Kinetics of convective crystal dissolution and melting, with applications to methane hydrate dissolution and dissociation in seawater

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Abstract

Large quantities of methane hydrate are present in marine sediment. When methane hydrate is exposed or released to seawater, it dissolves in seawater or dissociates into methane gas and water. There was some confusion in the literature about the kinetics of these processes. It is critical to realize that dissolution and dissociation are two different processes. Dissolution is due to instability in the presence of seawater (similar to dissolution of NaCl in water) and is controlled by mass transfer. Dissociation is due to inherent instability (similar to melting of ice) with or without water (although presence of warm water may increase the dissociation rate). Dissociation of methane hydrate into gas and water is similar to ice melting and is controlled by heat transfer. Hence dissolution is relatively slow and dissociation is rapid. In this work, we extend previous theory on convective crystal dissolution and melting to greater Reynolds numbers. We carry out laboratory experiments on the dissolution and descent of NaCl, KCl, NaBr and KBr in water to verify the applicability of our theory. We then apply our models as well as previous ones to estimate methane hydrate dissolution and dissociation rates for several cases, including dissolution of exposed methane hydrate floor, dissociation of hydrate as it rises through seawater. The results show: (i) convective dissolution rate of exposed hydrate floor is of the order 0.07 m/yr; (ii) convective dissolution rate of a rising hydrate crystal is 0.2–0.3 μm/s and a crystal of 5 mm radius is able to survive the rise through an 1800 m seawater column; and (iii) convective dissociation rate is high and depends on the difference between the ambient water temperature and the equilibrium dissociation temperature of hydrate. Starting from a depth when hydrate just reaches dissociation instability, a hydrate sphere of 5 mm radius would survive only a 47 m water column. Because hydrate is unstable in the surface ocean and would undergo rapid dissociation, only very large hydrate chunks (greater than about 0.09 m radius) would be able to survive a 530 m surface water column.

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Keywords: Sherwood number; crystal dissolution; methane hydrate dissociation

Notation list

a Crystal radius
C Concentration (in mol/l) of the principal component of the dissolving crystal
Cp, Drag coefficient
 ρ, Heat capacity
 D, Diffusivity of the dissolving component in seawater (m²/s)
 g, Acceleration due to the Earth’s gravity (9.8 m/s²)
 h, Survival distance of a dissolving crystal
 k, Heat conductivity of water (0.54 W/m/K)
 L, Latent heat for crystal melting or dissolution
 l, Length scale
 Nu, Nusselt number (can be simplified to 2α/δ)
 P, Pressure
 Pe, Compositional Peclet number (=2α/δ)
 Pe, Thermal Peclet number (=2α/κ)
 Re, Reynolds number (=2α/μ)
 S, Solubility (kg of solute per 100 kg of water)
 Sc, Schmidt number (=μ(ρL/D)=Pe/Re)
 Sh, Sherwood number (can be simplified to 2α/δ)
 T, Temperature (in K)
 t, Time, or survival time of dissolving crystals
 u, Velocity of crystal relative to seawater
 V, Dissolution rate
 Xa, Dissolution distance
 α, The parameter α is related to β through
 β, (CA−CS)/CSwhere C_s is the concentration in the solid
 Concept, C_s is the concentration in the starting water,
 C_s is in mol/l)
 β, ρ_v(T_s−T)/[ρ_v(C_s−C_s)+ρ_sL] where T_s is the temperature
 in seawater far away from the interface, T is the temperature
 in crystal far away from the interface
 δ, Average compositional boundary layer thickness
 δ, Average thermal boundary layer thickness
 κ, Heat diffusivity of water (1.26×10⁻⁵ m²/s)
 λ, Ostwald solubility coefficient (=CS/Bubble, where C is in
 mol/l)
 μ, Viscosity (Pa s)
 ρ, Density (kg/m³)
 ρ_l, Liquid density (kg/m³)
 Δρ, Density difference (kg/m³)

1. Introduction

Huge quantities of methane are stored in marine sediment in the form of methane hydrate, methane bubbles, and dissolved methane in pore water [1-3]. Various processes and conditions can lead to the release of methane hydrate into ocean water. For example, methane hydrate may be exposed onto the ocean floor, or released into seawater due to disturbance of marine sediment or oceanographic changes, such as methane bursting, landslide, faulting, or a rise in ocean bottom water temperature. Once hydrate is exposed to seawater, it becomes unstable with respect to either dissolution or dissociation. How long would an exposed layer of massive hydrate survive? How long would a piece of hydrate survive as it buoyantly rises through seawater? Would a piece of hydrate be able to survive the whole ocean column and reach the atmosphere? Would methane in hydrate dissolve in seawater or vent into the atmosphere? In this report, we investigate the kinetics and dynamics of the unstable hydrate decomposing to methane and water.

Methane can exist in the marine environment as hydrate, free gas or dissolved species in water. In order to understand the kinetics, it is necessary to first understand the stability of methane phases in the marine environment. Fig. 1 is a phase diagram of the CH₄-H₂O system at 4°C. The pressure to stabilize methane hydrate is 4.31 MPa, calculated from [27]. The solubility of CH₄ in water (line connecting solid dots) as a function of P is calculated from [28] and is limited by hydrate formation above 4.31 MPa. The solubility of CH₄ in water is too low to be clearly seen (see Fig. 2 for the solubilities).

Fig. 1. A calculated phase diagram of CH₄-H₂O at 4°C. The pressure to stabilize methane hydrate is 4.31 MPa, calculated from [27]. The solubility of CH₄ in water (line connecting solid dots) as a function of P is calculated from [28] and is limited by hydrate formation above 4.31 MPa. The solubility of CH₄ in water is too low to be clearly seen (see Fig. 2 for the solubilities).
given geotherm, hydrate is a stable phase (as long as CH₄ concentration is high) from 537 m depth to 3225 m depth (450 m below seafloor). At water depths shallower than 537 m, or at sediment depths greater than 450 m, methane hydrate is not a stable phase anymore, and would dissociate into methane and water.

For other locations, the corresponding phase diagram can be similarly constructed and is in general different because the temperature–depth profile depends on location. For example, if the seafloor depth is only 400 m and other conditions are the same, there would be no hydrate stability field. The phase diagram along a geotherm (such as that in Fig. 2) is essential in understanding the distribution of methane hydrate and gas in sediment, as well as the kinetic processes.

To understand the kinetics of heterogeneous reactions involving methane hydrate, it is necessary to distinguish different reaction regimes because the kinetic controls are very different. The different reaction regimes are introduced here, and some terms are defined below (also along the phase boundaries in Fig. 2) for convenience of reference. Methane hydrate instability can be either by dissolution into water without formation of gas bubbles, or by dissociation into CH₄ gas phase (bubbles) and water. Dissolution occurs when methane hydrate is inherently stable at the P–T conditions (e.g., when no water is present) but is undersaturated in seawater (similar to NaCl or CaSO₄·2H₂O dissolution in water). Because this instability is due to the presence of an external phase (seawater), it may be called external instability. The opposite process to dissolution is methane hydrate precipitation when dissolved CH₄ concentration in water is oversaturated with respect to hydrate.

Dissociation occurs when methane hydrate is inherently unstable at the P–T conditions (similar to ice melting). (Methane hydrate dissociation into gas and ice is not similar to melting, can be slow, and will not be discussed in this work.) Dissociation does not require the presence of water, although the rate may depend on whether water is present. Because in this case the phase is unstable regardless of external phases, this instability may be called inherent instability. The opposite process is condensation of CH₄ gas and liquid water to hydrate.

The kinetic control for dissolution is mass transfer and that for dissociation is heat transfer. Because the heat transfer rate is much greater than that of mass transfer, dissociation is expected to be much more rapid than dissolution.

Both dissolution and dissociation are encountered in the ocean environment (Fig. 2). Some authors confuse dissolution and dissociation and wonder why massive gas hydrate would not sublimate and dissociate when it comes into contact with deep water [5]. As shown in Fig. 2, in deep water (> 537 m depth), methane hydrate is inherently stable but externally unstable, and would undergo dissolution (instead of dissociation). Be-
cause dissolution is relatively slow, massive hydrate on the ocean floor may survive for many years. On the other hand, dissociation is rapid. Hence hydrate reaching shallow water (e.g., ≤ 537 m depth in Fig. 2) is expected to disappear rapidly. Dissolution and dissociation rates will be quantified in this work. In the following sections, we first review theories of crystal dissolution and melting (dissociation) under various conditions. Then we extend previous theoretical analyses to greater Reynolds numbers. We then carry out experiments to verify our new theories. We finally apply previous and our new theories to calculate methane hydrate dissolution and dissociation rates in seawater for several cases. The behavior of methane bubbles will be discussed in a future contribution.

2. General considerations and review of crystal dissolution in liquid

Crystal dissolution in a liquid requires both mass transfer (which includes diffusive and convective mass transfer) and interface reaction [6–15]. That is, the crystal dissolution rate may be controlled by either interface reaction, or mass transfer, or a combination of the two. When mass transfer controls the dissolution rate, i.e., when mass transfer is slow and interface reaction is rapid, there is a concentration gradient in the liquid (dashed curve in Fig. 3), and the interface liquid is roughly at equilibrium with the crystal, with very small undersaturation driving the dissolution. In this case, stirring the solution would increase the dissolution rate. When interface reaction controls the dissolution rate, i.e., when interface reaction rate is slow compared to mass transfer, the concentration gradient in the liquid is zero and the interface is undersaturated (solid horizontal line in Fig. 3). In this case, stirring the solution would not increase the dissolution rate. When both processes control the dissolution rate, the concentration profile would be between the dashed curve and the solid line in Fig. 3.

Because diffusion coefficients of different solute species in water do not vary greatly (≈ 10^{-9} m^2/s [16]), whether the dissolution of a crystal in water is controlled by interface reaction or by mass transfer is primarily determined by the interface reaction rate, which is primarily controlled by bond strength of the crystal. If the bonds in the crystal are weak and hence easy to break, then interface reaction rate would be high, and dissolution would be controlled by mass transfer. If the bonds are strong and hence difficult to break, then interface reaction rate would be low and dissolution would be controlled by the interface reaction rate. Since ice melting is controlled by heat transfer (e.g., [17]), it is expected that methane hydrate dissociation is also controlled by heat transfer, and hence dissolution (which is much slower than dissociation) is controlled by mass transfer.

2.1. Some dimensionless numbers

Some dimensionless numbers that are necessary for the theoretical development in this paper are summarized here.

The Reynolds number (Re) is defined as:

\[ \text{Re} = \frac{(2a)u \rho_f \gamma}{\mu} \]  

(1)

where \( a \) is the radius of the dissolving crystal (or effective radius for a nonspherical crystal), \( u \) is the
ascent or descent velocity of the crystal, $\rho_f$ is the density of the fluid (water or seawater in this study), and $\mu$ is the viscosity of the fluid. The Notation list explains the variables and parameters. The Rayleigh number is defined as:

$$\text{Ra} = \frac{8g\alpha^4|\Delta\rho|}{\mu D^2}$$  \hspace{1cm} (2)$$

where $g$ is acceleration due to Earth’s gravity, $|\Delta\rho|$ is the absolute density difference between far-field liquid and the gravitationally unstable liquid at the crystal–liquid interface, and $D$ is the diffusivity of the solute in the liquid.

The compositional Peclet number ($P_{ec}$), characterizing the relative importance of flow versus diffusion, is defined as:

$$P_{ec} = 2au/D$$  \hspace{1cm} (3)$$

The thermal Peclet number ($P_{et}$), characterizing the relative importance of flow versus heat conduction, is defined as:

$$P_{et} = 2au/\kappa$$  \hspace{1cm} (4)$$

where $\kappa$ is the heat diffusivity.

The Schmidt number ($Sc$) is defined as:

$$Sc = (\mu/\rho_f)/D \equiv Pe/Re$$  \hspace{1cm} (5)$$

2.2. Dissolution rates under various conditions

Mass transfer can be accomplished by either diffusion or convection (and advection). When mass transfer is by diffusion only (i.e., when convection is negligible), the dissolution distance can be modeled as follows [9,18]:

$$X_{\text{dis}} = 2\alpha\sqrt{Dt}$$  \hspace{1cm} (6)$$

where $X_{\text{dis}}$ is the dissolution distance, $t$ is the time, and $\alpha$ is solved from the following equation:

$$\sqrt{\pi}ae^{a^2}\text{erfc}(-a) = \beta_c$$  \hspace{1cm} (7)$$

where $\text{erfc}$ is the complementary error function, and $\beta_c$ is defined as:

$$\beta_c = (C_{\text{sat}}-C_w)/(C_{\text{crystal}}-C_{\text{sat}})$$  \hspace{1cm} (8)$$

where $C_{\text{sat}}$ is the concentration of the solute (e.g., CH$_4$ for methane hydrate) at the interface liquid at saturation, $C_w$ is the solute concentration in liquid far away from the crystal dissolution surface (if it is much smaller than $C_{\text{sat}}$, $C_w$ may be taken as zero), and $C_{\text{crystal}}$ is the solute concentration in the crystal to be dissolved; all concentrations are in mol/l.

The rate of dissolution ($V$) is:

$$V = -\frac{da}{dt} = dX_{\text{dis}}/dt = \alpha\sqrt{D/t}$$  \hspace{1cm} (9)$$

where $a$ is thickness or radius of the crystal.

In addition to diffusive dissolution, crystal dissolution may be aided by convection. Convection may arise due to various kinds of buoyancy instability (free convection, or natural convection), or due to motion of the crystal relative to the far-field liquid (forced convection) [15]. Convective dissolution of a solid floor or roof under free convection has been investigated [11]. Convective dissolution of a solid floor under forced convection due to fluid flow over it can be solved similar to heat transfer [19], leading to the following dissolution rate at high Re:

$$V = 0.03\beta_c D^{1/3}u^{4/5}(\mu/\rho_f)^{-7/15}l^{-1/5}$$  \hspace{1cm} (10)$$

where $l$ is the length scale of the system.

Convective dissolution of a crystal freely (buoyantly) rising or falling through a liquid has been investigated by Kerr [12]. His analysis is restricted to $Re \approx 1$. Since $Re$ for methane hydrate rising through seawater is often much greater than 1, we extend the theoretical analysis to $Re \leq 10^5$ in Section 3. We also verify the theoretical results by experiments.

Mathematically, melting can be treated in a similar fashion as dissolution except that mass transfer is replaced by heat transfer (including replacement of $\alpha$ by $\delta$, $P_{et}$ by $Pe_t$, Sherwood number by Nusselt number, etc.). Kerr [10] and McLeod and Sparks [20] investigated convective
3. Convective dissolution of a crystal rising or falling in water

For convective dissolution of a crystal as it buoyantly rises or falls through water, mass transfer is enhanced and typically dominated by forced convection due to buoyant descent or ascent of a crystal. The motion of the crystal induces a flow field, and the flow removes the liquid next to the crystal, resulting in a thin compositional boundary layer next to the dissolving crystal. The boundary layer thickness is thin on the leading side of the crystal and thick on the trailing side [21]. Although the thickness of the boundary layer is variable on different sides of the moving crystal, an average boundary layer thickness ($\delta_c$) is defined to characterize the average mass flux through the layer:

$$\delta_c = D\Delta C/F_c$$  \hspace{1cm} (11)

where $\Delta C = C_{\text{sat}} - C_\infty$ is the solute concentration difference between the interface liquid and far-away liquid, and $F_c$ is the compositional flux from the dissolving crystal.

Using this definition, convective dissolution rate can be modeled as [9,12]:

$$-d\alpha/dt = \beta_c D/\delta_c$$  \hspace{1cm} (12)

Diffusive crystal dissolution may also be treated using the concept of boundary layer thickness. By comparing Eqs. 9 and 12, it can be seen that diffusive crystal dissolution can be treated by Eq. 12 with a time-dependent boundary layer thickness:

$$\delta_{c,\text{dif}} = \frac{\beta_c}{\alpha} \sqrt{D t}$$  \hspace{1cm} (13)

From Eq. 12, if $D$ has been measured and $\beta_c$ can be estimated (see Appendix 1), the problem of obtaining the dissolution rate becomes the problem of obtaining the average boundary layer thickness $\delta_c$. As outlined by Kerr [12], for forced convection, $\delta_c$ can be estimated from the Sherwood number ($Sh$), which in turn can be estimated from $Pe_c$. $Sh$ is defined to be the ratio of the compositional flux ($F_c$) from the dissolving crystal to the mass flux scale:

$$Sh = \frac{F_c}{D\Delta C/(2\alpha)}$$  \hspace{1cm} (14)

Combining Eqs. 11 and 14, $Sh$ can be written as:

$$Sh = 2\alpha/\delta_c$$  \hspace{1cm} (15)

Kerr [12] developed the theory for convective crystal dissolution in which both the crystal ascent/descent velocity and $Sh$ are obtained using relations applicable only for $Re \leq 1$. In this section, we extend the analyses to cover $Re \leq 10^5$. Below, we first develop a unifying relation for the dependence of $Sh$ on $Pe_c$ and $Re$. We then present the analyses of convective crystal dissolution at both low and high $Re$. We then present laboratory experimental data to verify the theoretical analyses. Methane hydrate dissolution upon buoyant ascent in seawater will be modeled in Section 3.3.

3.1. A simple unifying expression for $Sh$ for forced convection

We first develop a simple expression for $Sh$ for a large range of $Re$ to simplify the theory for convective crystal dissolution. The expressions of $Sh$ under various conditions have been parameterized by Clift et al. [22] as follows:

For $Re < 1$, $Sh = 1 + (1 + Pe_c)^{1/3}$ \hspace{1cm} (16a)

For $1 \leq Re \leq 100$, $Sh = 1 + Z Re^{0.41}$ \hspace{1cm} (16b)

For $100 \leq Re \leq 2000$, $Sh = 1 + 0.752 Z Re^{0.472}$ \hspace{1cm} (16c)

For $2000 \leq Re \leq 100000$, $Sh = 1 + Z(0.44 Re^{0.5} + 0.034 Re^{0.71})$ \hspace{1cm} (16d)

where $Z = [(1 + 1/Pe_c)Sc]^{1/3}$. Eq. 16a is accurate to...
within 3% when \( \text{Re} \leq 1 \) and is the equation used by Kerr [12]. Eqs. 16b, 16c and 16d fit the experimental data (from different laboratories) well but the data themselves show substantial scatter [22].

The above four expressions for \( \text{Sh} \) are complicated and we simplify them below. The first step is to eliminate \( \text{Sc} \) in \( z \). Because \( \text{Sc} = \frac{\text{Pe}}{\text{Re}} \), \( Z = \left[ (1 + \frac{1}{\text{Pec}}) \text{Sc} \right]^{1/3} = \left[ (1 + \text{Pec}) / \text{Re} \right]^{1/3} \). Eqs. 16a, 16b, 16c and 16d can be rewritten as:

For \( \text{Re} < 1 \), \( \text{Sh} = 1 + (1 + \text{Pec})^{1/3} \) (17a)

For \( 1 \leq \text{Re} \leq 100 \),

\[
\text{Sh} = 1 + \left( 1 + \text{Pec} \right)^{1/3} \left( 0.44 \text{Re}^{0.51} + 0.034 \text{Re}^{0.71} - 1 \right) \quad (17b)
\]

For \( 100 \leq \text{Re} \leq 2000 \),

\[
\text{Sh} = 1 + \left( 1 + \text{Pec} \right)^{1/3} 0.752 \text{Re}^{0.472} - 1 \quad (17c)
\]

For \( 2000 \leq \text{Re} \leq 100000 \), \( \text{Sh} = 1 + \left( 1 + \text{Pec} \right)^{1/3} \left( 0.096 \text{Re}^{1/3} \right) \left( 1 + \frac{1}{7 \text{Re} - 2} \right) \) (17d)

The second step is to use one expression to represent the above four equations in their respective applicable range. After many trials, the above four equations can be combined as:

\[
\text{Sh} = 1 + \left( 1 + \text{Pec} \right)^{1/3} \left( 1 + \frac{0.096 \text{Re}^{1/3}}{1 + \frac{1}{7 \text{Re} - 2}} \right) \quad (18)
\]

Eq. 18 reproduces Eqs. 16a, 16b, 16c and 16d in their respective range to within 3%. Hence it is an excellent expression of \( \text{Sh} \) for \( \text{Re} \leq 10^5 \) and is recommended for future use.

3.2. Convective dissolution rate upon crystal ascent or descent in a large range of \( \text{Re} \)

For \( \text{Re} > 1 \), crystal ascent or descent velocity can no longer be calculated from Stokes’ law, and the expression of \( \text{Sh} \) using Eq. 16a must be replaced by Eq. 18. The following is an outline of our new model extending the model of Kerr [12]:

1. Given the radius of the crystal, calculate the ascent or descent velocity \( u \). For Stokes flow (\( \text{Re} < 1 \)), \( u = 2g \alpha^2 \Delta \rho / (9 \mu) \). If \( \text{Re} > 1 \), the Stokes law is no longer applicable; a more complicated formulation must be used. For \( \text{Re} \leq 3 \times 10^5 \), one formulation is to solve the three unknowns (\( u, \text{Re}, \text{drag coefficient} \ \text{C}_D \)) iteratively from Eq. 1 and the following two equations:

\[
\text{C}_D = \frac{24}{\text{Re}} \left( 1 + 0.15 \text{Re}^{0.687} \right) + \frac{0.42}{1 + 42500 \text{Re}^{-1.16}} \quad (19)
\]

\[
u = \sqrt{\frac{8g \alpha \Delta \rho}{3 \rho_{\text{water}} C_D}} \quad (20)
\]

Eq. 19 is from Cliff et al. [22] and the relative error is +6% to -4% for \( \text{Re} < 3 \times 10^5 \); Eq. 20 is from the definition of \( C_D \) and can be found in fluid dynamics books (e.g., eq. 6-230 in [23]). In the above formulation, the effect of denser interface fluid on descent velocity is ignored.

2. Knowing \( u \) from above, \( \text{Pec} \) can be calculated using Eq. 3. With \( \text{Re} \) (from Eq. 1) and \( \text{Pec} \), \( \text{Sh} \) for forced convection can be calculated from Eq. 18.

As shown by Kerr [12], for very tiny crystals (usually < 0.05 mm radius), free convection may be more important than forced convection. \( \text{Sh} \) for free convection is expressed as [12]:

\[
\text{Sh} = 2 + 0.6 \text{Ra}^{1/4} \quad (21)
\]

where \( \text{Ra} \) is the Rayleigh number (Eq. 2). The above equation applies for \( \text{Ra} \leq 10^9 \). For calculation of convective crystal dissolution rate, we calculate \( \text{Sh} \) for free convection and \( \text{Sh} \) for forced convection, and the greater value is used as \( \text{Sh} \) of the process. Only for very tiny crystals is \( \text{Sh} \) for free convection greater than that for forced convection and hence used in the calculation.

3. The value of \( \delta_i \) is calculated from \( \delta_i = (2a)/\text{Sh} \) (Eq. 15).

4. Then, the right-hand side of Eq. 12 is obtained, and \( a \) is solved from the differential equation (Eq. 12). Depth is solved by integrating \( u \) with respect to \( t \).
only be integrated numerically. The integration is carried out with a spreadsheet program.

Because we have extended the analyses of Kerr [12] from small Re (Re \( \leq 1 \)) to a large range of Re (Re \( \leq 10^5 \)), and because there are some simplifying assumptions and approximate equations, below we report laboratory experiments to verify the calculated results and assess the applicability of the model.

### 3.3. Experimental data on convective crystal dissolution to high Re

We carried out convective dissolution experiments in water using NaCl, KCl, NaBr, and...
Table 1
Experimental data for convective crystal dissolution

<table>
<thead>
<tr>
<th>NaCl (16.5-17°C)</th>
<th>KCl (21°C)</th>
<th>NaBr (17°C)</th>
<th>KBr (21°C)</th>
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<tbody>
<tr>
<td>0.103 15.5</td>
<td>0.383 0.043</td>
<td>7.06 0.117</td>
<td>0.309 8.3</td>
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<td>0.120 15.5</td>
<td>0.418 0.061</td>
<td>7.47 0.137</td>
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<td>0.135 15.4</td>
<td>0.455 0.083</td>
<td>8.84 0.194</td>
<td>0.429 9.5</td>
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<td>0.158 17.3</td>
<td>0.530 0.115</td>
<td>10.1 0.251</td>
<td>0.454 9.9</td>
</tr>
<tr>
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<td>0.635 0.121</td>
<td>10.47 0.270</td>
<td>0.648 10.5</td>
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<tr>
<td>0.217 20.1</td>
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<td>0.723 11.3</td>
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<td>0.219 20.0</td>
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<td>12.15 0.385</td>
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<td>13.44 0.465</td>
<td>1.025 12.7</td>
</tr>
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<td>1.092 13.5</td>
</tr>
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<td>0.999 0.340</td>
<td>14.85 0.516</td>
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<td>0.711 11.2</td>
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<td>6.75 0.120</td>
<td>0.920 11.2</td>
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<td>1.239 0.053</td>
<td>6.44 0.131</td>
<td>1.264 12.8</td>
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<td>1.239 0.053</td>
<td>6.44 0.131</td>
<td>1.264 12.8</td>
</tr>
<tr>
<td>0.519 21.0</td>
<td>0.519 0.519</td>
<td>16.93 0.706</td>
<td>0.622 9.7</td>
</tr>
<tr>
<td>0.513 27.1</td>
<td>1.204 KCl (25°C)</td>
<td>0.702 10.0</td>
<td>0.711 11.2</td>
</tr>
<tr>
<td>0.537 27.7</td>
<td>1.210 0.047</td>
<td>6.75 0.120</td>
<td>0.920 11.2</td>
</tr>
<tr>
<td>0.540 26.5</td>
<td>1.239 0.053</td>
<td>6.44 0.131</td>
<td>1.264 12.8</td>
</tr>
</tbody>
</table>

Crystals are cubic. $M$ is the mass of the crystal; $t_s$ is the survival time, and $h_s$ is the survival distance. Note that experimental data for NaCl dissolution at 20.5°C are shown in the last three columns. The uncertainty in temperature is less than 0.5°C. The uncertainty in the mass is 0.002 mg. The estimated uncertainty for the survival time from a digital stopwatch is 0.2 s. The uncertainty in the survival distance is 0.001 m. In plots, the effective radius ($a$) is used instead of the mass and is calculated from the mass and density of the crystal using $a = [3M/(4\pi \rho)]^{1/3}$. 

KBr crystals. The experimental apparatus consists of a glass cylinder 1.5 m long and 0.10 m in inner diameter. The experimental procedure follows that of Walker and Kiefer [8]. The experimental temperature (water temperature in the apparatus) is controlled by setting the room temperature to be either 17, 21 or 25°C, and waiting for \( \geq 24 \) h until measured water temperature in the cylinder reaches the room temperature. Crystals that are close to cubic and appear to be free of cracks and inclusions (but inspection is difficult due to surface pits) are used for experiments. We use cubic crystals (rather than prepare them into spheres) to assess the accuracy of the spherical model on cubic crystals because hydrate crystals are our focus and they are not spherical. A cubic crystal is weighed with a microbalance. From the mass an effective radius \( a \) of equal volume is calculated. The crystal is dropped into water and is watched as it descends and dissolves. The duration from the moment the crystal is dropped into water until it disappears in water is recorded as the surviving time \( t_s \). The total vertical distance that the crystal travels in water is recorded as the surviving distance \( h_s \). Because we require the crystal to be completely dissolved before it reaches the bottom and because the height of the water column is limited, the maximum Re number of the experiments is limited to \( \leq 350 \).

Some experiments were classified to be unsuccessful and discarded. (i) For a couple of experiments, a floating bubble appeared (presumably from a bubble inclusion in the crystal) as the crystal was dissolved. The results of these experiments were discarded. (ii) The larger the crystal, the more sideways wiggling there is as it falls down. We discarded the results if the crystal came very close (within a few mm by the naked eye) to the glass wall of the apparatus during its descent. The uncertainty for the crystal mass is 0.002 mg, that for the surviving time is 0.2 s (larger than the reading accuracy to account for human response time), and that for the surviving distance is 0.001 m. The scatter of the data in figures is greater than these uncertainties due to other experimental uncertainties, such as deviation from cubic shape, imperfection of a crystal (e.g., inclusions and cracks), etc.

All experimental data are listed in Table 1. Some data are shown in Figs. 4 and 5. Fig. 4 shows all experimental data on NaCl, as well as fits to the data. It also compares experimental data of Walker and Kiefer [8] with our data. The agreement between the two data sets is very good. The slightly larger scatter in the data of Walker and Kiefer [8] can be attributed to the unairconditioned July temperature (\( \sim 30\)°C) in their laboratory.

Experimental data and calculated results (see Fig. 5) show that the effective radius \( a \) and the surviving time \( t_s \) are roughly (but not exactly) proportional to each other over the experimental conditions of this study. To extend the results to zero crystal size, a better form is \( a = k t_s^{0.88} \) where \( k \) is a constant (see fits in Fig. 4). To extend to greater crystal size, \( a \) is roughly linear to \( t_s \). To cover both small and large crystal sizes, the following two-parameter equation, \( a = k_1 t_s^{1/3} + k_2 t_s^{1/2} \), fits the calculated results very well. For the relation between \( a \) and the surviving distance \( h_s \), a rough relation is that \( h_s \) is proportional to \( a^2 \). To extend to zero crystal size, a better form is \( h_s = q a^{2.3} \) where \( q \) is a constant (see fits in Fig. 4). To extend to greater crystal size, \( h_s \) is roughly linear to \( a^2 \). To cover both small and large crystal sizes, the following two-parameter equation, \( a = q_1 h_s^{1/5} + q_2 h_s^{1/2} \), fits calculated results very well.

Although the above two-parameter fitting functions can fit our \( a \) vs. \( t_s \) data and \( a \) vs. \( h_s \) data very well, we still primarily focus on the comparison between our model calculation and experimental data because there is no free parameter in the model calculation.

Fig. 5 compares all experimental data at 25°C with calculation using our model developed in Section 3.2. The constants necessary for the calculations are summarized in Appendix 2. For KCl, the calculated \( a \) vs. \( t_s \) curve and \( h_s \) vs. \( a \) curve are in good agreement with experimental data. For NaBr, the calculated \( a \) vs. \( t_s \) curve is in agreement with data, but the calculated \( h_s \) vs. \( a \) curve is above the data by up to 25% relative. For NaCl, the calculated \( a \) vs. \( t_s \) curve is above the data by up to 20% relative, and the calculated \( h_s \) vs. \( a \) curve is below the data by up to 15% relative. For KBr, the calculated \( a \) vs. \( t_s \) and \( h_s \) vs. \( a \) curve...
Fig. 5. Comparison of experimental data and calculated results on convective crystal dissolution. Note the curves are calculated (see Section 3.2) without any fitting parameters.
585 curves are both above the data by up to 20% relative.
586 Because there are no fitting parameters at all, this level of agreement for $Re \leq 350$ and for several types of crystals is good and implies that our model for crystal dissolution and descent captures the main controlling factors. Possible causes for the small disagreements include (in order of decreasing importance):
594 1. Some minor factors are ignored. Near the dissolving interface, the solute concentration is very high, and the effects on viscosity, density and diffusivity can be significant. There is also a minor thermal effect due to heat of solution. The effect of solute concentration on the diffusivity is small and complicated for these halides (usually first decreases and then increases with concentration). Viscosity of salt-bearing water strongly increases with NaCl and NaBr concentration (by about a factor of 2), but only depends weakly on KCl and KBr concentration (Appendix 2). The density of halide-saturated water is greater than that of pure water by $199 \text{ kg/m}^3$ for NaCl, $176 \text{ kg/m}^3$ for KCl, $533 \text{ kg/m}^3$ for NaBr, and $380 \text{ kg/m}^3$ for KBr (Appendix 2). A high viscosity would reduce the descent velocity, whereas a dense boundary layer would increase it, affecting the surviving distance. A change in the descent velocity would in turn affect $Re$, $Sh$, $\delta$, and the dissolution rate.
604 It appears that among the factors not incorporated into our model, viscosity and density variations in the boundary layer are the most important. For KCl, both effects are small, and calculations agree well with experimental results. For NaBr, the two effects (higher viscosity and higher density) tend to cancel each other. For NaCl, the viscosity effect dominates. For KBr, the density effect dominates. Incorporating the viscosity and density effects is difficult because they vary across the boundary layer. Hence we recognize the problems but choose to tolerate them.
612 2. Both Eqs. 18 and 19 have some uncertainties. Expressions for other parameters used in the calculations, such as diffusivity and solubility, also have small uncertainties. These uncertainties may lead to 10% relative uncertainties in the calculation.
620 3. The shape of crystals used for experiments is roughly cubic and some are prolate, whereas the calculation is done for spherical geometry. Because the theory is general to high Re number, and because there is good agreement between experimental data and theoretical calculation, we expect the theory to be approximately applicable to Re up to $10^5$. In Section 5.2, we apply the theory to calculate convective dissolution rate of methane hydrate upon free ascent in seawater.
638 4. Convective dissociation of a crystal rising or falling in water
644 In the regime of methane hydrate dissociation (e.g., at water depth less than 530 m in Fig. 2), the controlling factor is heat transfer instead of mass transfer. Kinetics of methane hydrate dissociation is expected to be similar to that of ice melting except for the generation of bubbles whose buoyant rise from the interface may enhance convection. Hence we use the theory for convective melting to approximate the theory for dissociation, but noting that the theory may only give a minimum dissociation rate.
652 Theory for crystal melting under forced convection as a crystal is falling or rising through a liquid can be developed by analogy with that for crystal dissolution under forced convection [12]. For $Re < 1$, the theory of convective melting has been developed by Kerr [10] and McLeod and Sparks [20]. Following Section 3.3 on convective dissociation, we extend the analysis of convective dissociation (or melting) to Re number up to $10^5$.
664 As a crystal melts, the necessary thermal flux is
672 \[ F_i = (\frac{-d\alpha}{dt})[\rho_s c_s (T_0 - T_s) + \rho_s L] \] (22)
680 where $(\frac{-d\alpha}{dt})$ is the melting rate, subscript ‘s’ means the solid phase, $c$ is heat capacity, $L$ is the latent heat for crystal melting or dissociation, $T_0$ is the interface temperature (assumed to be the equilibrium melting or dissociation temperature [17]), $T_s$ is the temperature inside the crystal far from
5. Dissolution and dissociation of methane hydrate as it rises through seawater

The primary motivation of this study is to understand methane hydrate dissolution and dissociation under various conditions although the above theories are general. In the following treatment, a piece of hydrate is assumed to behave as a perfect crystal. That is, the effects of grain boundaries, bubbles and other inclusions, cracks, and other defects of hydrate on dissolution rates are ignored. The necessary parameters needed for calculation are summarized in Appendix 1. Below, we consider dissolution of exposed hydrate floor, dissolution of a rising hydrate, and dissociation of a rising hydrate. We do not consider the unlikely case of dissociation of an exposed hydrate floor. It is unlikely because if hydrate is inherently unstable on the ocean floor, it is also inherently unstable in sediment due to temperature increase in sediment.

5.1. Dissolution of exposed hydrate floor

An exposed hydrate floor may stay at the ocean floor (that is, not rising through seawater) due to cohesion with sediment underneath or due to mix-
the overall density of hydrate and sediment is greater than that of seawater. In this section, we estimate the dissolution rates of such an exposed hydrate floor. The value of $L_c$ (Eq. 8) does not change much with water depth (Table A1). For a deep ocean floor temperature of 277.15 K, $L_c = 0.0094$, and $D$ for methane in water is roughly $1.09 \times 10^{-9}$ m$^2$/s (Appendix 1). The value of $\alpha$ can be solved from Eq. 7 to be 0.0053. From Eq. 6, the diffusive dissolution distance $X_{\text{dis}}$ (in m) is $3.5 \times 10^{-7}\sqrt{t}$ (where $t$ is in s), 0.10 mm in a day, 2.0 mm in a year, and 2 m in a million years. That is, diffusive dissolution is extremely slow.

The above dissolution rates are a minimum because dissolution of massive methane hydrate on the ocean floor is aided by convection, either free convection driven by the density difference between methane-bearing interface seawater and normal seawater, or forced convection due to oceanic current. Kerr [11] modeled floor dissolution controlled by free convection. Compared to far-field seawater, the boundary layer above a hydrate floor is slightly colder (which makes it more dense), and contains slightly higher CH$_4$ content (which makes it less dense). As estimated by Kerr (personal communication), the thermal effect that stabilizes the boundary layer is greater than the compositional effect. Hence there would be no free convection.

Hydrate floor dissolution rate under forced convection due to oceanic current can be estimated using Eq. 10. For hydrate floor exposed at Hydrate Ridge (44.57°N, 125.19°W), ocean current velocity $u$ is about 0.03 m/s (David Rea, personal communication), seawater viscosity at 277.15 K is about 0.00167 Pa s, the length scale $l$ is roughly taken as 1000 m (the dependence of dissolution on the length scale $l$ is weak). Hence the calculated dissolution rate $V$ is 0.00228 $\mu$m/s, or 0.072 m per year. A 100 m thick massive hydrate layer may survive for more than 1000 years.

5.2. Convective dissolution of methane hydrate upon free ascent

We now calculate convective dissolution rate as methane hydrate rises buoyantly through seawater (Table 2). Because the saturation concentration of CH$_4$ in water is low (Fig. 2), dissolved CH$_4$ is not expected to significantly affect the density, diffusivity and viscosity in the boundary layer. Hence we expect the theoretical calculation to have better accuracy than the case for NaCl and KBr descent and dissolution (Fig. 5). Since dissolution only occurs in deep water (dissociation occurs in shallow water) where temperature is roughly constant, for simplicity, a constant temperature of 277.15 K for deep water with a constant value of $\beta_c$ (0.0094) is used.

Fig. 6 shows some calculated results. The ascent velocity of methane hydrate increases with its size. The calculated ascent velocity of a hydrate with 50 mm radius is 0.53 m/s. Brewer et al. [24] observed the ascent velocity of natural hydrate of similar size to be 0.24 m/s. The difference is prob-
ably due to: (i) impurity in natural hydrate that increases its density, (ii) difficulty in determining the size, and (iii) non-spherical shape of natural hydrate.

The dissolution rate decreases with increasing effective radius of the crystal ($a$). The dissolution rate is 0.16 $\text{W/m/s}$ for $a = 50$ mm, 0.24 $\text{W/m/s}$ for $a = 5$ mm, and 0.30 $\text{W/m/s}$ for $a = 1$ mm. Brewer et al. [24] used variation in the ascent velocity to estimate the variation in the size of hydrate, and obtained a dissolution rate of 31 $\text{W/m/s}$, about two orders of magnitude greater than our results. This clearly shows that hydrate size cannot be estimated from ascent velocity. (Furthermore, there is an error in their eq. 1.) In another part of their paper [24], they argued that the dissolution rate is less than 6.7 $\mu\text{W/m/s}$, consistent with our calculation. The inconsistency between the two parts of their paper is not explained [24] but they have another submitted manuscript on the topic (Brewer, personal communication).

A larger hydrate piece rises more rapidly but dissolves more slowly. Hence per unit depth, dissolution distance is smaller for larger hydrate pieces. For the oceanic depth corresponding to Fig. 2, a piece of hydrate with radius greater than 5.5 mm would be able to survive the rise and dissolution from the ocean floor (2775 m) to reach the depth of 530 m where hydrate begins to dissociate. Solid curves in Fig. 7 show the size variation with depth for methane hydrate dissolution. As will be seen later, because hydrate dissociates in shallow seawater and the dissociation rate is much greater, only very large chunks of hydrate can survive dissociation and float to ocean surface.

Many hydrate grains may be released in a parcel of water. In this case the collective rise of hydrate-laden water must be considered. For example, consider a parcel of water 10 m in radius and containing 1 vol% of roughly uniformly distributed methane hydrate, lowering its density by 0.1% relative. The rising velocity of the parcel obtained from iterations of Eqs. 1 and 20 and the numerical standard drag curve ($C_D$ vs. Re) [22] (more general than Eq. 19) is 1.2 $\text{m/s}$. The parcel would rise by 2000 m in 0.47 h. Hydrate with radius greater than 0.5 mm would be able to survive such a rise. As hydrate reaches shallow depth, it becomes unstable and dissociates, which is discussed next.

### 5.3. Convective dissociation of methane hydrate upon free ascent

Using the theory in Section 4, methane hydrate dissociation rate can be calculated numerically. During methane hydrate dissociation, bubbles are produced at the dissociation interface. Buoyant rise of bubbles would intensify convection and hence increase the dissolution rate, but the effect is difficult to quantify. Hence the calculation using our theory only gives a minimum of the dissociation rate.

Before modeling the full process of ascent and dissociation, we first compare dissociation and dissolution rates. If $\Delta T = T_x - T_0 = 1 \text{ K}$ in Eq. 25, using the relevant parameters, the dissociation rate is calculated for each experimental condition and compared with the observed dissolution rate. The results are presented in Table 2.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Range of $a$ (mm)</th>
<th>Experimental $da/dt$ ($\mu\text{m/s}$)</th>
<th>Calculated $da/dt$ ($\mu\text{m/s}$)</th>
<th>Relative difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl, 17°C</td>
<td>0.22–0.39</td>
<td>13.1</td>
<td>16.4</td>
<td>25</td>
</tr>
<tr>
<td>NaCl, 21°C</td>
<td>10.15–0.39</td>
<td>14.7</td>
<td>18.2</td>
<td>24</td>
</tr>
<tr>
<td>NaCl, 25°C</td>
<td>0.20–0.42</td>
<td>15.8</td>
<td>19.4</td>
<td>23</td>
</tr>
<tr>
<td>NaBr, 17°C</td>
<td>0.30–0.55</td>
<td>33.7</td>
<td>31.7</td>
<td>−6</td>
</tr>
<tr>
<td>NaBr, 25°C</td>
<td>0.20–0.60</td>
<td>43.7</td>
<td>40.0</td>
<td>−8</td>
</tr>
<tr>
<td>KCl, 21°C</td>
<td>0.19–0.40</td>
<td>22.6</td>
<td>20.7</td>
<td>−8</td>
</tr>
<tr>
<td>KCl, 25°C</td>
<td>0.18–0.37</td>
<td>26.2</td>
<td>23.5</td>
<td>−10</td>
</tr>
<tr>
<td>KBr, 21°C</td>
<td>0.20–0.62</td>
<td>41.7</td>
<td>32.6</td>
<td>−22</td>
</tr>
<tr>
<td>KBr, 25°C</td>
<td>0.22–0.67</td>
<td>45.7</td>
<td>35.9</td>
<td>−21</td>
</tr>
</tbody>
</table>

Note: $a$ is the initial radius of a sphere with a volume equivalent to the halide grain used for experiments.
rate is about 30 times the dissolution rate (Eq. 29). If $v_T = 10$ K, then the dissociation rate is about 300 times the dissolution rate (Eq. 29). The conclusion is that the dissociation rate is much greater than the dissolution rate as long as $v_T$ is large enough, consistent with expectations.

Methane hydrate dissociation as it rises through seawater would begin when water pressure is smaller than the pressure to stabilize hydrate, which is equivalent to when water temperature is higher than the dissociation temperature of hydrate. Dissociation would begin when $T_\infty - T_0$ (Eq. 25) begins to exceed zero. Therefore, our numerical modeling starts with a hydrate at the depth of 530 m (the boundary between water+gas and water+hydrate in Fig. 2) where $T_\infty - T_0 = 0$ and a water temperature of 279.36 K. As hydrate rises, water temperature $T_\infty$ increases, and the pressure decreases so that the dissociation temperature $T_0$ decreases. The combined effect is that the difference $T_\infty - T_0$ increases and hydrate dissociation rate increases (Eqs. 24 and 25). In the model, $T_0$ is calculated from the pressure (depth), and $T_\infty$ is calculated by assuming it increases linearly upward with a gradient of 0.03 K/m so that the surface temperature is 295.15 K. After a rise of about 0.6 m (from the starting point of 530 m), $\Delta T$ increases to 0.033 K and the dissociation rate equals the dissolution rate. With further rise of hydrate, dissociation rate becomes greater and greater. Fig. 7 (dashed curve) shows some calculated results for hydrate dissociation in the surface water. Methane hydrate with an effective radius of 5 mm would dissociate completely in 370 s and with a survival distance of only 47 m. To survive the whole 530 m column, the hydrate sphere must have an initial radius of 0.09 m or more. Because bubbles produced during dissociation intensify convection and hence dissociation rate, and because large chunks of hydrate likely have grain boundaries and pores (hence not behaving as a single perfect crystal), to survive the surface layer would require larger hydrate pieces.

Brewer et al. [24] observed that at Hydrate Ridge, pieces of hydrate with 0.04–0.05 m radius can survive a 410 m surface column. Because the hydrate is not pure methane hydrate, there is not enough information to do the calculation. However, because the depth is shallower than our calculation above, and the temperature in surface water is only 287 K [25] leading to a temperature gradient of 0.02 K/m (smaller than 0.03 K/m we used above), a simple scaling of our calculated result roughly agrees with Brewer et al.’s observed result. Although temperature profiles in surface ocean vary with location, there is always a surface seawater layer where methane hydrate is unstable with respect to dissociation. Hence only large hydrate chunks (greater than about 50 mm radius depending on the local temperature profile) would be able to survive dissociation through this layer and reach the surface. Smaller hydrate grains and pieces would rapidly dissociate into bubbles and water. Hence if many methane hydrate grains (1–10 mm in radius) are released into ocean bottom water, many (depending on whether they rise individually or collectively) would likely survive dissociation in deep water, especially if the hydrate-bearing water parcel rises collectively. Upon reaching inherent instability depth, hydrate would...
dissociate rapidly into methane gas and water in shallow water, producing a bubble plume, which might power a methane-driven oceanic eruption [4]. This would be an efficient way to transport a large amount of CH₄ gas rapidly to the atmosphere.

6. Uncited references

[32]

Acknowledgements

We thank Bruce Buffett and Ross C. Kerr for constructive and insightful comments. Kerr also helped us to model floor dissolution rate under forced convection of ocean currents. We thank David Rea for helping with oceanography. Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for support of this research. This work is also partially supported by the US National Science Foundation (EAR-0125506 and EAR-0228752).

Appendix 1. Values of various parameters for hydrate

In this appendix, we summarize estimation of various parameters. Assuming an ideal formula for methane hydrate, CH₄(H₂O)₅₇.₅, the molecular mass of hydrate is 0.11963 kg/mol and the concentration of CH₄ in hydrate is 13.4 wt%. The density of methane hydrate is taken to be that of ice, 920 kg/m³. Hence the molar volume of hydrate is 0.130 l/mol, and concentration of CH₄ in methane hydrate is 

\[ C_{\text{hydrate}} = \frac{7.69 \text{ mol}}{\text{l}} \]

The diffusivity of CH₄ in seawater is assumed to be the same as that in pure water, and is expressed as [26]:

\[ D_{\text{CH}_4} = \exp(-15.066 - 1545/T) \] (A1)

where \( D_{\text{CH}_4} \) is in m²/s and \( T \) is in K. Note that \( D \) at 25°C from the above equation is 1.61×10⁻⁹ m²/s, which does not agree with 1.49×10⁻⁹ m²/s [16]. The small inconsistency (8% relative) is not important to the results presented in this work.

The pressure for hydrate formation in seawater is based on data from Dickens and Quinby-Hunt [27], and is given as a function of temperature as follows:

\[ P = \exp(30.718 + 8103.4/T) \] (A2)

where \( T \) is in K and \( P \) is in MPa.

The latent heat of dissociation of methane hydrate \((L \text{ in Eqs. 22 and 25})\) is taken to be that for ice melting, 333.6 kJ/kg. The heat capacity of methane hydrate \((c_s \text{ in Eqs. 22 and 25})\) is taken to be that of ice, 2100 J/kg/K.

The pressure for hydrate formation in seawater is given as a function of temperature as follows:

\[ P = \exp(30.718 + 8103.4/T) \] (A2)

The solubility of CH₄ in seawater in equilibrium with methane hydrate is calculated from the model of Duan et al. [28]. For approximate calculation, the Ostwald solubility coefficient is assumed to be a function of \( T \) only and is roughly expressed as:

\[ \lambda = \exp(-31.25 + 14450/T - 1849000/T^2) \] (A3)

When hydrate is stable, CH₄ solubility is limited by hydrate formation. In order to calculate the solubility at a given \( P \) and \( T \), we examine the following solubility reaction:

\[ \text{CH}_4(H_2O)_{5.75} \text{ (solid)} = \]

\[ \text{CH}_4(aq) + 5.75H_2O \text{ (liq)} \] (A4)

The equilibrium constant for the above reaction is

\[ K = C_{\text{CH}_4}^{\text{sat}} \]

where \( C_{\text{CH}_4}^{\text{sat}} \) is CH₄ solubility in seawater in equilibrium with methane hydrate. To calculate \( C_{\text{CH}_4}^{\text{sat}} \) at a given \( P \) and \( T \) and hydrate formation pressure, we recognize that at the pressure ofhydrate formation, the chemical potential of CH₄ in the hydrate, in the gas phase at \( P \), and in seawater must be the same. Hence the CH₄ solubility of hydrate equals the solubility of methane gas in water at the same \( T \) and \( P \). At the same \( T \) and higher \( P \), \( \ln K \) would change with pressure as \(-\Delta \nu dP/(RT)\). According to the solubility model of Duan et al. [28], the partial molar volume of CH₄ in water at 273.15 K is about 32 cc/mol. \( \Delta V \) of the above reaction (Eq. A4) is hence about 6
cc, meaning that $K$ would decrease with $P$. From 1 to 30 MPa (about 3000 m depth), $\ln K$ would decrease by 0.08. The accuracy of this calculation is not certain but it shows that the effect of pressure on hydrate solubility is small and can be ignored. Thus, at a given $T$, hydrate solubility at any $P$ is roughly the same as that at $P$ of hydrate formation. That is, the solubility of hydrate is only a function of $T$ and roughly independent of $P$. Fitting the calculated solubility of hydrate (from gas solubility) at various temperatures, we have the following expression for CH$_4$ solubility of methane hydrate:

$$C_{\text{sat}} = \exp\left(10.063 - 4674.1/T\right)$$

(A5)

where $C_{\text{sat}}$ is mass fraction.

The viscosity of water ($\mu$ in Pa s) [29] is parameterized as follows:

$$\ln \mu = -16.34073 + 6.4877x - 1.991x^2 + 0.26384x^3$$

(A7)

where $x = 1000/T$. Thermal conductivity ($k$) of water is 0.54 W/m/K. The heat diffusivity ($\kappa$) of water [29] is:

$$\kappa = k/(\rho_{\text{water}}c) = 1.29 \times 10^{-7} \text{ m}^2/\text{s}$$

(A8)

where $c$ is heat capacity of water and is 4184 J/kg/K.

### Seawater

The salinity of seawater is taken to be 35%. For simplicity, density of seawater ($\rho_{\text{seawater}}$) is taken to be 1.0263 times that of pure water, and viscosity of seawater is taken to be 1.067 times that of pure water [29]. At 4$^\circ$C, viscosity of seawater is 0.00167 Pa s. The pressure effect on density and viscosity of seawater is ignored. The surface tension, thermal conductivity and heat diffusivity of seawater are approximated by those of pure water.

### NaCl

The solubility of NaCl in water ($S$ in kg of NaCl per 100 kg of water [30]) at 273.15–373.15 K is parameterized as follows:

$$S = 35.7 + 0.00515(T-273.15) + 0.000295(T-273.15)^2$$

(A9)

The solubility in terms of mass fraction of dis-
solved NaCl is \( w = S/(100+S) \). The density of NaCl-bearing water at 298.15 K is assumed to be the same as that at 293.15 K \([29]\), depending linearly on \( w \) as:

\[
\rho_{\text{NaCl solution}} = \rho_{\text{water}} + 749.6w_{\text{NaCl}} \quad (A10)
\]

where \( \rho_{\text{water}} = 998.21 \text{ kg/m}^3 \). The density of the saturated solution \( (\rho_{\text{sat}}) \) can hence be calculated. The solubility in terms of mol/kg is \( \rho_w \) where \( \rho \) is molar mass of NaCl. The solubility in terms of mol/l \( (C_{\text{sat}}) \) is \( C_{\text{sat}} = 0.001\rho_{\text{sat}}w \). Then, the parameter \( \beta = (C_{\text{sat}} - C_w)/(C_{\text{crystal}} - C_{\text{sat}}) \) can be estimated to be 0.171 (Table A2) for \( C_w = 0 \). Because the solubility of NaCl does not vary much with temperature, the value of \( \beta \) is roughly constant (it varies from 0.170 to 0.172 between 0 and 40°C).

\[
D_{\text{NaCl}} = \exp(-13.725 - 1950/T) \quad (A11)
\]

Viscosity of NaCl solution at 293 K increases by 98.6% as NaCl concentration increases from 0 to 26 wt% \([29]\). The ratio of the viscosity of the saturated solution at 25°C to that of pure water \( (\mu_{\text{sat}}/\mu_0) \) is obtained by extrapolation to be about 2.0.

### KCl

The solubility of KCl in water \([30]\) at 273.15–313.15 K is parameterized as follows:

\[
S = 80.3 + 0.403(T - 273.15) + 0.000661(T - 273.15)^2 \quad (A15)
\]

where \( T \) is in K. The density of NaBr-bearing water at 298.15 K is assumed to be the same as that at 293.15 K \([29]\), which depends linearly on \( w_{\text{KBr}} \) and is parameterized as follows:

\[
\rho_{\text{KCl solution}} = \rho_{\text{water}} + 670.6w_{\text{KCl}} \quad (A13)
\]

From the above information, the parameter \( \beta = (C_{\text{sat}} - C_w)/(C_{\text{crystal}} - C_{\text{sat}}) \) can be estimated (Table A2) for \( C_w = 0 \). The value of \( \beta \) for KCl dissolution depends on temperature as follows:

\[
\beta = 0.64 - 136/T. \quad (A12)
\]

The diffusivity of KCl is \([31]\):

\[
D_{\text{KCl}} = \exp(-13.906 - 1831.5/T) \quad (A14)
\]

Viscosity of KCl solution at 293 K first decreases by about 1% and then increases to 4% greater than viscosity of pure water as KCl concentration increases to 24 wt% \([29]\).

### NaBr

The solubility of NaBr in water \([30]\) at 273.15–313.15 K is parameterized as follows:

\[
S = 80.3 + 0.403(T - 273.15) + 0.000661(T - 273.15)^2 \quad (A15)
\]

where \( T \) is in K. The density of NaBr-bearing water at 298.15 K is assumed to be the same as that at 293.15 K \([29]\), which depends on \( w_{\text{NaBr}} \) and is parameterized as follows:

\[
\rho_{\text{NaBr solution}} = \rho_{\text{water}} + 732w_{\text{NaBr}} + 752w_{\text{NaBr}}^2 \quad (A16)
\]

### Table A2

<table>
<thead>
<tr>
<th>Phase</th>
<th>W molar mass</th>
<th>Crystal density</th>
<th>( C_{\text{crystal}} )</th>
<th>( S )</th>
<th>( w )</th>
<th>( \rho_{\text{sat}} )</th>
<th>( C_{\text{sat}} )</th>
<th>( \beta )</th>
<th>( \mu_{\text{sat}}/\mu_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.058443</td>
<td>2165</td>
<td>37.04</td>
<td>36.0</td>
<td>26.5</td>
<td>1197</td>
<td>5.42</td>
<td>0.171</td>
<td>2.0</td>
</tr>
<tr>
<td>KCl</td>
<td>0.074551</td>
<td>1984</td>
<td>26.61</td>
<td>35.5</td>
<td>26.2</td>
<td>1174</td>
<td>4.12</td>
<td>0.183</td>
<td>1.06</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.102894</td>
<td>3205</td>
<td>31.15</td>
<td>94.5</td>
<td>48.6</td>
<td>1531</td>
<td>7.23</td>
<td>0.302</td>
<td>2.7</td>
</tr>
<tr>
<td>KBr</td>
<td>0.119002</td>
<td>2752</td>
<td>23.13</td>
<td>67.8</td>
<td>40.4</td>
<td>1378</td>
<td>4.68</td>
<td>0.254</td>
<td>1.01</td>
</tr>
</tbody>
</table>

The density of NaBr-bearing water at 298.15 K is assumed to be the same as that at 293.15 K \([29]\), depending linearly on \( w_{\text{NaBr}} \) and is parameterized as follows:

\[
\rho_{\text{NaBr solution}} = \rho_{\text{water}} + 732w_{\text{NaBr}} + 752w_{\text{NaBr}}^2 \quad (A16)
\]
The value of $\beta_k$ for NaBr dissolution depends on temperature as follows: $\beta_k = 0.2579 + 0.00133(T - 273.15) + 0.0000172(T - 273.15)^2$ where $T$ is in K. The diffusivity of NaBr in water at 25°C is $1.62 \times 10^{-9}$ m²/s [16,29]. Assuming the activation energy is the same as that for NaCl, the diffusivity of NaBr can be expressed as:

$$D_{NaBr} = \exp\left(-13.70 - 1950/T\right)$$  \hspace{1cm} (A17)

Viscosity of NaBr solution at 293 K increases by 86% as NaBr concentration increases from 0 to 40 wt% [29].

The solubility of KBr in water [30] as a function of temperature can be expressed as:

$$S = 160.34 \ln(T/195.35)$$ \hspace{1cm} (A18)

The density of KBr-bearing water at 298.15 K is assumed to be the same as that at 293.15 K [29], which depends on $w$ as:

$$\rho_{KBr \, solution} = \rho_{water} + 684w_{KBr} + 632w_{KBr}^2$$ \hspace{1cm} (A19)

The value of $\beta_k$ for KBr dissolution depends on temperature as follows: $\beta_k = 0.6023 \ln(T/195.77)$ where $T$ is in K. The diffusivity of KBr in water at 25°C is $2.02 \times 10^{-9}$ m²/s [16,29]. Assuming the activation energy is the same as that for KCl, the diffusivity of KBr can be expressed as:

$$D_{KBr} = \exp\left(-13.877 - 1831.5/T\right)$$ \hspace{1cm} (A20)

Viscosity of KBr solution at 293 K first decreases by 5.9% as KCl concentration increases from 0 to 23 wt% and then increases to pure water viscosity at 39 wt% KCl [29].

References


