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A consistent and verifiable macroscopic model for the dissolution of liquid CO_2 in water under hydrate forming conditions

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Abstract

Direct injection of liquid CO_2 into the ocean has been proposed as one method to reduce the emission levels of CO_2 into the atmosphere. When liquid CO_2 is injected (normally as droplets) at ocean depths >500 m, a solid interfacial region between the CO_2 and the water is observed to form. This region consists of hydrate clathrates and hinders the rate of dissolution of CO_2. It is, therefore, expected to have a significant impact on the injection of liquid CO_2 into the ocean. Up until now, no consistent and predictive model for the shrinking of droplets of CO_2 under hydrate forming conditions has been proposed. This is because all models proposed to date have had too many unknowns. By computing rates of the physical and chemical processes in hydrates via molecular dynamics simulations, we have been able to determine independently some of these unknowns. We then propose the most reasonable model and use it to make independent predictions of the rates of mass transfer and thickness of the hydrate region. These predictions are compared to measurements, and implications to the rates of shrinkage of CO_2 droplets under varying flow conditions are discussed.

Keywords: CO_2 sequestration; Clathrate hydrate; Mass transfer

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Nomenclature

C_0	concentration of pure liquid CO_2
C_{H1}	concentration of CO_2 in a fully occupied hydrate
C_{H2}	concentration of CO_2 in hydrate at equilibrium
C_i	concentration of CO_2 at the water–hydrate interface
C_α	concentration of CO_2
$C_{CO_2,sat.}$	concentration of CO_2 at equilibrium
D	diameter of CO_2 droplet
D_H	diffusivity of CO_2 in clathrate hydrate phase
D_L	diffusivity of CO_2 in water
k_L	mass transfer coefficient at hydrate–water interface
P	pressure
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
t	time
t_{ss}	time to approach steady state
T	temperature
u	flow velocity
δ	hydrate film thickness
v	kinematic viscosity

1. Introduction

The viability of ocean storage as a green house gas mitigation option is a topic of ongoing research and debate [1]. The ocean represents a large potential sink for anthropogenic CO_2, and in fact, it has been predicted that eventually over 80% of anthropogenic CO_2 will end up in the ocean due to equilibrium effects [2]. Environmental impact and economics are the driving factors in determining the acceptability of ocean sequestration of CO_2. There have been several methods proposed for injecting CO_2 into the ocean. A leading candidate is to transport the CO_2 in a pipe to moderate ocean depths (from 1000 to 2000 m), where upon release as liquid droplets, it will form a plume and dissolve [3]. In this case, there is formation of clathrate hydrate (a crystalline solid that includes CO_2 molecules in cages formed by water molecules, see e.g., Ref. [4]) at the interface of CO_2 and sea-water, which impacts the dissolution of CO_2 in the ocean. In order to predict accurately and assess the ecological ramifications due to the proposed scheme, a multi-scale modeling and understanding of the CO_2 sequestration process is necessary, which include: (a) physico-chemical interactions of CO_2 and sea-water, and (b) the fate of the CO_2 hydrate and the CO_2 dissolved in sea-water.

Equilibrium properties of the CO_2/sea-water system have been well researched from an experimental standpoint [5–9]. In particular, the clathrate hydrate forming conditions ($T < 285$ K and $P > 4$ MPa) are well established. For a complete phase diagram see e.g., Ref. [7]. Several experiments have been performed under conditions mimicing the direct injection process and have attempted to measure the dissolution rate of CO_2 in sea-water for a variety of state conditions as well as flow conditions [10–22]. Under the direct injection conditions, the injected CO_2 is in the form of a liquid droplet and a thin spherical shell of CO_2 clathrate hydrate is observed to form around the CO_2 drop, separating it from the sea-water. In spite of the presence of the hydrate shell, there is mass transfer of CO_2 to the sea-water phase, and the diameter of the CO_2 drop is observed to decrease with time. The rate of decrease of the diameter is related to the CO_2 flux into the sea-water phase and can be related to the mass transfer coefficient, the equilibrium properties of the hydrate/sea-water interface and the ambient concentration of CO_2 in sea-water. However, these relations pre-suppose that a mechanism to transport the CO_2 molecules through the crystalline hydrate phase exists. Under steady state conditions, the flux of CO_2 through the hydrate equals that at the hydrate/water interface, resulting in a constant thickness of the hydrate film, while the diameter of the drop decreases linearly with time [10–22]. In an effort to make the above mass transfer scheme self-consistent, several researchers have proposed a variety of mechanisms for the transport of CO_2 through the hydrate phase [18,21–30]. The proposed mechanisms can be broadly categorized into three classes (for a review see Ref. [21]): (a) hydrate-in-suspension models (b) micro-perforated plate models and (c) permeable solid-plate models.

1.1. *Hydrate-in-suspension models*

The hydrate in suspension models [24–28] treat the hydrate phase as a colloidal suspension of tiny hydrate particles in the liquid CO_2/H_2O phase, rather than a crystalline material (the CO_2 transport mechanism through the hydrate then becomes a simple case of liquid phase diffusion). The assumption, however, is in direct contradiction to experimental results [31,32] that clearly establish the crystalline nature of the hydrate shell. Therefore, the predictive capability of such models is limited.

1.2. *Micro-perforated plate models*

The micro-perforated plate models [22,23] assume that the hydrate shell is not perfectly crystalline but is comprised of pores (or micro-perforations) that act as capillaries to transport CO_2/H_2O molecules. Within the framework of the micro-perforated plate models, the transport through the hydrate phase is assumed to be a pressure driven flow through the micro-perforations, the pressure difference being caused by the surface tension of the liquid phase that wets the hydrate. Aside from the complexity in verifying the porous nature of the hydrates by experimentally investigating the hydrate morphology, the micro-perforated plate models have too many unknown model parameters (porosity, diameter of the perforations, tortuosity and the hydrate shell thickness) and only one equation (the flux balance) relating them. In principle, one can argue that the thickness of the hydrate film can be independently measured by experiment and, therefore, is not an unknown model parameter. Nevertheless, a self-consistent transport model must be capable of predicting a quantity, such as hydrate film thickness, that can be compared to experiment. In any case, the utility value of the micro-perforated plate models is limited owing to the number of unknown model parameters.

1.3. Permeable solid-plate models

The permeable solid-plate models [18,30] assume that the transport of CO_2 molecules across the hydrate is simply that of diffusion of CO_2 molecules in the crystalline (or poly-crystalline) hydrate structure. However, these models were not pursued because the mechanism for the diffusion of the guest molecules through the hydrate was not known, and there was a prevalent consensus that the diffusivity of CO_2 molecules in hydrate crystals would be too small for such models to predict accurately the CO_2 flux and thickness of the hydrate film observed in the direct injection experiments. The estimate of diffusivity of CO_2 in the hydrate phase was not available from experimental or theoretical studies.

Recently, our group reported a theoretical study [33] using molecular simulations, in which a mechanism for the diffusion of CO_2 molecules in the hydrate phase was proposed. The outcome of the study was the estimate of D_H, the self-diffusion coefficient of the CO_2 molecules in the hydrate phase, to be 1.1×10^{-12} m^2/s at 273 K, a value that is three orders of magnitude smaller than typical liquid phase diffusivity, but three orders of magnitude larger than typical diffusion coefficients in solids. In this paper, the above estimate for D_H is used to provide a self-consistent model with a sound physical basis for the dissolution rate of CO_2 in water at steady state under direct injection conditions. It will be shown that our model accurately predicts the CO_2 flux and thickness of the hydrate film under a variety of flow conditions reported in the literature [10–22]. In Sections 2 and 3, we summarize the macroscopic aspects and the microscopic theory [33] on which our model is based. In Section 4, we compare the results of our model with the published experimental measurements and offer our conclusions.

2. Macroscopic model

The macroscopic transport mechanism is pictorially depicted in Fig. 1. A hydrate film of thickness δ separates the CO_2 drop of diameter D from the water phase. The hydrate film nucleates and covers the CO_2/water interface almost instantaneously (within the first few seconds of introduction of the drop [19,20]), therefore the nucleation process is expected to have a negligible effect on the mass transfer rate of CO_2, a process which occurs on a time scale of a few hours. The concentration of CO_2 in the drop is denoted by C_0, which corresponds to pure CO_2 and does not change with time, as the equilibrium concentration of water in liquid CO_2 is negligible (water mole fraction is 2×10^{-4} [6]). For this reason, the CO_2 phase is considered to be saturated with water, and hence, there is no driving force for the transport of water into the CO_2 phase. However, there exists a driving force for the transport of CO_2 into the water phase as long as the ambient concentration of CO_2 in water, C_α, is less than the equilibrium concentration, $C_{CO_2,sat}$. The interface between the outer surface of the hydrate shell and water is assumed to be at equilibrium (a good assumption considering that the hydrate continuously dissolves and reforms at this interface [21]), and therefore, the concentration of CO_2 in water at the interface, C_i, is equal to the equilibrium concentration of CO_2 in water $C_{CO_2,sat}$. It should be noted that the equilibrium concentration of CO_2 in water, $C_{CO_2,sat}$, in the presence of hydrate is less by approximately a factor of two than a hypothetical extrapolated value at the same conditions, but in the absence of hydrate. Therefore,

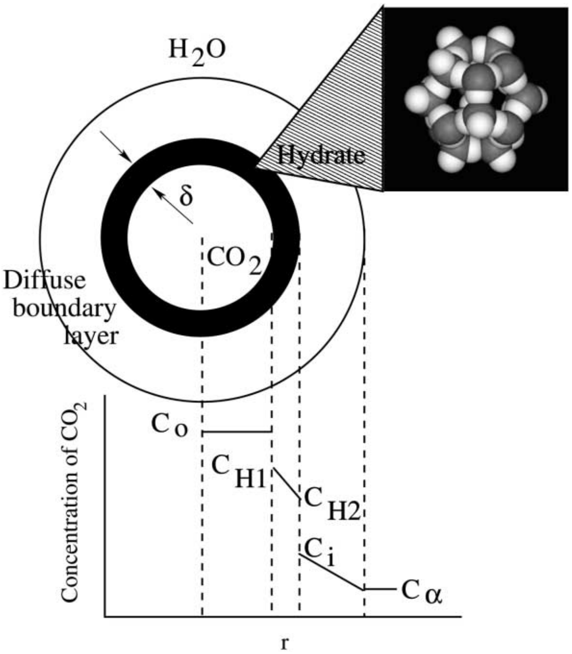

Fig. 1. Representation of the macroscopic transport model. The thickness of the hydrate film is δ. The different concentrations are C_0 = concentration of liquid CO_2; C_{H1} = concentration of CO_2 in a fully occupied hydrate; C_{H2} = concentration of CO_2 in hydrate at equilibrium; C_i = equilibrium concentration of CO_2 in water in the presence of hydrate; C_α = ambient concentration of CO_2 in water.

$C_{CO_2,sat}$ is a strong function of temperature near the hydrate forming temperature [9]. The flux of CO_2 is then given by the equation

$$CO_2 \text{ flux in water} = k_L(C_i - C_\alpha) \tag{1}$$

where k_L is the mass transfer coefficient at the hydrate–water interface. Under conditions where there is no net flow around the drop (a neutrally buoyant situation or when the drop is held fixed, e.g. in a Du-Nouy ring, and the flow turned off), $k_L = 2D_L/D$, which corresponds to a value of Sherwood number, $Sh = k_L D/D_L = 2$. D_L is the liquid phase diffusivity of CO_2 in water. Under flow conditions (a water velocity of u m/s), k_L is estimated using the equation [9]

$$Sh = 2 + 0.5 \times Re^{1/2} \times Sc^{1/3} \tag{2}$$

where $Re = uD/v$ and $Sc = v/D_L$ are the Reynolds number and Schmidt numbers respectively, and v is the kinematic viscosity of liquid water. The rate of decrease of diameter, dD/dt is then given by

$$\frac{dD}{dt} = 2 \times C_0 \times CO_2 \text{ flux in water} \tag{3}$$

The flux of CO_2 in the hydrate phase, which is the main focus of this paper, is given by the equation

$$\mathrm{CO_2 \text{ flux in hydrate}} = \frac{D_H}{\delta}(C_{H1} - C_{H2}) \tag{4}$$

where C_{H1} is the concentration of CO_2 in the hydrate region near the liquid CO_2 phase and C_{H2} is the concentration of CO_2 in the hydrate region near the water phase. C_{H1} corresponds to the CO_2 concentration in a fully occupied hydrate (all the cages occupied by CO_2 molecules). Since the interface of CO_2 and hydrate is saturated with respect to CO_2, any unoccupied cage near that interface is expected to be filled instantaneously. C_{H2} corresponds to the equilibrium concentration of CO_2 in the hydrate, determined by the chemical potential of the guest molecule and temperature. C_{H2} is related to the percentage of occupancy of the guest molecules in the hydrate cages and is obtained from neutron diffraction experiments. For the case of CO_2 hydrate, we use the published results of Henning et al. [34] to calculate C_{H2}. According to their study, at a temperature of 273 K, 50–70% of small cages and about 90% of large cages are occupied by CO_2 molecules in the hydrate.

For a given temperature, pressure and flow condition, k_L is calculated using Eq. (2), and the flux of CO_2 is calculated using Eq. (1). At steady state, the flux of CO_2 through the hydrate is equal to that at the interface. Therefore, we predict the steady state thickness δ using Eq. (4). We obtain the value of D_H that goes into Eq. (4) from molecular simulations [33], as outlined in the following Section 3.

3. Microscopic diffusion model

In a molecular dynamics study, Demurov et al. [33] showed that the diffusion of CO_2 molecules in an ideal clathrate lattice with 95% CO_2 occupancy was negligible in a time scale of 1 ns. However, they observed hopping of CO_2 molecules in the presence of a water vacancy in the lattice. Using a Monte Carlo approach, the authors [33] then quantified their proposed hopping mechanism by (a) calculating the concentration of water vacancies in the clathrate lattice by calculating the free energy of defect formation and (b) calculating the free energy barrier for the hopping of a CO_2 molecule between different cages. They calculated the diffusion coefficient of CO_2 in the hydrate at 273 K to be 1.1×10^{-12} m^2/s. We use this estimate for D_H, in Eq. (4) to calculate the thickness of the hydrate film, as outlined in Section 2.

4. Results and discussion

The experimental results under different state conditions and flow conditions [10–22] are summarized in Table 1. In Table 2, we compare the results of our model to the results obtained in the experiments. The thickness of the hydrate film was measured for only a few state and flow conditions [35–37] and is a strong function of the flow conditions. For experiments in which no net flow was present, the hydrate film thickness at steady state was of the order of a few tens of microns. Under flow conditions (water velocity of a few cm/s), the steady state film thickness reduces to a tenth of a micron. The difference springs from the strong dependence of k_L on flow (see Eq. (2)). The results in Table 2 indicate that our model predicts the right order of magnitude

Table 1
Experimental measurements of CO_2 dissolution rate

Experimental group, Ref.	P (MPa)	T (K)	Water velocity (cm/s)	Initial diameter (mm)	Final diameter (mm)	Diameter shrinkage rate (m/s)	Hydrate shell formed?
[10]	5.5	283–293	0	25–30	<10	3.9×10^{-7}	Yes
						8.5×10^{-7}	No
[11]	28&35	280	0	13–15	3	5×10^{-7}	Yes
[12]	30	274–285	2–3	6–8	0	$5–15 \times 10^{-7}$	Yes
						1.6×10^{-6}	No
[17]	30	275	3	15	NA	8×10^{-7}	Yes
						1.6×10^{-6}	No
[13]	4.2–8.3	277–279	3	15	NA	8×10^{-6}	Yes
[22]	9.8–39.2	276–286	1.5–7	9	7	$4–19 \times 10^{-7}$	Yes
						$1.3–3 \times 10^{-6}$	No
[18]	10–15	278	0	5–10	NA	$1.2–5.6 \times 10^{-8}$	Yes
[20]	5.5	278	1–2.5	2	1	$1–3 \times 10^{-8}$	Yes

Table 2
Comparison between model and experimental results

Flux, Ref.	δ, Ref.	Flow/no flow	$\delta/10^{-6}$ m expt.	$\delta/10^{-6}$ m model	dD/dt m/s expt.	dD/dt m/s model
[10]	[35]	No flow	17	25	4.0×10^{-7}	2.0×10^{-8}
	[36]		32			
[11]		No flow		7	5×10^{-7}	5×10^{-8}
[12]		Flow		0.15	1.5×10^{-6}	2×10^{-6}
[17]		Flow		0.25	1.6×10^{-6}	1×10^{-6}
[13]		Flow		0.22	8×10^{-6}	1×10^{-6}
[22]	[37]	Flow	0.43	0.21	1.9×10^{-6}	1.9×10^{-6}
[18]		No flow		600	1.2×10^{-8}	2×10^{-9}
[20]		Flow		0.12	3×10^{-6}	3×10^{-6}
[19]	[19]	No flow	50	21	5×10^{-7}	2×10^{-8}

for the thickness of the hydrate film under different flow conditions. Our model also predicts the rate of shrinkage of the CO_2 drop (dD/dt) very accurately for conditions in which there is net flow present. However, there is a systematic one order of magnitude difference in the values of dD/dt between the results of our model and the experiments, when there is no net flow.

It should be recognized that the source of the difference in the shrinkage rate between model and experiment is in the value of k_L. In what follows, we offer a few possible explanations for this discrepancy: (1) A small flow of 0.3 cm/s causes a factor of 10 increase in the value of k_L. Therefore any small disturbance in the experimental cell leads to an increased rate of mass transfer. (2) Our model gives the shrinkage rate and the thickness of the hydrate film at steady state. All of the experiments assume that steady state is achieved almost immediately. However, the approach to steady state is governed by the equations

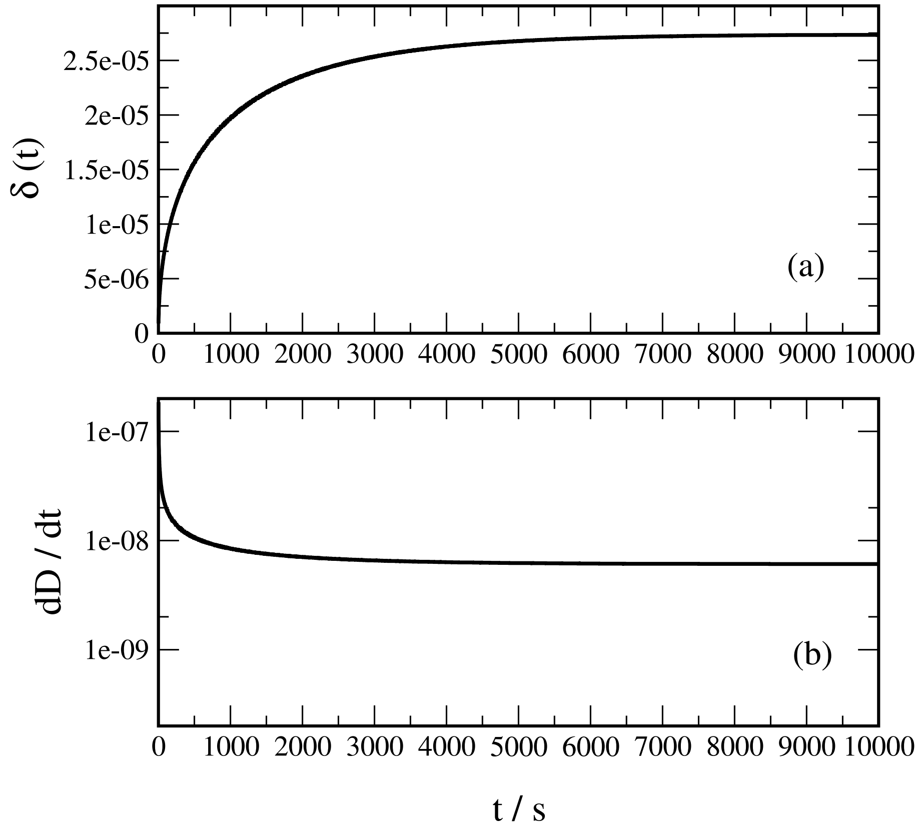

Fig. 2. Approach to steady state for a droplet of initial diameter, $D = 30$ mm, at $T = 278$ K, $P = 5.5$ MPa, under zero flow: (a) showing $\delta(t)$, (b) showing $\mathrm{d}D/\mathrm{d}t$. The time taken to reach steady state, t_{ss} is $\approx$1.5 h.

$$C_{\mathrm{H1}}\frac{\mathrm{d}\delta(t)}{\mathrm{d}t} = \frac{D_{\mathrm{H}}}{\delta(t)}(C_{\mathrm{H1}} - C_{\mathrm{H2}}) - k_{\mathrm{L}}(C_{\mathrm{i}} - C_{\alpha}) \tag{5}$$

$$\frac{\mathrm{d}D}{\mathrm{d}t} = -\frac{2D_{\mathrm{H}}}{C_0\delta(t)}(C_{\mathrm{H1}} - C_{\mathrm{H2}}) \tag{6}$$

Eqs. (5) and (6) were solved numerically under typical experimental conditions [10], $T = 278$ K, $P = 5.5$ MPa, droplet diameter $D = 30$ mm and zero net flow, and the results are plotted in Fig. 2. It is clear from Fig. 2 that the time taken to approach steady state, t_{ss}, is $\simeq$1.5 h. [1] In the experiments performed under no flow conditions, the total time over which data was collected was about 5 h with no time allocated for equilibration. During the equilibration process, the rate of decrease of diameter of the CO_2 drop, $\mathrm{d}D/\mathrm{d}t$ is 1–10 times larger than the steady state value (see Fig. 2(b)), although the CO_2 flux at the interface is equal to the steady state flux. The excess CO_2 goes to make up the expanding hydrate film. Since the equilibration process is not taken into

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[1] Solving the same equations for a flow velocity of 1 cm/s yields a value of $t_{\mathrm{ss}} \approx 2$ min.

account in the experimental results, the experiments over predict the flux and hence the shrinkage rate by up to a factor of 10. This effect could account for the discrepancy between the experiments and the model. In summary, our model together with our computed D_H [33], provides a reasonably good estimate of the hydrate film thickness and the CO_2 flux under steady state conditions. It should be noted that the close agreement between the model and experiments goes to validate the diffusion mechanism proposed by Demurov et al. [33]. Other possible defect structures, viz. grain boundaries and dislocations, could also affect diffusion in the hydrate layer. Our results indicate, however, that such effects may be negligibly small compared to the water vacancy and CO_2 hopping mechanism.

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