed from a supersaturated state prepared by rapid cooling or decompression along with the corresponding formation Gibbs energy of hydrate.

Theory and methods

Since we have presented most part of the methods to calculate the phase behaviours of



CO₂ hydrate and the solubility of water in our previous papers¹⁴⁻¹⁸, they are described below only briefly. A CO₂ hydrate coexists with either an aqueous solution or a CO₂-rich liquid. The compositions in the aqueous solution and liquid CO₂ are denoted by z'_c (mole fraction of CO₂) and by $z''_w = 1 - z''_c$ (mole fraction of water), respectively. Those in CO₂ hydrate are represented by the mole fraction of CO₂ as y'_c on the phase boundary between the aqueous solution and hydrate (water/hydrate boundary) and as y''_c on the phase boundary between the hydrate and liquid CO₂ (hydrate/CO₂ boundary).

Thermodynamic conditions for hydrate formation

The phase behaviour of CO₂ hydrate is represented in the space of temperature, T , pressure, p , and composition, y . The original vdWP theory has been proposed to calculate the dissociation pressure of hydrate at the three-phase equilibrium, where the water, hydrate, and liquid CO₂ phases coexist in a certain range of temperature.¹⁹ Actually, it is a locus of the intersections between the two two-phase boundaries (water/hydrate and hydrate/CO₂) projected onto T - p plane.^{12,13} The dissociation pressure for CO₂ hydrate is depicted against temperature in Fig. 1. The present theoretical calculation successfully recovers experimental measurements.²⁶⁻²⁸ The upper-left area delimited by the curve is the stable zone of the hydrate. The highest temperature of the three-phase coexistence for CO₂ hydrate is around 297 K.



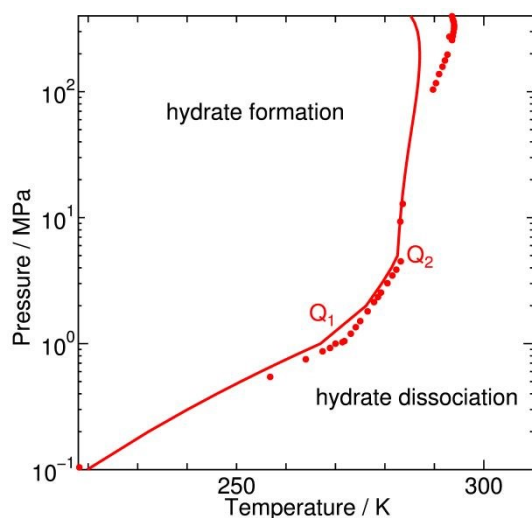


Fig. 1 Dissociation pressure of CO₂ hydrate, by which CO₂ hydrate formation and dissociation zones are separated, obtained from the theoretical calculation (solid line). Experimental results are shown by filled circles.

Agreement of the dissociation pressures at high pressure is moderate compared with those at low pressure for a range of $p < 20$ MPa. Although the reentrant character in experimental observation is reproduced with our theoretical calculations, the deviation from the experimental measurement becomes large in the very high-pressure region above 200 MPa. As will be described below, the equilibrium condition is determined using the chemical potential of ice Ih. However, this ice is no longer stable under such high pressures. Thus, it is reasonable to consider our calculations are sound and at least semi-qualitatively correct at pressures lower than ~ 100 MPa.

Phase diagram for binary mixture of water and CO₂

In Fig. 2, we display a global phase diagram of the binary mixture of water and CO₂ at 10 MPa. This figure shows all the phases in T - y space involved in the present study. The stable phase at low composition of CO₂ is the aqueous solution occupying the left region



separated by the blue line. It shrinks to zero below the freezing temperature of water for no incorporation of CO₂ in ice. The stable phase in the middle is the hydrate phase, which is not given as a single line but is surrounded by the boundary of the aqueous solution with the hydrate (water/hydrate) and that of the hydrate with the CO₂-rich solution (hydrate/CO₂). The CO₂-rich solution including the gaseous phase, called hereafter liquid CO₂, exists at high composition of CO₂, though it occupies only a narrow region beyond the red line. When the temperature is higher than the dissociation temperature denoted by the horizontal dotted line, no hydrate forms, and the aqueous phase coexists with liquid CO₂ (water/CO₂). The hydrate intervenes between the aqueous phase and the liquid CO₂ phase below the dissociation temperature. Each phase boundary is determined by the equivalence of the chemical potential of either water or CO₂ between the two phases. CO₂ is regarded as the solute species in the aqueous solution while it is treated as the solvent in liquid CO₂. The hydrate, guest liquid, aqueous, and ice phases are designated by superscripts (*hy*), (*lq*), (*aq*), and (*ice*) in the following description of the phase equilibria.

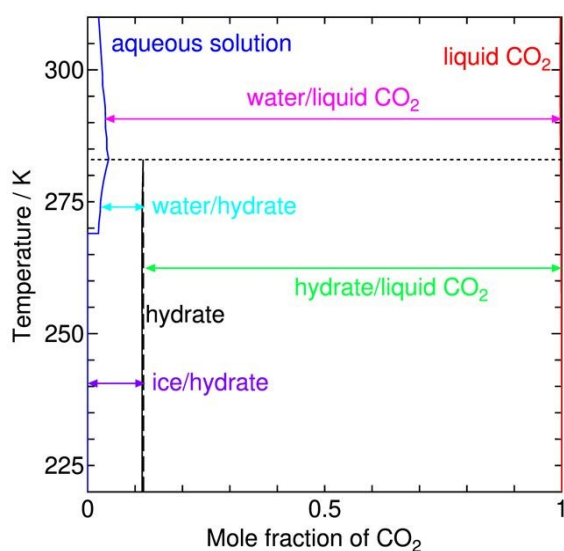


Fig. 2 Phase diagram of the binary mixture of water and CO₂ at 10 MPa. The boundaries of the stable phases are represented by blue line for the aqueous solution, black lines for



the hydrate, and red line for liquid CO₂. The horizontal dotted line indicates the dissociation temperature of CO₂ hydrate.

Liquid CO₂ in equilibrium with aqueous solution without CO₂ hydrate

First, we consider thermodynamic conditions where T is high and/or p is low, and therefore CO₂ hydrate is not formed. Liquid CO₂ is in direct contact with the aqueous solution. It is assumed that the chemical potential of water in the aqueous solution, $\mu_w^{(aq)}(T, p, z'_c)$, is approximated to that of the pure water, $\mu_w^0(T, p)$. Likewise, that of CO₂ in liquid CO₂, $\mu_c^{(lq)}(T, p, z''_c)$, is assumed to be equal to that of pure liquid CO₂, $\mu_c^0(T, p)$. The rationale of these approximations is based on the low mutual solubilities.²²⁻²⁵ The methods to calculate the chemical potentials of the two pure substances are given elsewhere.¹⁷ The equilibrium condition for each two-phase coexistence is calculated from

$$\mu_j^0(T, p) = \mu_j^{(k)}(T, p, z) = k_B T \ln(\rho_j \lambda_j^3) + \mu_j^e(T, p) + f_j^{(r)}(T), \quad (1)$$

where k_B denotes the Boltzmann constant and $\mu_j^{(k)}(T, p, z)$, ρ_j , λ_j , $f_j^{(r)}$, and $\mu_j^e(T, p)$ stand for the chemical potential in solvent k , number density, thermal de Broglie wavelength, free energy of the rotational motion of the rigid model for the solute, and excess chemical potential arising from the interaction of the solute with surrounding solvent molecules for species j . The excess chemical potential, $\mu_j^e(T, p)$, is calculated assuming infinite dilution of the solute in the solvent of the counterpart species. In the practical calculation, the density of the solute is given by

$$\rho_j(T, p) = \lambda_j^{-3} \exp\left[\frac{\mu_j^0(T, p) + \epsilon_j - \mu_j^e(T, p) - f_j^{(r)}(T)}{k_B T}\right], \quad (2)$$

where ϵ_j is an energy correction associated with the self-polarization. It is set to 7.8 kJ



mol⁻¹ for $j = w$ (water) with the TIP4P/ice model and 0 kJ mol⁻¹ for $j = c$ (CO₂) with the TraPPE model taking account of the different environments.^{17, 29,30} The solubility of solute species j in solvent k is

$$z_j(T,p) = \frac{\rho_j(T,p)}{\rho_j(T,p) + \rho^{(k)}(T,p)} \approx \frac{\rho_j(T,p)}{\rho^{(k)}(T,p)} \quad (3)$$

where $\rho^{(k)}$ is the density of the pure liquid of k .

CO₂ hydrate in equilibrium with either aqueous solution or liquid CO₂

Cooling and compression promote formation of CO₂ hydrate. Such a hydrate has the two boundaries in the composition (mole fraction) space at a given T and p . It coexists with the aqueous phase on one boundary at y' and with the liquid CO₂ phase on the other boundary at y'' .

The water/hydrate boundary is obtained from the equivalence of the chemical potentials of water in the aqueous solution and in the hydrate as

$$\mu_w^{(hy)}(T,p,y'_c) = \mu_w^0(T,p). \quad (4)$$

The chemical potential of water changes by $\Delta\mu_w^{(hy)}$ while traversing from the water/hydrate boundary fixed by eqn (4) to the hydrate/CO₂ boundary. The chemical potential of water on the hydrate/CO₂ boundary is given by

$$\mu_w^{(hy)}(T,p,y''_c) = \mu_w^0(T,p) + \Delta\mu_w^{(hy)}, \quad (5)$$

which should be equal to $\mu_w^{(lq)}(T,p,z''_c)$.^{13,16}

On the hydrate/CO₂ boundary, the chemical potential of CO₂ in the hydrate equals that in the liquid CO₂ phase. The composition in the hydrate on this boundary is calculated from

$$\mu_c^{(hy)}(T,p,y''_c) = \mu_c^0(T,p). \quad (6)$$

The chemical potential of CO₂ changes by $\Delta\mu_c^{(hy)}$ due to the decrease in composition from



the hydrate/CO₂ boundary determined by eqn (6) to the water/hydrate boundary. The chemical potential of CO₂ on the water/hydrate boundary is given as

$$\mu_c^{(hy)}(T, p, y'_c) = \mu_c^0(T, p) + \Delta\mu_c^{(hy)}, \quad (7)$$

which should be equal to $\mu_c^{(aq)}(T, p, z'_c)$.¹⁷

Eqn (5) and (7) have the same form. Therefore, the density of CO₂ in the liquid water phase and the density of water in the liquid CO₂ phase in the presence of the hydrate are calculated using the common form given by

$$\rho_j(T, p) = \lambda_j^{-3} \exp \left[\frac{\mu_j^0(T, p) + \epsilon_j + \Delta\mu_j^{(hy)} - \mu_j^e(T, p) - f_j^{(r)}(T)}{k_B T} \right]. \quad (8)$$

Excess chemical potential of water in liquid CO₂

The excess chemical potential of solute species j is calculated according to the particle insertion³¹ as

$$\mu_j^e(T, p) = -k_B T \ln \left[\frac{\langle V \exp(-\phi_j/k_B T) \rangle_{T, p}}{\langle V \rangle_{T, p}} \right], \quad (9)$$

where ϕ_j is the interaction potential energy of a randomly inserted solute molecule with all the surrounding solvent molecules and V indicates the volume of the pure solvent. A molecular dynamics (MD) simulation is performed for 5 to 110 ns to generate molecular coordinates at each T and p for liquid water and CO₂.³²⁻³⁴ The numbers of water and CO₂ molecules are set to 1024 and 864, respectively. The number of solute insertions is maximally 8×10^{12} for each thermodynamic condition. All the intermolecular interactions are smoothly truncated at 1.2 nm by multiplying a switching function³⁵ so that the lattice dynamics for the free energy calculation of the host hydrate and ice³⁶ is performed without suffering from the discontinuities associated with the abrupt cutoff of the interaction.



Composition of CO₂ hydrate

The vdWP theory¹⁹ establishes a relation between the occupancy of cage of type j , x_j , and the chemical potential of water in hydrate, $\mu_w^{(hy)}(T, p, y)$, with the aid of the chemical potential of water in empty hydrate, $\mu_h^0(T, p)$, as

$$\mu_w^{(hy)}(T, p, y) = \mu_h^0(T, p) + k_B T \sum_j \alpha_j \ln(1 - x_j) \quad (10)$$

where α_j is the ratio of the number of j type cages to that of water molecules. This is applicable even to a thermodynamic condition where only the hydrate exists as a stable phase.¹²⁻¹⁸ The occupancy is calculated according to

$$x_j = \frac{\exp\left[\frac{(\mu_g - f_j)}{k_B T}\right]}{\exp\left[\frac{(\mu_g - f_j)}{k_B T}\right] + 1} \quad (11)$$

where μ_g and f_j stand for the chemical potential of the guest in the hydrate and the free energy of occupation of the type j cage, which is either large 14- or small 12-hedron for CS-I CO₂ hydrate. The free energy of cage occupation, f_j , for the linear rigid CO₂ molecule is given by

$$f_j = -k_B T \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \frac{2\pi I k_B T}{s h^2} \iint \exp\left(-\frac{\psi_j(\mathbf{R}, \boldsymbol{\Omega})}{k_B T}\right) d\mathbf{R} d\boldsymbol{\Omega} \right], \quad (12)$$

where m and I are the mass and the moment of inertia, h is the Planck constant, and s is the symmetry number, which is 2 for CO₂. In this equation, $\psi_j(\mathbf{R}, \boldsymbol{\Omega})$ represents the interaction energy of the guest CO₂ molecule at position \mathbf{R} and orientation $\boldsymbol{\Omega}$ with all surrounding water molecules. The free energy of cage occupation is significantly affected by the host-guest interaction and the shape of the cage. A set of occupancies, x_j , is connected with the composition, y , as



$$y = \frac{\sum_j \alpha_j x_j}{\sum_j \alpha_j x_j + 1}. \quad (13)$$

One of the significant differences from the original vdWP theory is that the chemical potential of guest species in the hydrate is calculated from eqn (13) combined with eqn (11) via the occupancies for each given composition, y . The chemical potential of the guest species in eqn (11) is substituted with that in its pure fluid state to determine the hydrate/CO₂ boundary using eqn (10).^{12,13,29}

Chemical potentials of ice, empty hydrate, and liquid water

The chemical potential of occupied hydrate is calculated according to eqn (10) once that of the empty hydrate and the occupancies are given. The free energy of empty hydrate, $A(T, V, N_w)$, is assumed to be the sum of the cohesive energy, $U_q(V, N_w)$, the harmonic vibrational free energy, $F_H(T, V, N_w)$, and the residual entropy term, $TS_r(N_w)$, given as¹⁸

$$A(T, V, N_w) = U_q(V, N_w) + F_H(T, V, N_w) - TS_r(N_w), \quad (14).$$

The harmonic vibrational free energy is calculated from a set of the frequencies, ν_j , as

$$F_H(T, V, N_w) = k_B T \left\langle \sum_j \ln \left(\frac{h\nu_j}{k_B T} \right) \right\rangle, \quad (15)$$

where $\langle \rangle$ indicates the average over the generated hydrogen-disordered structures. The residual entropy does not affect the phase boundary since it is a function of only N_w . To obtain the equilibrium volume, $\langle V \rangle$, the following function is minimized with respect to V :

$$Y(T, V, N_w, p) = A(T, V, N_w) + pV. \quad (16)$$

The chemical potential of empty hydrate, $\mu_h^0(T, p)$, is simply calculated as



$$\mu_h^0(T,p) = \frac{A(T,\langle V \rangle, N_w) + p\langle V \rangle}{N_w}. \quad (17)$$

The same method is used to calculate the chemical potential of ice Ih. The anharmonic free energies of ice and hydrate are likely to be comparable. Since this component cancels out in eqn (4), we exclude it from eqn (14).

An extension to higher temperatures beyond the melting point of ice is required. The chemical potential of pure liquid water, $\mu_w^0(T,p)$, at temperature $T = T_m + \Delta T$ and pressure p can be estimated as

$$\mu_w^0(T,p) \approx \mu_{ice}(T,p) - \Delta s(T_m,p)\Delta T - \frac{\Delta c_p(T_m,p)}{2T_m}\Delta T^2, \quad (18)$$

where $\Delta s(T_m,p)$ and $\Delta c_p(T_m,p)$ are the differences in the entropy and heat capacity per molecule at constant pressure between ice and liquid water. Those properties are rather easily calculated from MD simulations.¹⁸

The phase boundary between water and hydrate is found by equating the chemical potential of water in hydrate in eqn (10) with that of ice (or liquid water) according to eqn (4). The occupancy at this equilibrium is calculating from eqn (11) and (13). The other boundary between hydrate and guest species is given by the equivalence of the chemical potential of the guest species according to eqn (6).

Intermolecular interactions and structures of hydrate and ices

A hydrate is composed of host water and guest molecules. The water-water interaction is described by the TIP4P/ice model²⁹, which is superior in reproducing the melting temperature of ice Ih and several properties of hydrates.^{37,38} We adopt the TraPPE model for CO₂³⁰, which is a rigid rotor with three interaction sites, and the united-atom OPLS model for CH₄.³⁹ Capability of this CO₂ model to recover the phase diagram around the



triple point gives a rationale for its use under CO₂-rich conditions rather than the other models.^{40,41} Those parameters are listed in Table 1. A deviation from the Berthelot rule is introduced for the Lennard-Jones (LJ) interactions of the unlike pairs of molecules^{13,16,42-44} while the Lorentz rule is always applied. A scaling factor, χ , is multiplied to the LJ energy parameter value from the Berthelot rule to recover the experimental dissociation pressure around 273 K.

Table 1 Potential models for CO₂ and CH₄. Partial charge (q), LJ size parameter (σ), and LJ energy parameter (ε), in the potential models for CO₂ and CH₄. A scaling factor, χ , is multiplied to the value of the Berthelot rule for the interactions with the oxygen atom of water. The C-O distance is fixed to 0.1160 nm.

site	q/e	σ/nm	$\varepsilon/\text{kJ mol}^{-1}$	χ
C	0.7000	0.2800	0.2245	1.13
O	-0.3500	0.3050	0.6568	1.13
CH ₄	0.0	0.3730	1.231	0.980

One hundred hydrogen-disordered CS-I structures are generated using the GenIce tool^{45,46} for the calculation of the free energy and other properties of the hydrate. The CS-I structure consists of 368 water molecules. The generated configurations satisfy the ice rules having no net polarization.^{47,48} The chemical potentials of ice, empty hydrate, and liquid water were calculated previously.¹²⁻¹⁷

Results and discussion

Solubilities of CO₂ in water and water in liquid CO₂

In Fig. 3, we show the solubility of CO₂ in the aqueous phase and the solubility of water in the liquid CO₂ phase at 10 MPa. The aqueous phase is assumed to be in



equilibrium with the hydrate or liquid CO₂ in the whole range of temperature examined here while the liquid CO₂ is to be in equilibrium with the hydrate or aqueous solution. Thus, each curve is extended to the range of metastable state.¹⁷ As the temperature increases, the solubility curve shifts from the solid one to the dotted one at the crossover, the three-phase coexistence condition, indicated by the arrow. Agreement with the experimental measurements²² is excellent in the solubility of water in liquid CO₂, once an appropriate value of the self-polarization energy of the TIP4P/ice²⁹ model, $\epsilon_j = 7.8$ kJ mol⁻¹, is chosen.¹⁷ Experimental values at 0.1 MPa^{24,25} are compared to the theoretical ones in the inset of Fig. 3. The solubility of CO₂ is reproduced within the range of accuracy required for our later discussion.

The solubility of CO₂ in liquid water coexisting with liquid CO₂ decreases with raising temperature. This behaviour is commonly observed in the solubility of solute substance having a low boiling point. However, the solubility increases with raising temperature when the aqueous solution coexists with CO₂ hydrate. The crossover of the solubility curves against temperature has also been observed experimentally.⁴⁹ The difference in the solubility between the dotted and solid curves arises from the decrease in the chemical potential of CO₂ associated with traversing from the hydrate/CO₂ boundary to the water/hydrate boundary in composition space, $\Delta\mu_c^{(hy)}$ in eqn (7).^{13,16} From a qualitative viewpoint, this is simply accounted for by the fact that the mole fraction of CO₂ on the water/hydrate boundary is lower than that on the hydrate/CO₂ boundary. As for the solubility of water in liquid CO₂, the chemical potential of water on the water/hydrate boundary is higher and therefore the solubility of water in the presence of the hydrate is lower than the value in the absence of the hydrate. A more quantitative argument on the difference in the solubility between CO₂ and water will be made below in relation to the



phase behaviours of the CO₂ hydrate.

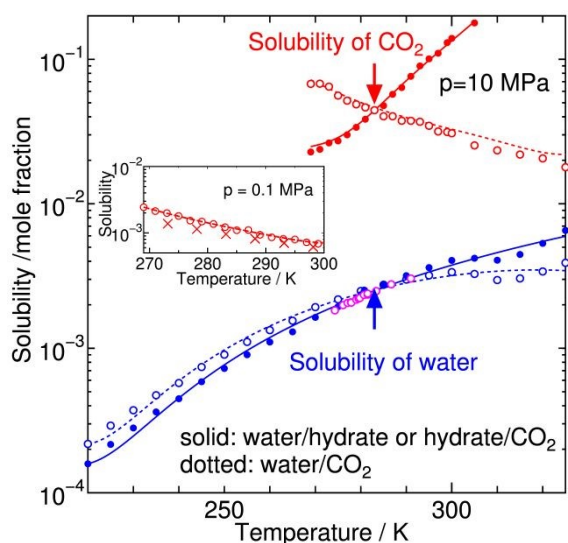


Fig. 3 Solubility of CO₂ in the aqueous solution (red) and that of water in the liquid CO₂ (blue) in the presence (solid line) and absence (dotted line) of CO₂ hydrate plotted against temperature at 10 MPa. The crossover of the coexistence curve is indicated by the arrow. Experimental values of the solubility of CO₂ at 0.1 MPa (cross) are compared to the theoretical ones (open circle and dotted line) in the inset. The magenta open circles are experimental values of the solubility of water at 10.1 MPa.²²

The solubility curves excluding the metastable regions are depicted in Fig. 4a. Agreement with experiments at 10.1 MPa is remarkably good as shown previously.^{17,22} The solubility of CO₂ in the absence of hydrate considerably depends on temperature. Formation of the hydrate not only changes the sign of the slope against temperature but also decreases the magnitude of the pressure dependence as seen in Fig. 4a.¹⁶ This trend is also observed in experimental measurements.⁵⁰ On the other hand, formation of hydrate alters to some extent the slope of the solubility curve of water against temperature.¹⁷ Compression leads to a higher solubility of water even in the presence of hydrate.^{22,51}



The standard deviations are calculated for the solubilities of water in CO₂ dividing a set of excess chemical potential values into 10 blocks. The error bars are shown in Fig. 4b. The standard deviations are fairly large at 100 MPa, which arises from the fact that the particle insertion is difficult for very condensed liquids. On the other hand, those at low pressures such as 10 MPa are small. Fig. S1 demonstrates that our MD simulations are sufficiently long to obtain statistically reliable results even near the critical point where the molar volume fluctuates to a large extent.

It is appropriate to compare our results with solubility curves obtained from fitting of accumulated experimental measurements.²³ This comparison is made in Fig. 4b. They are not in good agreement compared with those by Seo *et al.*²² However, it is noted that the individual measurements used for the fitting differ from each other. In fact, the solubility values at 285 K and 10 MPa vary among sources: approximately 2.8×10^{-3} in the present study and ref. 22, 2.0×10^{-3} in ref. 23, and 2.6×10^{-3} in ref. 52 where an equation of state was used to calculate the solubility. This inevitably leads to a fairly large standard deviation. Therefore, we must be satisfied with the situation that the general feature on the temperature and pressure dependence is at least semi-qualitatively reproduced. Another key issue in the fitting method is that the break in the solubility curve resulting from hydrate formation is effectively averaged out within a single smoothed curve.



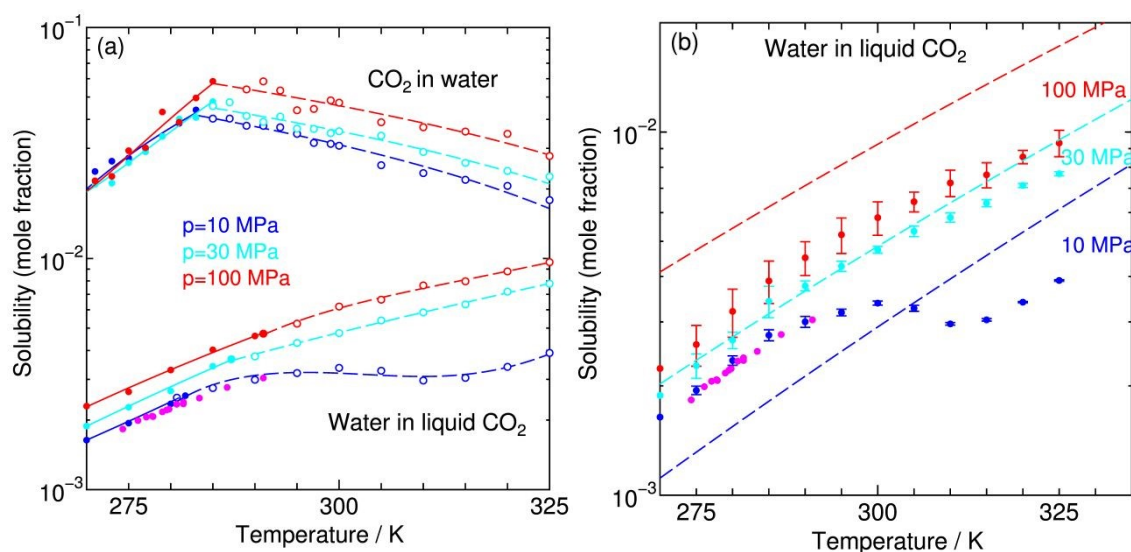


Fig. 4 (a) Solubilities of CO₂ in liquid water (upper) and water in liquid CO₂ (lower) at 10 (blue), 30 (cyan), and 100 (red) MPa in the presence (solid line) and absence (dashed line) of CO₂ hydrate plotted against temperature along with those by experimental measurement at 10.1 MPa (magenta circle).²² (b) Solubilities of water in liquid CO₂ with error bars at the same pressures along with those obtained from the fitting of experimental data (dashed line).²³

Nonstoichiometric properties of CO₂ hydrate

We examine some properties of hydrates which affect the solubility curve due to the non-stoichiometric nature characteristic to hydrates. Here, we compare our results for CO₂ hydrate with those for CH₄ hydrate. While CH₄ hydrate was examined in our previously^{14,15} using the OPLS model³⁹, those for CO₂ are newly obtained using the TraPPE model,³⁰ which is capable of reproducing the phase behaviour of pure CO₂ and therefore is advantageous to describe liquid CO₂ containing a tiny amount of water.

One of the intriguing properties representing the non-stoichiometry is the number of



water molecules per guest species called the hydration number. It has often been explored in studying the composition of hydrates.^{53,54} The pressure and temperature dependences of the hydration numbers along the three-phase coexistence curve are depicted for CO₂ and CH₄ hydrates in Fig. 5. The hydration number of CO₂ hydrate is generally large. It decreases with compression for CO₂ hydrate while it has a peak around 0.3 MPa for CH₄ hydrate. While the hydration number of CO₂ hydrate relies heavily on the condition (temperature or pressure), that of CH₄ hydrate is rather constant.⁵³ The three-phase coexistence pressure of CO₂ hydrate increases with temperature significantly around 280 K as shown in Fig. 1. A high pressure inevitably leads to encapsulation of the small cages. This results in the abrupt drop of hydration number in CO₂ hydrate shown in Fig. 5.

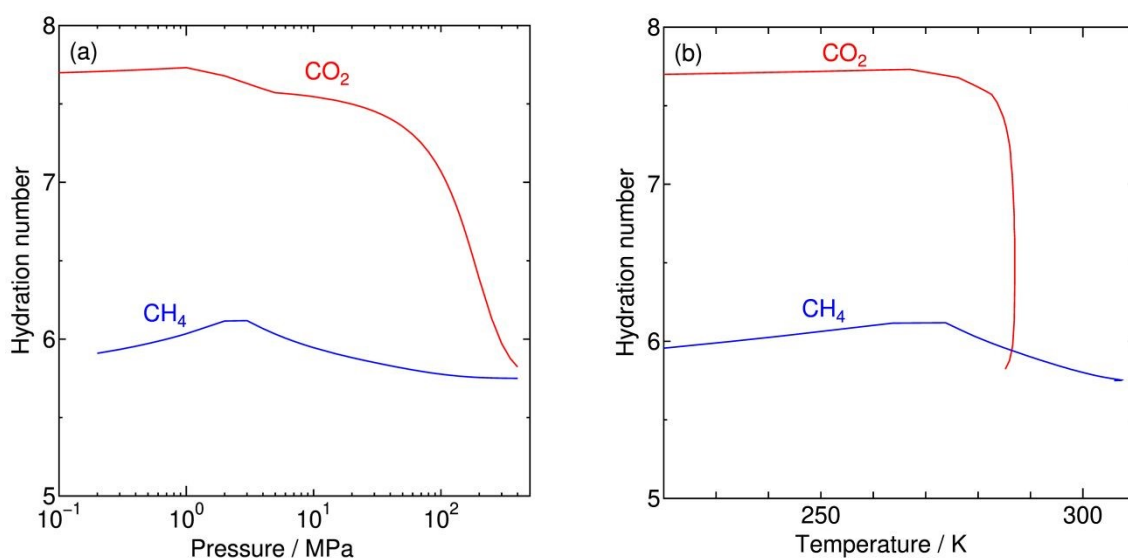


Fig. 5 Hydration numbers of (red) CO₂ and (blue) CH₄ hydrates along the three-phase coexistence curve as a function of (a) pressure and (b) temperature.

CO₂ hydrate forms spontaneously in the upper-left area of the dissociation curve in Fig. 1. When the pressure is fixed at a certain value, the hydrate is in equilibrium with either the aqueous phase or the liquid CO₂ phase depending on the composition. The aqueous



solution coexists on the water/hydrate boundary while the liquid CO₂ phase does on the hydrate/CO₂ boundary. These two sorts of the boundaries in temperature (T)-composition (y) space are depicted in Fig. 6a, and the corresponding results for CH₄ hydrates are shown in Fig. 6b. The size of the stable region of CO₂ hydrate in the T - y plane is comparable to that of CH₄ at low pressures. The shape of the region, however, differs from CH₄ and looks rather like C₂H₆ hydrate.^{13,18} The area increases with increasing pressure due to gradual encapsulation of CO₂ molecules in the small cages and therefore the extent of increase by compression is more pronounced than that for CH₄ hydrate. The composition of the enclosed region for CO₂ hydrate calculated with the TraPPE model^{14,16,30} is lower than that estimated from a different potential model.⁵⁵ The water/hydrate boundary curve has a break caused by the melting of ice except for 1 MPa. Formation of hydrate rather than ice is a practical concern for flow assurance in the high pressure region having the break.

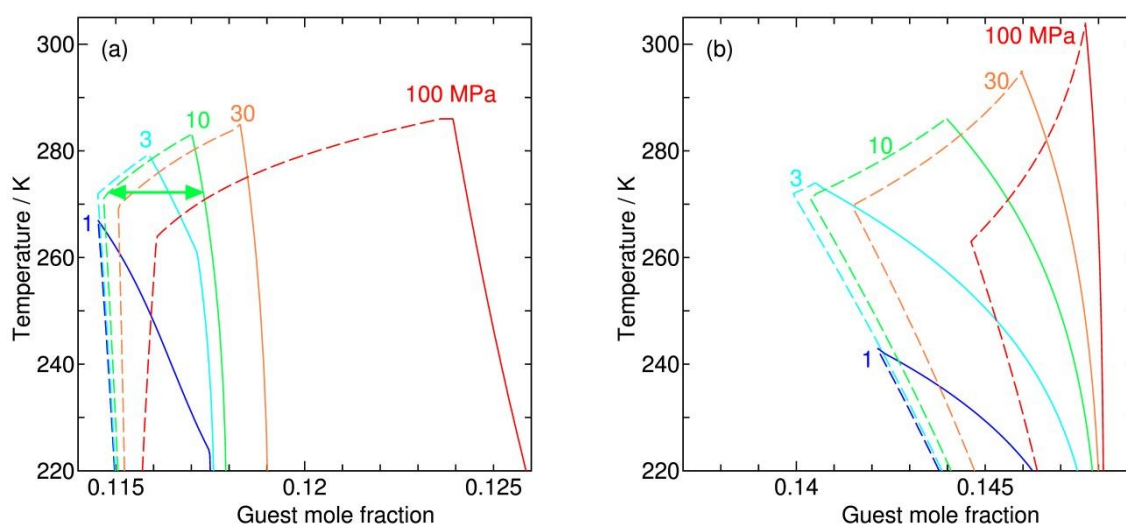


Fig. 6 Phase boundaries of (a) CO₂ and (b) CH₄ hydrates with the guest fluid (solid line) and water (dashed line) on the temperature-composition diagram at 1 (blue), 3 (cyan), 10 (green), 30 (orange) and 100 (red) MPa. The green bidirectional arrow denotes the composition range where the CO₂ hydrate alone is stable at 273 K and 10 MPa.



The phase diagram shown in Fig. 6a is helpful to explore the origin of the change in the solubility upon formation of CO₂ hydrate below the dissociation temperature as represented in Fig. 3. The chemical potential of water decreases in moving from the water/hydrate boundary to the hydrate/CO₂ boundary along the green arrow in Fig. 6, i.e., $\Delta\mu_w^{(hy)} < 0$ in eqn (5). The chemical potential of CO₂ decreases ($\Delta\mu_c^{(hy)} < 0$ in eqn (7)) in moving in the opposite direction. The magnitudes of the changes in the chemical potentials are constrained by the Gibbs-Duhem equation as

$$(1 - y_c) \frac{\partial \mu_w^{(hy)}}{\partial y_c} + y_c \frac{\partial \mu_c^{(hy)}}{\partial y_c} = 0. \quad (19)$$

which implies that $\left| \frac{\partial \mu_w^{(hy)}}{\partial y_c} \right|$ is smaller than $\left| \frac{\partial \mu_c^{(hy)}}{\partial y_c} \right|$ because y_c is smaller than 0.15 for CS-I hydrate ruling out the multiple occupancy of cages. This relation, together with eqn (8), explains why the change in the solubility of water upon formation of hydrate is smaller than that of CO₂. In fact, the difference in the chemical potentials between the two boundaries for CO₂, $|\Delta\mu_c^{(hy)}|$, is several times larger than that for water, $|\Delta\mu_w^{(hy)}|$, as tabulated in Table 2. The chemical potential difference plays a decisive role in determining the magnitude of the effect of hydrate formation on the solubility.

Table 2 Chemical potential differences between the two boundaries for CO₂, $\Delta\mu_c^{(hy)}$, and for water, $\Delta\mu_w^{(hy)}$, at 10 MPa.

T / K	$\Delta\mu_c^{(hy)} / \text{kJ mol}^{-1}$	$\Delta\mu_w^{(hy)} / \text{kJ mol}^{-1}$
273	-2.03	-0.32
277	-1.25	-0.22
281	-0.44	-0.11



The composition of hydrate is associated with partial filling of each cage. The occupancies for the individual cage types are calculated according to eqn (11). The occupancy substantially depends on the cage types, guest species, and thermodynamic conditions as depicted in Fig. 7. Compression and/or cooling enhance the occupancies. Those for the large cage in CO₂ hydrate at two pressures nearly overlap each other. The large cages are more preferentially occupied in both CO₂ and CH₄ hydrates although the magnitude of the preference is different from each other. While the large cages are almost fully occupied in CO₂ hydrate so as to lower the chemical potential of water according to eqn (10), the small cages are of little use to stabilise the hydrate. This is in sharp contrast to the stabilization mechanism of CH₄ hydrate where both the large and small cages contribute to decrease the chemical potential of water in the hydrate.

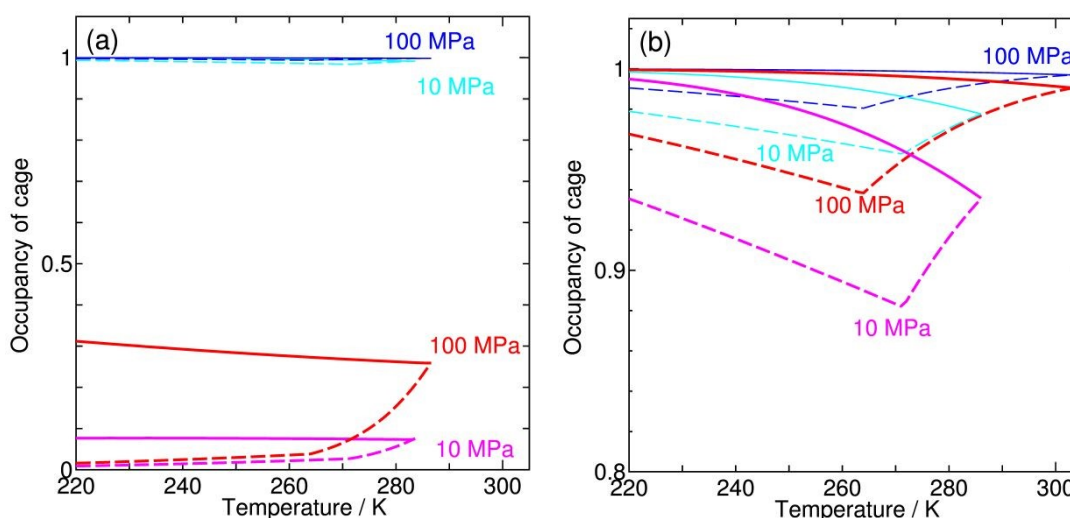


Fig. 7 Temperature dependence of cage occupancies for (a) CO₂ and (b) CH₄ hydrates at 10 (cyan: large, magenta: small) and 100 (blue: large, red: small) MPa. The solid and dashed lines represent the hydrate/guest and water/hydrate boundaries, respectively.

The preferential occupation of the large cages by CO₂ molecules is substantiated by the orientationally averaged interaction energy of a guest with the surrounding water



molecules, $\psi'_j(r)$, against the radial distance, r , from the cage center defined as

$$\psi'_j(r) = \frac{\iint \psi_j(\mathbf{R}, \boldsymbol{\Omega}) \delta(|\mathbf{R}| - r) d\mathbf{R} d\boldsymbol{\Omega}}{\iint \delta(|\mathbf{R}| - r) d\mathbf{R} d\boldsymbol{\Omega}}, \quad (20)$$

It is depicted in Fig. 8a along with the resultant temperature dependences of the free energies of cage occupation in Fig. 8b. It is evident that a CO₂ molecule in the small cage has a higher interaction energy than that in a large cage due to its large molecular size. This leads to a much higher free energy of cage occupation as shown in Fig. 8b. A CH₄ molecule in a small cage is stabilized by the surrounding water to a similar extent as that in large cage. Consequently, the difference in the free energy of occupation between them is small.

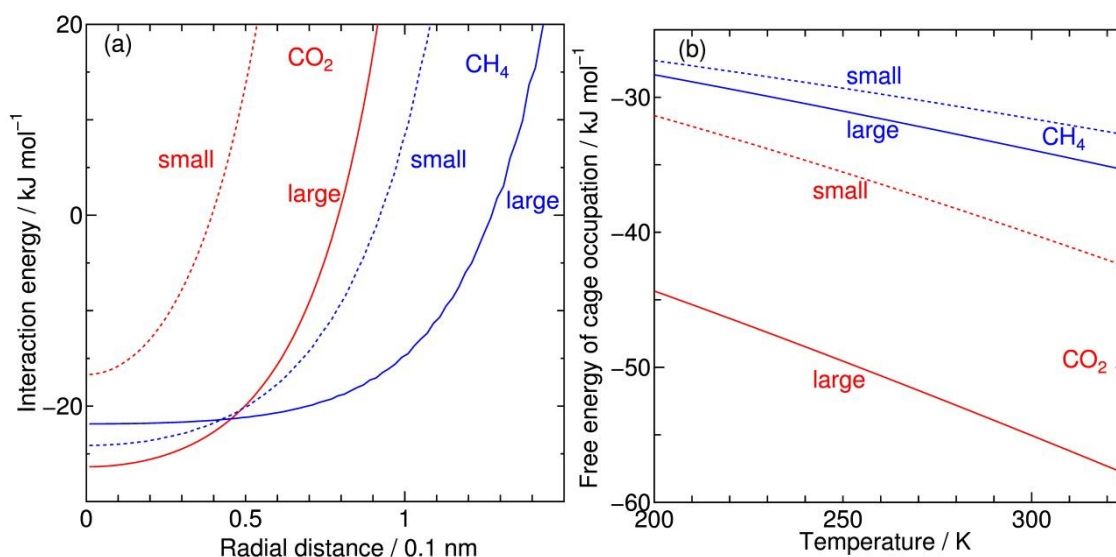


Fig. 8 (a) Orientationally averaged interaction energy of a guest with surrounding water molecules plotted against the radial distance from the cage center, (b) Free energies of cage occupation of (red) CO₂ and (blue) CH₄ for the (solid line) large and (dotted line) small cages.

Precipitation of CO₂ hydrate under rapid cooling or decompression

Our main concern is the phase behaviour of liquid CO₂ with an impurity of water,



which corresponds to the region near $z_c = 1$ in Fig. 2. The magnified temperature-composition diagram is depicted in Fig. 9. The diagram is divided into three regions, liquid (including gaseous) CO_2 with a small amount of dissolved water, liquid CO_2 coexisting with the hydrate (hydrate/ CO_2), and liquid CO_2 coexisting with the aqueous solution (water/ CO_2). The regions are separated by the dotted line corresponding to the dissociation temperature of the hydrate and by the solid line corresponding to the solubility of water. The phase diagram is also shown in Fig. S2 for each pressure.

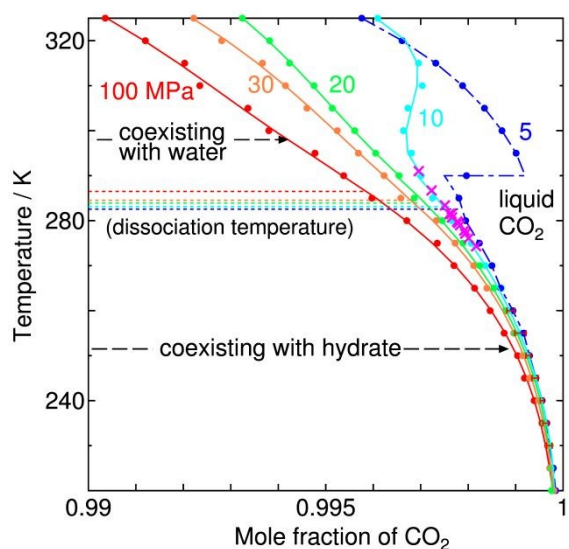


Fig. 9 Magnified phase diagram of the binary mixture of water and CO_2 for a region close to pure CO_2 at 5 (blue), 10 (cyan), 20 (green), 30 (orange), and 100 MPa (red). The stable region of fluid CO_2 is separated by the solid curve. Liquid CO_2 coexists with either the aqueous solution or CO_2 hydrate in the left region of each solid curve. Each dotted line indicates the dissociation temperature above which no hydrate is stable and the CO_2 fluid is in equilibrium with the aqueous solution. The blue dot-dash line depicts the interpolated solubility curve taking account of the breaks due to the vaporization of liquid CO_2 at 5 MPa. The magenta crosses denote the experimental solubilities at 10.1 MPa.²²



The liquid CO₂ phase is in equilibrium with the aqueous solution at higher temperatures in the left region separated by the solubility curve in Fig 9. The solubility of water in liquid CO₂, $z''_w = (1 - z''_c)$, decreases with decreasing temperature. Compression generally gives rise to a higher solubility of water. The curve at 10 MPa is nearly vertical around 310 K. This behaviour originates from the critical point of CO₂ (304.2 K and 7.38 MPa) around which the density changes harshly. At 5 MPa, CO₂ undergoes the phase transition from the liquid to gaseous state. This accompanies a sudden decline of the solubility as drawn in Fig. 9 in which two adjacent points are smoothly connected by the solid curve but the phase transition is represented by the dash-dot curve. The solubility of water in the gaseous CO₂ phase is the vapor pressure of the pure liquid water to a good approximation and therefore is expected to decrease by compression according to the present definition of the solubility given by eqn (3) through an increase in $\rho^{(k)}$.

The Gibbs energy difference between the reactants (water and CO₂) and the product (hydrate) plays an essential role in determining the rate of hydrate formation. It is also known as the thermodynamic driving force for formation of hydrate and has been calculated with available thermodynamic properties from MD simulations.^{37,38} We have shown that it can also be calculated in a relatively simple way from the chemical potentials, which are available from the method we developed.¹⁶ The Gibbs energy of formation in our definition is measured on a per water molecule (mole) basis reflecting the non-stoichiometric nature of hydrate. As stated above, we make a little rough approximation for the chemical potentials of water and CO₂ such that water in hydrate on the water/hydrate boundary has the same chemical potential of pure water although it contains a certain amount of CO₂, and the guest species in the hydrate on the hydrate/CO₂ has the same chemical potential of pure CO₂. The Gibbs energy of formation at a



composition of y_c is given as

$$\Delta G_f = \mu_w^{(hy)}(T,p,y_c) - \mu_w^0(T,p) + \frac{y_c}{1-y_c} [\mu_c^{(hy)}(T,p,y_c) - \mu_c^0(T,p)]. \quad (21)$$

This quantity converges to zero on approaching to the three-phase equilibrium. There are two extreme cases for the composition of the product hydrate, y_c . In the first one, we consider formation of the hydrate under a water-rich condition, i.e., on the water/hydrate boundary where the composition of the guest in the hydrate is y'_c . The Gibbs energy of formation is given by

$$\Delta G_f = \frac{y'_c}{1-y'_c} [\mu_c^{(hy)}(T,p,y'_c) - \mu_c^0(T,p)]. \quad (22)$$

This is plotted in Fig. 10 against temperature. In the second, the hydrate is assumed to be formed under a guest-rich condition, on the hydrate/guest boundary at a composition of y''_c . The Gibbs energy of formation is given by

$$\Delta G_f = \mu_w^{(hy)}(T,p,y''_c) - \mu_w^0(T,p). \quad (23)$$

This is also shown in Fig. 10. It differs only slightly from that according to eqn (22).

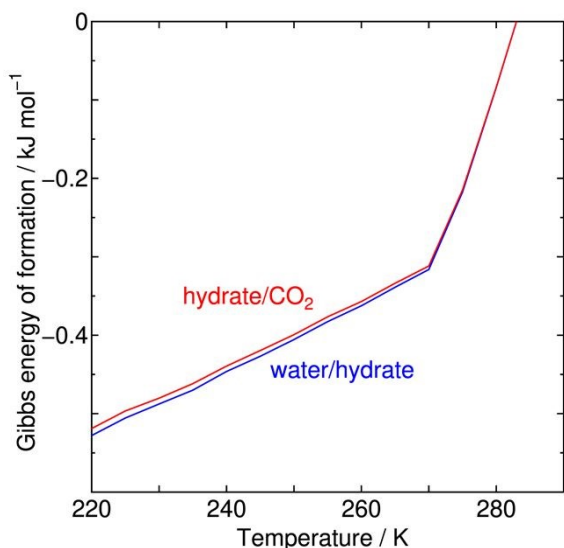


Fig. 10 Gibbs energy of formation of CO₂ hydrate against temperature at a pressure of 10 MPa on the hydrate/CO₂ (red) and water/hydrate (blue) boundaries.



Thus far, the initial state is chosen to be pure water and CO₂ at a given temperature and pressure. We may consider a different formation process in which the initial state is liquid CO₂ supersaturated with water prepared by a temperature drop. This process is schematically drawn in Fig. 11. The temperature is dropped vertically from a certain point on the phase boundary to a point below the dissociation temperature of CO₂ hydrate. Consequently, an excessive amount of water precipitates as a CO₂ hydrate.

The liquid CO₂ at the initial state contains a certain amount of saturated water whose density is ρ_w or equivalently composition of the corresponding solubility, z_c . Since $\mu_w^0(T, p)$ in eqn (23) should be replaced with $\mu_w^{(lq)}(T, p, z_c)$ in this process, the Gibbs energy of formation is calculated from $\mu_w^{(hy)}(T, p, y''_c) = \mu_w^{(lq)}(T, p, z''_c)$ as

$$\begin{aligned} \Delta G_f &= \mu_w^{(hy)}(T, p, y''_c) - \mu_w^{(lq)}(T, p, z_c) = \mu_w^{(lq)}(T, p, z''_c) - \mu_w^{(lq)}(T, p, z_c) \\ &= k_B T \ln \left(\frac{\rho''_w}{\rho_w} \right), \quad (24) \end{aligned}$$

where ρ''_w is the equilibrium density of water in liquid CO₂ coexisting with CO₂ hydrate at T and p .

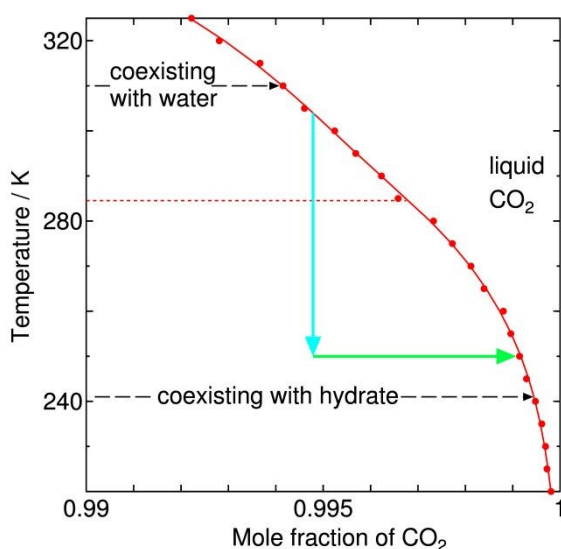


Fig. 11 Isobaric cooling in temperature-composition diagram. The red solid and dotted lines indicate the phase boundary of liquid CO₂ and the dissociation temperature of CO₂ hydrate. The temperature is dropped along the vertical line from a point on the red solid curve to an arbitrary temperature, T in eqn (24).

This Gibbs energy of formation, the sign of which is limited to negative, is depicted as a function of the degree of cooling in Fig. 12 for (a) the initial temperature from which liquid CO₂ undergoes rapid cooling and for (b) the final one to which it will be settled. It decreases as the degree of cooling or equivalently the supersaturation is intensified. In other words, supersaturation significantly induces formation of CO₂ hydrate to achieve the equilibrium between hydrate and liquid CO₂ at the final temperature. The Gibbs energy change is almost linear in both panels. A higher initial temperature requires a deeper cooling to have the same energy value as is seen in panel (a). CO₂ hydrate does not appear at 300 and 320 K at a pressure of 10 MPa and therefore the corresponding curves shift to the left side. The Gibbs energies for the various final temperatures seem to be laid on a common straight line passing through the origin in panel (b) under the fixed final temperature condition.

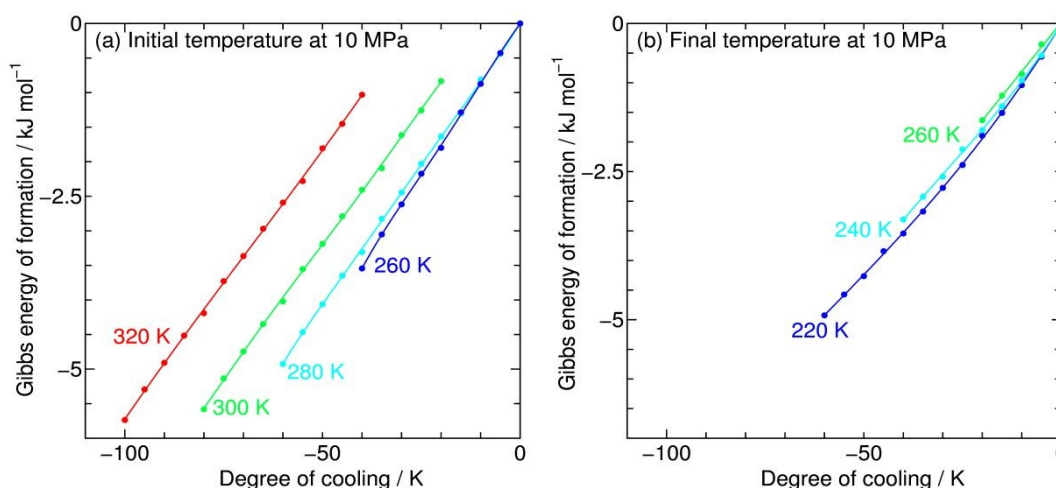


Fig. 12 Gibbs energy of formation of CO₂ hydrate plotted against the degree of cooling at 10 MPa for (a) four initial temperatures and (b) three final temperatures.

Another intriguing quantity from an industrial viewpoint is an amount of hydrate precipitated from liquid CO₂ supersaturated with water. Formation of hydrate incurs blockage of pipelines in liquid CO₂ transportation. The amount of hydrate from the one mole of liquid CO₂ is plotted in Fig. 13 as a function of temperature drop. Again, we examine it for either (a) the initial temperature from which liquid CO₂ is cooled down or (b) the final one to which it will be settled. As plotted in Fig. 13a, the amount of water increases simply with deepening the cooling but a relation between the amount and the initial temperature at a given degree of cooling is complicated. On the other hand, the amount simply decreases with decreasing the final temperature at a given degree of cooling as seen in Fig. 13b.

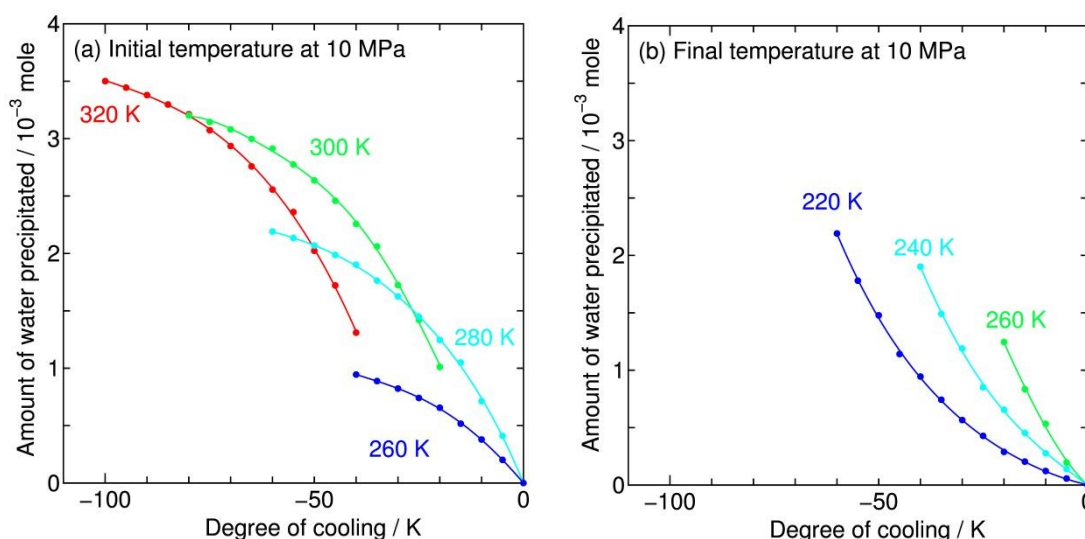


Fig. 13 Amount of water precipitated from one mole of liquid CO₂ as a hydrate at 10 MPa plotted against the degree of cooling for (a) four initial temperatures and (b) three final temperatures.



Next, we consider a pressure drop of liquid CO_2 . This may also happen in a pipeline going to downstream. Here, we assume the pressure drop takes place isothermally as drawn in Fig. 14. We calculate the amount of hydrate precipitated in this process in the same way as in the case of the temperature drop. The amount of precipitation due to the decompression is shown in Fig. 15. The amount is small compared with that of the cooling process even when the initial pressure is an order magnitude larger than the final pressure. As is expected from Fig. 9, it becomes larger with increasing temperature.

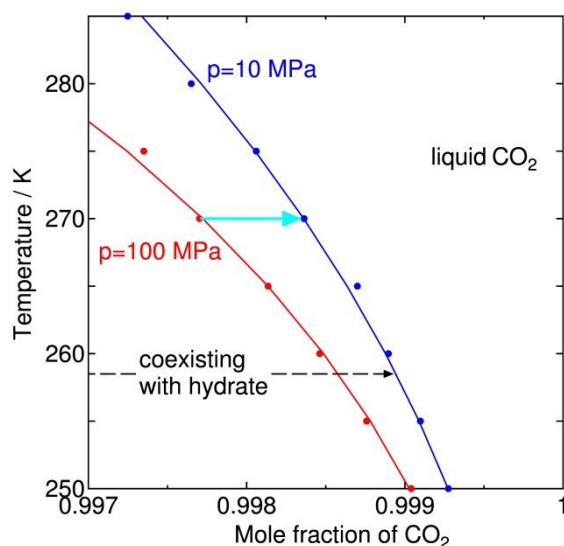


Fig. 14 Isothermal decompression in temperature-composition diagram. The red and blue solid lines indicate the phase boundaries of liquid CO_2 . The pressure drops along the horizontal line from an initial point on the red curve to the final point on the blue one.



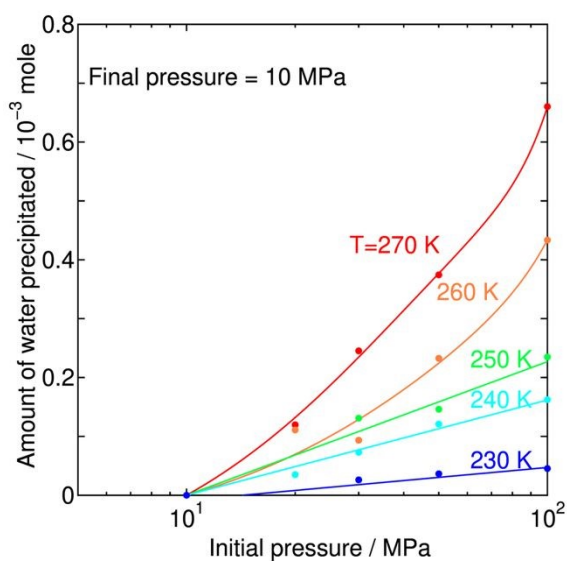


Fig. 15 Amount of water precipitated from one mole of liquid CO₂ as hydrate by rapid decompression to the final pressure of 10 MPa plotted against the initial pressure at 230 (blue), 240 (cyan), 250 (green), 260 (orange), and 270 K (red).

Conclusions

The solubility of water in liquid CO₂ is calculated using atomistic intermolecular potential models. Liquid CO₂ coexists with liquid water and CO₂ hydrate above and below the dissociation temperature of the hydrate, respectively. The solubility of water in liquid CO₂ increases with increasing temperature and compression enhances the solubility regardless of the presence or absence of hydrate.

Several properties of CO₂ hydrate are examined focusing on the water/hydrate and hydrate/CO₂ two-phase coexistences. Whereas CH₄ hydrate is stabilised by a moderate occupancy of large cages and the same degree of occupancy of small cages, the stability of CO₂ hydrate is mostly due to the preferential occupation of large cages.

CO₂ hydrate forms not only by the temperature drop but also by a pressure drop of liquid CO₂ containing water as an impurity. The amount is seemingly small but can pose



a risk of pipeline blockage. Another important factor for flow assurance is nucleation kinetics of CO₂ hydrate, but it is out of scope in the present study.

The temperature and pressure ranges differ for each operational condition. The solubility of water and the amount of precipitated hydrate are heavily dependent on temperature and pressure. Hence, the allowable content of water in liquid CO₂ may be set flexibly, avoiding overly conservative constraints. The Gibbs energy of formation and the associated properties in the present study are expected to provide a valuable insight into conditions for safe CO₂ transportation without hydrate formation.

Author contributions

Hideki Tanaka: conceptualization, methodology, investigation, interpretation, and writing original draft.

Masakazu Matsumoto: methodology, constructive discussions, writing review-editing, and funding acquisition.

Takuma Yagasaki: methodology, interpretation, constructive discussions, and writing review-editing.

Munetaka Takeuchi: constructive discussions, interpretation, and writing review-editing.

Yoshihito Mori: constructive discussions, interpretation, and writing review-editing.

Takumi Kono: constructive discussions, project administration, and funding acquisition.

Conflict of interest

The authors have no conflicts to disclose.

Data availability



The data that support the findings of this study are available from the corresponding author upon reasonable request. All relevant figures are included in the supplementary information.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. All relevant figures are included in the supplementary information.

