

Methane hydrate stability in pore water: A simple theoretical approach for geophysical applications

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Abstract. Geophysicists have recently expressed an interest in understanding how pore water composition affects CH₄ hydrate stability conditions in the marine environment. It has previously been shown in the chemical engineering literature that CH₄ hydrate stability conditions in electrolyte solutions are related to the activity of water (a_w). Here we present additional experimental data in support of this relationship and then use the relationship to address issues relevant to geophysicists. Pressure and temperature conditions of CH₄ hydrate dissociation were determined for 10 solutions containing variable concentrations of Cl⁻, SO₄²⁻, Br⁻, Na⁺, K⁺, Mg²⁺, NH₄⁺, and Cu²⁺. The reciprocal temperature offset of CH₄ hydrate dissociation between the CH₄-pure water system and each of these solutions (and for other electrolyte solutions in literature) is directly related to the logarithm of the activity of water ($\ln a_w$). Stability conditions for CH₄ hydrate in any pore water system therefore can be predicted simply and accurately by calculating $\ln a_w$. The effect of salinity variation and chemical diagenesis on CH₄ hydrate stability conditions in the marine environment can be evaluated by determining how these processes affect $\ln a_w$ of pore water.

Introduction

Clathrate hydrates of methane (CH₄ hydrates) occur naturally in sediment pore space along many continental margins [Kvenvolden, 1988, 1993]. These hydrates exist in a depth zone that is dictated by pressure-temperature conditions of a CH₄-hydrate-water equilibrium curve [Kvenvolden, 1988, 1993]. Because CH₄ hydrate in the marine environment exists in association with saline pore waters that are chemically distinct from seawater (and pure water), a present line of inquiry is the effect that variations in pore water chemistry have on the stability conditions of CH₄-hydrate-water equilibrium curves [Hyndman *et al.*, 1992; Westbrook *et al.*, 1994; Ussler and Paull, 1995; Kastner *et al.*, 1995]. The issue is relevant to current geophysical literature, inasmuch as it has a direct bearing on (1) methods to estimate the distribution of CH₄ hydrate [Kvenvolden, 1988; Kvenvolden and Grantz, 1990; MacDonald, 1990; Gornitz and Fung, 1994], (2) use of bottom-simulating reflectors (BSRs) to estimate geotherms and heat flow [Cande *et al.*, 1987; Minshull and White, 1989; Davis *et al.*, 1990; Hyndman *et al.*, 1992; Brown and Bangs, 1995], and (3) approaches to modeling hydrate dissociation during past climate change [Nisbet, 1990; MacDonald, 1990; Paull *et al.*, 1991; Hatzikiriakos and Englezos, 1994; Dickens *et al.*, 1995].

The activity of water (a_w) of a solution is a measure of the effective concentration of water in the solution. It is defined as

$$a_w = e^{\frac{\mu_w - \mu_w^0}{RT}}, \quad (1)$$

where μ_w is the chemical potential of water in the solution, μ_w^0 is the chemical potential of pure water, R is the gas constant, and T is temperature (in kelvins), or

$$a_w = \gamma_w x_w, \quad (2)$$

where γ_w is the activity coefficient of water, and x_w is the mole fraction of water in the solution. The a_w of an electrolyte solution can be accurately calculated with several constants and a series of equations [e.g., Pitzer, 1991] (see also Appendix 1 of this paper).

The reciprocal temperature offset between the CH₄-hydrate-water equilibrium curve in pure water and that in an electrolyte solution should be linearly related to the logarithm of the activity of water ($\ln a_w$) of the solution at a given pressure [cf. Piroen, 1955; Menten *et al.*, 1981]. This simple theoretical relationship can be verified with limited experimental data for artificial and actual seawater as well as for solutions containing Cl⁻, K⁺, Na⁺, and Ca²⁺ [de Roo *et al.*, 1983; Dholabhai *et al.*, 1991; Dickens and Quinby-Hunt, 1994]. Here we demonstrate that the relationship is also valid for additional solutions containing Cl⁻, SO₄²⁻, Br⁻, Na⁺, K⁺, Mg²⁺, NH₄⁺, and Cu²⁺. Thus pressure-temperature conditions that define a CH₄-hydrate-water equilibrium curve in any pore water can be estimated by calculating the $\ln a_w$ of the pore water.

Background

Methane hydrate is restricted to an uppermost depth zone of sediment columns in the marine environment. This zone, at

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any given location, lies between the sediment-water interface and the subbottom depth where the geotherm intersects a CH₄-hydrate-water equilibrium curve (Figure 1) [Kvenvolden and McMenamin, 1980].

Most BSRs on seismic reflection profiles are inferred to represent an interface between an overlying zone of CH₄ hydrate and an underlying zone of free CH₄ [e.g., Singh et al., 1993; Lee et al., 1994; Katzman et al., 1994; Singh and Minshull, 1994]. This interpretation is strongly supported by recent investigations of the Ocean Drilling Program (ODP) at the Chile Triple Junction (Leg 141 [Bangs et al., 1993; Brown and Bangs, 1995]), at the Cascadia Margin (Leg 146 [MacKay et al., 1994; Davis et al., 1995]), and at the Blake Ridge (Leg 164 [Paull et al., 1996; Holbrook et al., 1996]). Thus BSRs are widely believed to be depth coincident with an intersection of a geotherm and a CH₄-hydrate-water equilibrium curve.

Pressures and temperatures that define a CH₄-hydrate-water equilibrium curve in any given system depend on trace gas and dissolved ion concentrations [Sloan, 1990]. Incorporation of trace gases (e.g., CO₂, H₂S, ethane, and propane) into the hydrate lattice displaces the CH₄-hydrate-water equilibrium curve such that hydrate will form and/or dissociate at a higher temperature at any given pressure. Addition of dissolved ions to water shifts the CH₄-hydrate-water equilibrium curve such that

hydrate will form and/or dissociate at a lower temperature at any given pressure.

Most hydrate in the marine environment contains >98.5% CH₄ [Kvenvolden, 1993]. Thus for a given geotherm the depth range over which CH₄ hydrate is stable and the depth of a BSR are expected to depend on pore water composition. The effect of dissolved ions upon the stability range of CH₄ hydrate in the marine environment is significant. For example, at a location with a water depth of 675 m, a bottom water temperature of 5.5°C, and a geotherm of 0.051°C/m the total depth of the CH₄ hydrate stability zone would be decreased from approximately 100 m to 75 m if pure CH₄ hydrate was formed from seawater rather than pure water (Figure 1). Recent investigations at the Chile Triple Junction, Cascadia Margin, and Blake Ridge indeed have documented significant shoaling of the hydrate stability zone from that expected for the CH₄-pure water system [Brown and Bangs, 1995; Davis et al., 1995; Paull et al., 1996].

Pore waters in which CH₄ hydrate is formed are compositionally much different from seawater (and pure water) because of chemical diagenesis, ionic diffusion and fluid flow. Therefore it is of interest to investigations of natural CH₄ hydrate to know how variations in pore water composition affect the pressure and temperature conditions that define CH₄-hydrate-water equilibrium curves [Hyndman et al., 1992; Westbrook et al., 1994; Ussler and Paull, 1995; Kastner et al., 1995].

Pieroen [1955] presented a simple relationship to describe the reciprocal temperature offset (at a given pressure) between the CH₄-hydrate-water equilibrium curve of the CH₄-pure water system and that of certain CH₄-water-alcohol systems:

$$\ln a_w = \frac{\Delta H_{DIS}}{nR} \left(\frac{1}{T_d^0} - \frac{1}{T_d} \right), \quad (3)$$

where ΔH_{DIS} is the enthalpy of dissociation of CH₄ hydrate, n is the number of water molecules in the hydrate formula (CH₄· n H₂O), R is the gas constant, and T_d^0 and T_d are the temperatures at which CH₄ hydrate dissociates in pure water and in a water-alcohol solution, respectively. The equation is a formal expression of the Hammerschmidt Equation and is easily derived from classical thermodynamic theory given the following assumptions: (1) negligible CH₄ exists in water, (2) negligible water exists in gaseous CH₄, (3) ΔH_{DIS} is constant over small temperature ranges, and (4) the effect of adding alcohol is only to reduce a_w . Experimental data were shown by Pieroen [1955] to verify equation (3) for water-alcohol solutions.

Several authors [e.g., Hollister and Burruss, 1976; Menten et al., 1981; Englezos and Bishnoi, 1988; Diamond, 1994] have suggested that, similar to alcohol, the only effect of dissolved ions upon CH₄ hydrate stability conditions is to reduce a_w . Equation (3) therefore should also apply to electrolyte solutions (as mentioned by Menten et al. [1981]) and offers a very simple method to estimate pressure-temperature conditions of a CH₄-hydrate-water equilibrium curve in any given pore water (note that Englezos and Bishnoi [1988] and Dholabhai et al. [1991] have offered an alternative, yet relatively involved, statistical thermodynamic method).

Approach and Method of Study

The experimental portion of this investigation was designed to test two related hypotheses: (1) that the reciprocal temperature offset of CH₄ hydrate dissociation, $1/T_d^0$ minus

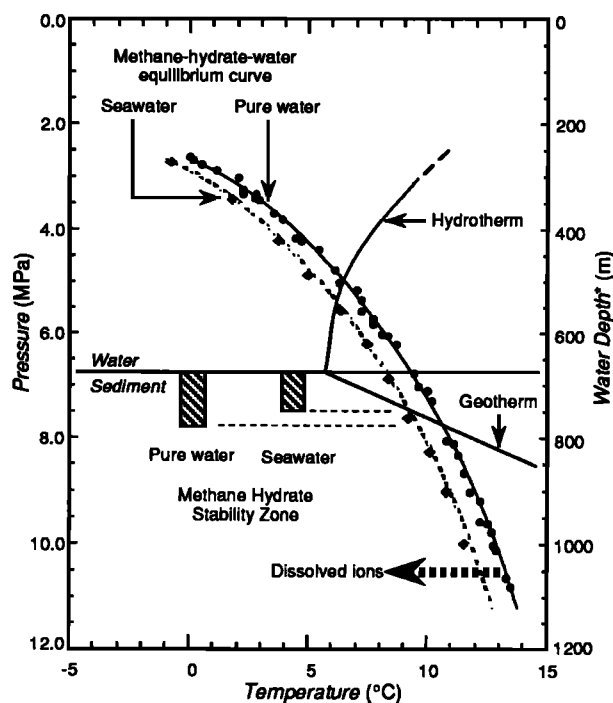


Figure 1. The zone of CH₄ hydrate stability in the marine environment lies between the sediment-water interface and the intersection of the geothermal gradient and a CH₄-hydrate-water equilibrium curve [after Kvenvolden and McMenamin, 1980]. The sediment-water interface (675 m below sea level) and geothermal gradient (5.5°C + 0.051°C/m below the seafloor) on this diagram are those for Ocean Drilling Program (ODP) Site 892 [Westbrook et al., 1994]. The depth axis on this diagram assumes a hydrostatic pressure gradient of 0.010 MPa/m. The CH₄-hydrate-water equilibrium curves for the pure water and seawater systems are from Sloan [1990] and Dickens and Quinby-Hunt [1994], respectively. Note that dissolved ions shift the CH₄-hydrate-water equilibrium curve such that the zone of CH₄ hydrate stability is shallower than would be expected from consideration of the CH₄-pure water system.

$1/T_d$, for any electrolyte solution, is linearly related to $\ln a_w$ at a given pressure; and (2) if so, that the "slope" of this relationship is equivalent to $\Delta H_{DIS}/n$. Our experimental approach was as follows.

Pressure and temperature conditions of CH_4 -hydrate-water equilibrium curves for a variety of CH_4 -water-electrolyte systems, including solutions containing SO_4^{2-} , Br^- , Mg^{2+} , NH_4^+ , and Cu^{2+} , were determined by using the experimental apparatus and procedure described by Dickens and Quinby-Hunt [1994]. The above ions were chosen because they are of particular interest to investigations in the marine environment and because previous experimental work regarding CH_4 hydrate stability conditions in electrolyte solutions have focused only on solutions containing Cl^- , Na^+ , K^+ , and Ca^{2+} (with the exception of artificial and actual seawater). Errors in reported temperatures and pressures are within 0.2°C and 0.07 MPa , and previous work has shown that our apparatus and procedure give pressures and temperatures for the CH_4 -hydrate-water equilibrium curve of the CH_4 -pure water system that are within analytical precision of those obtained by using other apparatus and procedures [cf. Sloan, 1990; Dickens and Quinby-Hunt, 1994]. Note, however, that two recent experimental investigations concerning CH_4 hydrate stability in electrolyte solutions [de Roo *et al.*, 1983; Dholabhai *et al.*, 1991] have used apparatus and procedures different from ours.

Electrolyte solutions were prepared by dissolving known masses of various salts into 250 ml of deionized water. Masses of salt were determined by using a balance with an accuracy greater than 0.001 g . Salts used in these experiments were obtained from Baker (B), Fisher (F), and Mallinkrodt (M) and included $\text{NaCl}_{(B)}$, $\text{KCl}_{(B)}$, $\text{MgSO}_{4(M)}$, $\text{NaBr}_{(M)}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}_{(F)}$, $\text{NH}_4\text{Cl}_{(B)}$, $\text{Na}_2\text{SO}_{4(B)}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}_{(B)}$. All salts have re-

ported purities in excess of 99.7% except $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which has a reported purity of 98%. Methane used in these experiments was supplied through Airco Gases and has a reported purity in excess of 99.99%.

The reciprocal temperature offset (at a constant pressure) and $\ln a_w$ were determined for each of the 10 electrolyte solutions analyzed here and for those presented by de Roo *et al.* [1983], Dholabhai *et al.* [1991], and Dickens and Quinby-Hunt [1994]. A fourth published experimental data set concerning CH_4 hydrate stability conditions in electrolyte solutions [Kobayashi *et al.*, 1951] appears to be (for an unexplained reason) incorrect [Diamond, 1994] and is not discussed in this paper. The value $1/T_d^0$ minus $1/T_d$ was determined at a constant pressure, as shown in Figure 2. The a_w for single-electrolyte solutions was calculated via the Pitzer technique

Table 1. Methane Hydrate Dissociation Temperature at Constant Pressure for Solutions Examined in This Study

Solution	T, K	P, MPa
(A) 1.998 m NaCl + 2.001 m NaCl	268.2	4.21
	269.4	4.90
	270.8	5.52
	272.8	6.89
	273.6	7.72
	274.5	8.34
(B) 1.000 m NaCl + 1.001 m KCl	271.3	3.45
	274.6	4.55
	276.3	5.58
	277.9	6.76
	279.0	7.58
	279.5	7.93
(C) 1.001 m KCl + 1.000 m MgSO_4	272.3	3.45
	274.6	4.27
	276.3	5.24
	278.6	6.69
	279.6	7.45
	279.9	7.58
(D) 1.000 m NaBr	271.8	2.69
	275.0	3.86
	277.5	5.03
	279.6	6.21
	280.5	6.89
	274.9	3.52
(E) 1.096 m MgSO_4	276.7	4.21
	279.3	5.58
	281.6	6.89
	282.3	7.65
	269.4	3.52
	271.0	4.21
(F) 1.001 m MgCl_2 + 1.000 m NH_4Cl	273.8	5.58
	274.9	6.27
	275.7	6.83
	274.4	4.21
	275.7	4.83
	277.1	5.52
(G) 0.889 m MgCl_2	278.2	6.21
	279.4	7.10
	275.8	4.14
	277.3	4.83
	279.2	5.86
	280.5	6.89
(H) 1.001 m NH_4Cl	275.1	3.45
	277.1	4.14
	278.2	4.83
	279.9	5.52
	281.3	6.55
	275.1	3.45
(I) 0.333 m CuCl_2	277.1	4.27
	278.2	4.90
	280.9	6.21
	282.1	7.03
(J) 0.394 m Na_2SO_4		

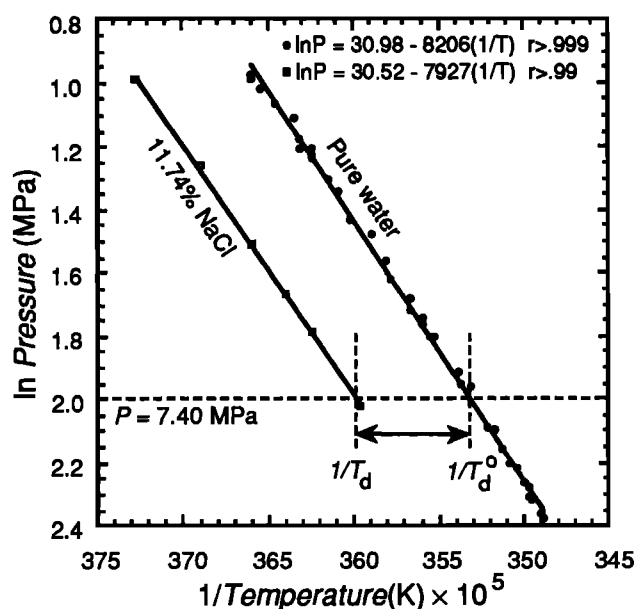


Figure 2. The reciprocal absolute dissociation temperature varies nearly linearly with the logarithm of pressure for any electrolyte solution. The reciprocal temperature offset, $1/T_d^0$ minus $1/T_d$, produced by dissolved ions in an electrolyte solution can be estimated at a given pressure from least squares error curve equations through experimental data for CH_4 hydrate stability in pure water and that in the electrolyte solution. Shown here are experimental data for CH_4 hydrate stability conditions in pure water (compiled by Sloan [1990]) and a 11.74 wt % NaCl solution [de Roo *et al.*, 1983].

(summarized by Pitzer [1991] and in Appendix 1). The a_w for mixed electrolyte solutions was calculated according to the Patwardhan and Kumar [1986] approximation (Appendix 1). This latter approach has a predictive accuracy of within 2% [Patwardhan and Kumar, 1986] and is much simpler than the rigorous ion interaction method for determining a_w of mixed electrolyte solutions [Pitzer, 1991; Clegg and Whitfield, 1991]. The Debye-Hückel parameter and virial coefficients needed for the above a_w calculations were taken from Pitzer [1991] and are for 0.1 MPa and 25°C. The choice of using the Debye-Hückel parameter and virial coefficients at standard temperature and pressure (STP) arises because values at lower temperature and, especially, higher pressure are not well constrained for many salts and because pressure-temperature corrections to these values result in slight (although significant as discussed below) changes to a_w .

Results and Experimental Discussion

Pressures and temperatures at which CH₄ hydrate dissociates in the 10 CH₄-water-electrolyte systems are reported in Table 1. The pressure-temperature conditions that define the CH₄-hydrate-water equilibrium curve for each of these electrolyte solutions (Figure 3) as well as those of de Roo *et al.* [1983], Dholabhai *et al.* [1991], and Dickens and Quinby-Hunt [1994] demonstrate that $1/T$ varies nearly linearly with $\ln P$ ($r^2 > 0.99$ for all electrolyte solutions). The slope (m) and y intercept (b) for least squares error curve equations through data in $1/T$ versus $\ln P$ space are presented in Table 2. Table 2 also lists the calculated $\ln a_w$ (at STP) for each of the experimental solutions and the observed reciprocal temperature offset between the CH₄-hydrate-water equilibrium curve of the CH₄-pure water system (compilation of Sloan [1990]) and that of CH₄-water-electrolyte systems at two pressures, $P = 3.32$ and 7.40 MPa.

The slope m is not constant for all solutions and may be explained by experimental error. For example, the observed range in m for the 10 solutions of this study is 554 (K), and this range is about that expected for our estimated analytical errors and number of analyses (≤ 6 for any solution). The observed range in m for solutions of de Roo *et al.* [1983] (799 (K)) and Dholabhai *et al.* [1991] (895 (K)), however, exceeds that expected for their reported analytical errors. Because m approximates the value $\Delta H_{\text{DIS}}/R$, the range in m therefore may suggest that CH₄ hydrate being examined in the various experiments has a range of ΔH_{DIS} (implying that n is not constant). This, in turn, could signify an inability to form CH₄ hydrate of constant composition with current apparatus and procedures, or (as suggested by de Roo *et al.* [1983]) that n and ΔH_{DIS} depend on the distribution of dissolved ions in the solution. Note, however, that data presented here and by Dholabhai *et al.* [1991] display no significant correlation between m and calculated a_w .

For the entire suite of electrolyte solutions (i.e., all those listed in Table 2 and including seawater) the observed value $1/T_d^\circ$ minus $1/T_d$ correlates well with calculated $\ln a_w$ ($r^2 > 0.996$) at any pressure spanned by the experimental data. At pressures at the limits of the data set, $P = 3.32$ MPa and 7.40 MPa, the relationship between the reciprocal temperature of dissociation and calculated $\ln a_w$ (at STP) can be described by the following empirical equations (Figure 4):

$$\ln a_w + 0.00207 = 1118(\text{K}) \left(\frac{1}{T_d^\circ} - \frac{1}{T_d} \right), P = 3.32 \text{ MPa}, \quad (4)$$

and

$$\ln a_w + 0.00624 = 1089(\text{K}) \left(\frac{1}{T_d^\circ} - \frac{1}{T_d} \right), P = 7.40 \text{ MPa}, \quad (5)$$

where K is kelvin.

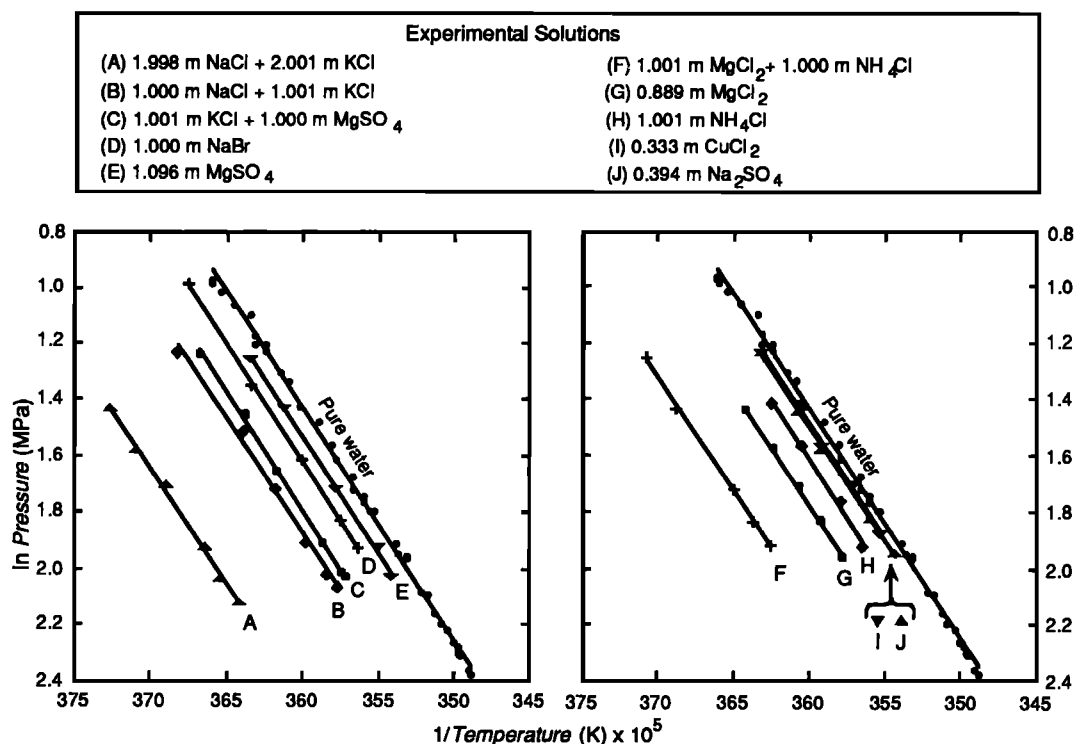


Figure 3. Methane hydrate stability conditions (in $1/T$ versus $\ln P$ space) for the 10 solutions analyzed in this study. Data for the CH₄-pure water system are from Sloan [1990].

Table 2. Parameters Describing Experimental Methane Hydrate Stability Conditions in Pure Water and Mixed Electrolyte Solutions and the Offset Between Predicted and Observed Methane Hydrate Dissociation Temperature at Two Pressures

Experimental Solution	Reference	<i>m</i>	<i>b</i>	$\ln a_w$	$1/T^\circ - 1/T, \times 10^5$		$T_{\text{observed}} - T_{\text{predicted}}, ^\circ\text{C}$	
					3.32 MPa	7.40 MPa	3.32 MPa	7.40 MPa
Deionized water	1	-8206	30.98	0.0000	0.00	0.00		
Monterey seawater (~33.5‰)	2	-8103	30.72	-0.0180	-1.47	-1.34	-0.02	-0.20
Synthetic seawater (~35‰)	3	-8343	31.59	-0.0189	-1.36	-1.52	0.11	-0.28
0.529 <i>m</i> NaCl	3	-7595	28.86	-0.0176	-1.35	-0.57	0.03	0.38
0.546 <i>m</i> NaCl + 0.428 <i>m</i> KCl	3	-7495	28.61	-0.0322	-2.85	-1.93	-0.12	0.36
0.951 <i>m</i> NaCl + 0.747 <i>m</i> KCl	3	-8144	31.15	-0.0575	-4.94	-4.86	0.02	-0.12
1.006 <i>m</i> NaCl + 1.575 <i>m</i> KCl	3	-8153	31.41	-0.0894	-7.72	-7.66	0.07	-0.01
1.069 <i>m</i> NaCl + 2.515 <i>m</i> KCl	3	-8118	31.55	-0.1281	-10.99	-10.89	0.20	0.23
2.196 <i>m</i> NaCl + 2.064 <i>m</i> KCl	3	-8113	31.76	-0.1620	-13.87	-13.76	0.31	0.41
3.330 <i>m</i> NaCl + 1.392 <i>m</i> KCl	3	-8390	33.00	-0.1897	-16.25	-16.47	0.37	0.28
0.546 <i>m</i> NaCl + 0.288 <i>m</i> CaCl ₂	3	-7945	30.28	-0.0329	-3.13	-2.81	-0.28	-0.29
1.128 <i>m</i> NaCl + 0.297 <i>m</i> CaCl ₂	3	-7971	30.52	-0.0553	-4.96	-4.67	-0.14	-0.13
1.967 <i>m</i> NaCl + 0.311 <i>m</i> CaCl ₂	3	-7898	30.48	-0.0908	-7.90	-7.52	0.03	0.19
2.030 <i>m</i> NaCl + 0.641 <i>m</i> CaCl ₂	3	-7884	30.66	-0.1205	-10.87	-10.47	-0.20	0.02
0.590 <i>m</i> NaCl + 1.036 <i>m</i> CaCl ₂	3	-8010	30.89	-0.0851	-7.81	-7.57	-0.28	-0.25
1.222 <i>m</i> NaCl + 1.073 <i>m</i> CaCl ₂	3	-8235	31.96	-0.1191	-10.69	-10.73	-0.16	-0.27
2.276 <i>m</i> NaCl	4	-7927	30.52	-0.0820	-7.06	-6.72	0.07	0.19
3.537 <i>m</i> NaCl	4	-7940	31.01	-0.1378	-12.62	-12.29	-0.34	-0.15
4.687 <i>m</i> NaCl	4	-8449	33.34	-0.1970	-17.53	-17.81	-0.06	-0.21
5.427 <i>m</i> NaCl	4	-8726	34.74	-0.2395	-21.50	-22.08	-0.17	-0.46
1.000 <i>m</i> NaCl + 1.001 <i>m</i> KCl		-7899	30.33	-0.0683	-5.87	-5.49	0.04	0.17
1.001 <i>m</i> KCl + 1.000 <i>m</i> MgSO ₄		-8084	30.91	-0.0566	-4.71	-4.56	0.06	-0.02
1.998 <i>m</i> NaCl + 2.001 <i>m</i> KCl		-7978	31.19	-0.1498	-13.03	-12.75	0.14	0.33
1.000 <i>m</i> NaBr		-8183	31.10	-0.0345	-2.56	-2.54	0.25	0.05
1.096 <i>m</i> MgSO ₄		-8026	30.45	-0.0211	-1.60	-1.39	0.07	-0.02
1.001 <i>m</i> NH ₄ Cl		-8301	31.51	-0.0325	-2.34	-2.45	0.29	-0.03
0.889 <i>m</i> MgCl ₂		-7943	30.38	-0.0513	-4.55	-4.23	-0.11	-0.07
0.394 <i>m</i> Na ₂ SO ₄		-7809	29.64	-0.0151	-1.29	-0.80	-0.09	0.02
1.001 <i>m</i> MgCl ₂ + 1.000 <i>m</i> NH ₄ Cl		-7748	30.02	-0.1034	-9.15	-8.57	-0.06	0.27
0.333 <i>m</i> CuCl ₂		-7956	30.15	-0.0153†	-1.07	-0.75	0.10	0.07

References are (1) compilation by Sloan [1990], (2) Dickens and Quinby-Hunt [1994], (3) Dholabhai *et al.* [1991], and (4) de Roo *et al.* [1983]. The parameters *m* (slope) and *b* (y intercept) are from least squares error curve equations through experimental data in $1/T$ versus $\log P$ space (Figure 4), with *T* in kelvins, and *P* in megapascals. The activity of water (a_w) has been calculated according to Pitzer [1991] for single-salt solutions and Patwardhan and Kumar [1986] for mixed electrolyte solutions. The Debye-Hückel parameter and virial coefficients used to calculate a_w are from Pitzer [1991] and are for 0.1 MPa and 25°C.

†The purity of the salt used (~98%) may introduce a significant error (~0.002) into the calculation of $\ln a_w$.

The coefficients of $1/T_d^\circ$ minus $1/T_d$ in the above equations should be equivalent to $\Delta H_{\text{DIS}}/nR$ if the assumptions behind equation (3) are valid and $\ln a_w$ for each solution has been calculated correctly. Handa [1986] determined via calorimetry that ΔH_{DIS} for $\text{CH}_4 \cdot (6.0 \pm 0.01)\text{H}_2\text{O}$ is 54.2 ± 0.28 kJ/mol (at 273 K), and these values constrain $\Delta H_{\text{DIS}}/nR$ for $\text{CH}_4 \cdot 6.0\text{H}_2\text{O}$ to between 1079 and 1093 (K). The coefficient of equation (5) therefore is within the range of $\Delta H_{\text{DIS}}/nR$ determined by calorimetry, whereas the coefficient of equation (4) is slightly (but significantly) greater than this range. These observations are explained in part by pressure-temperature effects on calculated $\ln a_w$.

Virial coefficients for NaCl and the Debye-Hückel parameter at pressures of 0.1 and 20 MPa and temperatures of 0°C, 10°C, and 25°C have been tabulated by Pitzer *et al.* [1984]. Although these values are not current (i.e., virial coefficients at STP are not identical to those of Pitzer [1991]), they can be used to evaluate general pressure-temperature effects upon calculated $\ln a_w$ (Figure 5). As exemplified by a 2.276 *m* NaCl solution, the $\ln a_w$ adjusted for pressure and temperature is slightly less than that calculated at STP when temperatures and pressures are low. With increasing pressure and temperature, however, the $\ln a_w$ adjusted for pressure and temperature approaches and surpasses that calculated at STP. Given that the magnitude of this effect is proportional to $\ln a_w$ and assuming that this effect is

similar for all electrolyte solutions, the relationship between $1/T_d^\circ$ minus $1/T_d$ and $\ln a_w$ at STP (i.e., the slope in the above equations) should be greater than that expected at low pressure and temperature, similar to that expected at moderate pressure and temperature, and less than that expected at high pressure and temperature. A variable coefficient of $1/T_d^\circ$ minus $1/T_d$ in equations such as those above reflects the use of virial coefficients and Debye-Hückel parameters at STP for conditions other than STP.

Agreement between the slopes of linear empirical equations (such as those above) and the $\Delta H_{\text{DIS}}/nR$ determined by calorimetry verifies the assumptions underlying equation (3) and clearly demonstrates that the only effect of dissolved ions on the stability of CH_4 hydrate is to reduce a_w . The agreement also implies (1) that $\Delta H_{\text{DIS}}/n$ is nearly constant over a wide range of *n* and/or (2) that the average hydrate being formed in the various experiments has a composition approximating $\text{CH}_4 \cdot 6\text{H}_2\text{O}$. Furthermore, verification of equation (3) implies that there is a linear relationship between the reciprocal temperature offset of the CH_4 -hydrate-water equilibrium curve and the freezing point depression of ice in any electrolyte solution (as alluded to by Menten *et al.* [1981]). The equation that describes the temperature depression of ice in an electrolyte solution (relative to that in pure water) is similar to equation (3):

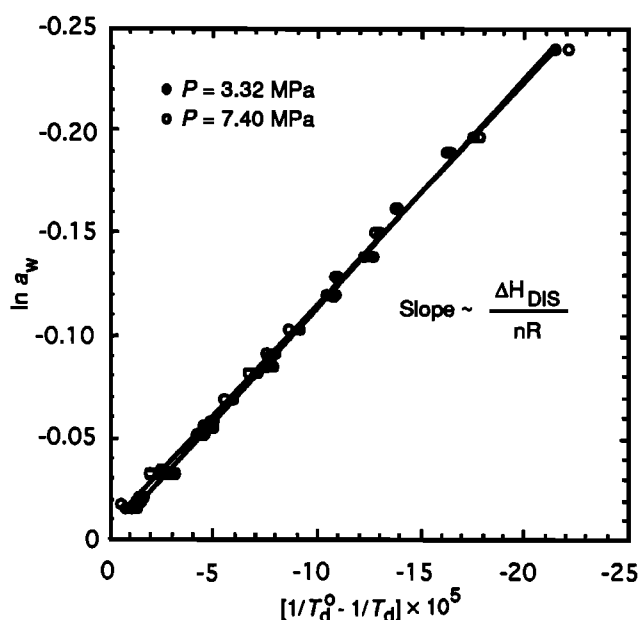


Figure 4. The relationship between the observed reciprocal temperature offset of CH_4 hydrate dissociation in an electrolyte solution and calculated $\ln a_w$ (according to Patwardhan and Kumar [1986] and Pitzer [1991]) of the solution at two pressures, 3.32 and 7.40 MPa. The correlation coefficient (r^2) between the two parameters exceeds 0.996 at any pressure between 3.32 and 7.40 MPa. The slope of this relationship is 1118 (K) at 3.32 MPa and 1089 (K) at 7.40 MPa. These slopes should be equivalent to $\Delta H_{\text{DIS}}/nR$, which is between 1079 and 1093 (K) [Handa, 1986].

$$\ln a_w = \frac{\Delta H_{\text{FUS(I)}}}{R} \left(\frac{1}{T_f^0} - \frac{1}{T_f} \right), \quad (6)$$

except that $\Delta H_{\text{FUS(I)}}$ is the enthalpy of fusion for pure water to ice (6008 J/mol at 273.2 K) and T_f^0 and T_f are the fusion (melting) temperatures of ice in pure water and an electrolyte solution, respectively. Hence, by combining and rearranging equations (3) and (6) the relationship between the temperature offset of the CH_4 -hydrate-water equilibrium curve and that of the ice-water equilibrium curve in any electrolyte solution (at constant pressure) is

$$\left(\frac{1}{T_d^0} - \frac{1}{T_d} \right)_{\text{Hydrate}} = \frac{n\Delta H_{\text{FUS(I)}}}{\Delta H_{\text{DIS}}} \left(\frac{1}{T_f^0} - \frac{1}{T_f} \right)_{\text{Ice}}. \quad (7)$$

This relationship may be of interest to shipboard investigations, inasmuch as the CH_4 -hydrate-water equilibrium curve of a particular pore water might be estimated quickly from the freezing point of the pore water.

A linear equation can be used to predict the stability conditions along a CH_4 -hydrate-water equilibrium curve in any electrolyte solution (e.g., pore waters) provided that $\ln a_w$ can be determined. The accuracy of using this approach to estimate the CH_4 -hydrate-water equilibrium curve (via $\ln a_w$ calculations according to the techniques of Patwardhan and Kumar [1986] and Pitzer [1991]) is such that a linear equation (e.g., equation (4) or (5)) can predict the CH_4 hydrate dissociation temperature within 0.46°C from that observed for any experimental solution and at any pressure between 3.32 and 7.40 MPa (Table 2). Moreover, we suggest that the primary cause

for inaccuracy (i.e., the difference in temperature between an observed value and a value predicted by a linear equation) arises from the range in m of experimental solutions and not from assumptions behind equation (1) or techniques for calculating $\ln a_w$ (indeed, there is a moderate correlation between inaccuracy and m). As such, any of the aforementioned explanations for the observed range in m could explain the inaccuracy of the method to predict stability conditions along the CH_4 -hydrate-water equilibrium curve. There are, however, two important points. If the observed range in m principally reflects experimental error, then the accuracy of using a linear equation (e.g., equation (4) or (5)) to predict a CH_4 hydrate dissociation temperature is better than 0.46°C. Likewise, if the observed range in m principally reflects differences in the ΔH_{DIS} of $\text{CH}_4 \cdot n\text{H}_2\text{O}$, then for a hydrate of a given ΔH_{DIS} (and n) the accuracy of using a linear equation to predict a CH_4 hydrate dissociation temperature is better than 0.46°C.

Methane Hydrate Stability in the Marine Environment

The stability conditions of CH_4 hydrate (assuming a fixed composition, n) in association with any marine pore water should be directly related to activity of the pore water. The inquiry of how various marine processes affect the pressure-temperature conditions of the CH_4 -hydrate-water equilibrium curve [Hyndman et al., 1992; Westbrook et al., 1994; Ussler and Paull, 1995; Kastner et al., 1995] is therefore a question of how these same processes affect a_w . Two relatively basic scenarios concerning how the CH_4 -hydrate-water equilibrium curve varies with salinity and chemical diagenesis are considered here.

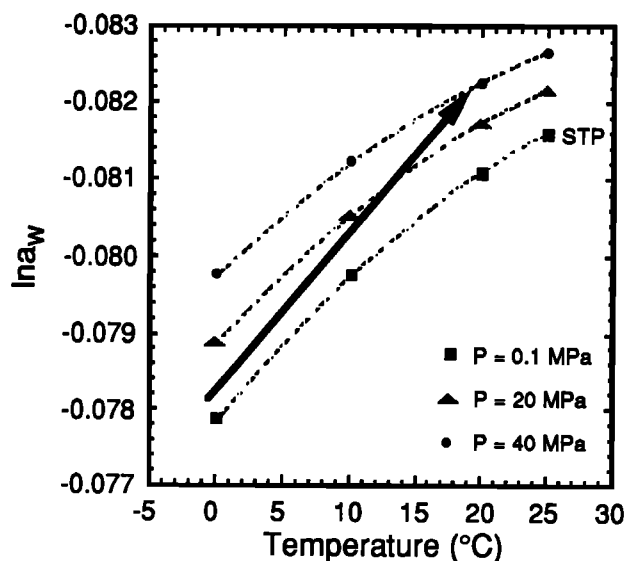


Figure 5. The effect of pressure and temperature upon calculated $\ln a_w$ for a 2.276-m NaCl solution according to data of Pitzer et al. [1984]. At relatively low pressure and temperature the $\ln a_w$ of a solution is slightly less than that calculated for the same solution at STP. However, with increasing pressure and temperature the $\ln a_w$ of a solution approaches and surpasses that calculated for the same solution at STP. Thus the linear relationship between reciprocal temperature offset of CH_4 hydrate dissociation and calculated $\ln a_w$ at STP (equations (4) and (5)) is slightly dependent on the pressure/temperature regime of interest (see text).

Table 3a. Approximate Composition of 30‰ Oxic and Euxinic Seawater in Terms of Molarity (M) and Molality (m)

Constituent Ion	Oxic Seawater		Euxinic Seawater	
	M, mol/L	m, mol/kg	M, mol/L	m, mol/kg
Cl ⁻	0.48009	0.48492	0.50700	0.51210
Na ⁺	0.41182	0.41596	0.44400	0.44847
Mg ²⁺	0.04685	0.04732	0.02780	0.02808
SO ₄ ²⁻	0.02482	0.02507	0.00000	0.00000
Ca ²⁺	0.00909	0.00918	0.00600	0.00606
K ⁺	0.00871	0.00880	0.00760	0.00768
HCO ₃ ⁻	0.00205	0.00207	0.01500	0.01515
Br ⁻	0.00072	0.00073	(0.00320)	0.00323
F ⁻	0.00006	0.00006	(0.00006)	0.00006
Sr ²⁺	0.00008	0.00008	(0.00004)	0.00004
NH ₄ ⁺	0.00000	0.00000	0.00600	0.00606

Molarity concentrations for oxic seawater are extrapolated from *Clegg and Whitfield* [1991], and molarity concentrations for euxinic seawater are from ODP Site 892 [*Westbrook et al.*, 1994]. Concentrations for Br⁻, F⁻, and Sr²⁺ are estimated for the euxinic seawater. Boric acid and trace elements are not considered here.

In determining the $\ln a_w$ of natural waters it typically is convenient to describe the mixed electrolyte solution in terms of the component neutral salts that could be combined to make the solution [e.g., *Clegg and Whitfield*, 1991]. Table 3 gives the composition of "artificial" seawater at 30‰ salinity in terms of its component neutral salts (extrapolated from *Clegg and Whitfield* [1991]) and the $\ln a_w$ of this mixed electrolyte solution (at STP) calculated by two different methods. The value -0.0161 is estimated by both a rigorous ion interaction method that includes a treatment for boric acid [*Clegg and Whitfield*, 1991] and the *Patwardhan and Kumar* [1986] approximation (using data of *Pitzer* [1991]) with no treatment for boric acid (because borate species are not amenable to this particular approach). Using equations (4) and (5) (and the parameters for the CH₄-hydrate-water equilibrium curve in the CH₄-pure water system from *Sloan* [1990]), we predict that CH₄ hydrate will dissociate in 30‰ sea water at 1.51°C at 3.32 MPa and 9.34°C at 7.40 MPa (the significant digits imply that the accuracy of equations (4) and (5) is better than 0.46°C).

Table 3b. Approximate Composition of 30‰ Oxic and Euxinic Seawater in Terms of Component Neutral Salts

Component Salt	Oxic Seawater, mol/kg	Euxinic Seawater, mol, kg
NaCl	0.36369	0.43200
Na ₂ SO ₄	0.02507	0.00000
NaHCO ₃	0.00207	0.01510
NaF	0.00006	0.00006
KCl	0.00807	0.00600
KBr	0.00073	0.00170
MgCl ₂	0.04732	0.02810
CaCl ₂	0.00918	0.00606
SrCl ₂	0.00008	0.00004
NH ₄ Cl	0.00000	0.00610
NaBr	0.00000	0.00150
$\ln a_w$	-0.0161	-0.0169

Calculated $\ln a_w$ is via the techniques of *Patwardhan and Kumar* [1986] and *Pitzer* [1991].

Table 4. Calculated $\ln a_w$ and Theoretical Methane Hydrate Dissociation T_d at 3.32 and 7.40 MPa in Various Salinities of Seawater

Seawater	Calculated $\ln a_w$	T_d at 3.32 MPa, °C	T_d at 7.40 MPa, °C
Pure water	0.0000	2.60	10.53
5‰	-0.0027 (PK)	2.41	10.33
	-0.0030 (CW)	2.39	10.31
10‰	-0.0054 (PK)	2.23	10.13
	-0.0050 (CW)	2.26	10.16
15‰	-0.0081 (PK)	2.05	9.93
	-0.0080 (CW)	2.05	9.94
20‰	-0.0103 (PK)	1.90	9.77
	-0.0101 (CW)	1.91	9.78
25‰	-0.0134 (PK)	1.69	9.54
	-0.0131 (CW)	1.71	9.56
30‰	-0.0161 (PK)	1.51	9.34
	-0.0161 (CW)	1.51	9.34
35‰	-0.0189 (PK)	1.32	9.14
	-0.0192 (CW)	1.30	9.11
40‰	-0.0216 (PK)	1.14	8.94
	-0.0222 (CW)	1.10	8.89
45‰	-0.0244 (PK)	0.95	8.73
50‰	-0.0272 (PK)	0.76	8.53
55‰	-0.0301 (PK)	0.56	8.32
60‰	-0.0330 (PK)	0.37	8.11

For calculation of $\ln a_w$, PK refers to the *Patwardhan and Kumar* [1986] approximation technique, and CW refers to ion interaction method described by *Clegg and Whitfield* [1991]. The CH₄ hydrate dissociation temperatures are determined according to equations (2) and (3) in text.

Using the same approach, CH₄ hydrate dissociation temperatures for seawater at salinities other than 30‰ can be easily calculated (Table 4). Note that the predicted dissociation temperatures for 35‰ seawater are identical to those extrapolated from "artificial" 35‰ seawater data and within 0.1°C less than those extrapolated from "actual" Monterey Bay 33.5 ± 0.5‰ seawater data (Table 2).

Bacterial methanogenesis of organic matter is believed to be the source of CH₄ for most marine hydrate [*Kvenvolden*, 1988, 1993]. Methanogenesis, however, is typically the last of a series of organic matter oxidation pathways in the marine environment [e.g., *Froelich et al.*, 1979]. Prior to methanogenesis, organic matter is degraded by oxic respiration, denitrification, Fe-Mn oxide reduction, and sulfate reduction. Each of these reactions significantly changes the chemical composition of seawater such that in sediment where methanogenesis occurs, pore waters are markedly different from seawater. They invariably are depleted in O₂ and SO₄²⁻, deficient in Ca²⁺ and Mg²⁺ (via carbonate precipitation), enriched in NH₄⁺ and various trace metals, and elevated in Br⁻ (released from organic matter). It is expected, and indeed it has been documented [*Kvenvolden and Kastner*, 1990; *Kastner et al.*, 1990; *Von Breymann et al.*, 1990; *Westbrook et al.*, 1994; *Kastner et al.*, 1995; *Paull et al.*, 1996], that CH₄ hydrate in the marine environment should occur in association with these "euxinic" (O₂ and SO₄²⁻ depleted) seawater solutions.

Table 3a provides molarities determined on ship for various ions in a ~30‰ euxinic pore water that was collected near hydrated sediment at ODP site 892 [*Westbrook et al.*, 1994]. Table 3a also gives the molalities of these ions. Table 3b gives the approximate concentrations of component neutral salts that can form such a solution. Concentrations of Br⁻, F⁻,

and Sr^{2+} were not determined on ship for this pore water; we thus have assumed molarities for these ions in accord with concentrations observed in other euxinic pore waters [Kastner *et al.*, 1990; Von Breymann *et al.*, 1990] such that the sum of component neutral salts can form the solution. Of interest in Table 3 is that the calculated $\ln a_w$ of this euxinic pore water is close to the calculated $\ln a_w$ of a similar salinity seawater solution. Hence the stability conditions of CH_4 hydrate in this particular euxinic pore water are similar to those in oxic seawater, even though the actual composition of the pore water is significantly different. Note, however, that pore water compositions determined on ship are not at in situ pressure-temperature conditions and that "core retrieval" effects on the chemical composition of pore water are poorly constrained (such as from CO_2 degassing during pressure loss; see inorganic geochemistry section, Sites 994 and 995, Paull *et al.* [1996]).

A recurring issue in geophysical literature concerns which CH_4 -hydrate-water equilibrium curve is appropriate for understanding the sedimentary zone of CH_4 hydrate and the depth of BSRs [e.g., Hyndman *et al.*, 1992; Westbrook *et al.*, 1994; Brown and Bangs, 1995; Kastner *et al.*, 1995; Davis *et al.*, 1995]. It should be clear from the work presented here that there is no unique answer to this question. A range of CH_4 -hydrate-water equilibrium curves should be expected in the marine environment. The magnitude of this range will be dictated by the natural variability of $\ln a_w$ of pore water.

Two general processes are of interest to geophysicists because they may significantly change the $\ln a_w$ of pore water from that of seawater and hence the CH_4 -hydrate-water equilibrium curve from that of the seawater system. This effect can be understood by considering the two basic parameters that affect $\ln a_w$ (equation (2)). An increase/decrease in the mole fraction of water (x_w) of an electrolyte solution will increase/decrease $\ln a_w$. Thus processes that significantly increase/decrease the salinity of a solution (even without changing the relative ionic distribution) will decrease/increase the stability of CH_4 hydrate (as discussed above and shown in Table 4). Such processes include advection and diffusion of ions that have been suggested to occur in sediment columns with CH_4 hydrate [Kastner *et al.*, 1990, 1995; Paull *et al.*, 1996].

An increase/decrease in the activity coefficient of water (γ_w) of an electrolyte solution also will increase/decrease $\ln a_w$. The γ_w of an electrolyte solution is highly dependent on the distribution of dissolved ions within the solution (because of ion-ion interactions). Thus processes that change pore water composition (even without changing the mole fraction of water) can affect pressure-temperature conditions of the CH_4 -hydrate-water equilibrium curve. For example, a 0.5 *m* MgSO_4 solution ($\ln a_w \approx -0.0095$) has a significantly higher γ_w than a 0.5 *m* MgCl_2 solution ($\ln a_w \approx -0.0255$). Anion exchange of SO_4^{2-} and 2Cl^- therefore represents a mechanism that can significantly change the stability of CH_4 hydrate in pore water.

The process of sulfate reduction should decrease $\ln a_w$ and CH_4 hydrate stability conditions in pore water. However, the $\ln a_w$ of the aforementioned euxinic pore water is similar to that of equivalent salinity oxic seawater (Table 3). It is suggested that much of this similarity arises because sufficient Ca^{2+} and Mg^{2+} have been removed from the euxinic solution (via carbonate precipitation) to compensate for the lack of SO_4^{2-} (via sulfate reduction). Suppression of carbonate precipitation (and retention of dissolved Ca^{2+} and Mg^{2+}) with low

pH and high pCO_2 is an intriguing theoretical mechanism to decrease the stability of CH_4 hydrate in euxinic pore water in relation to that in oxic seawater (assuming that pCO_2 is sufficiently low that CO_2 does not enter the hydrate lattice).

Previous workers have used experimental data for pure CH_4 -NaCl solutions in order to estimate pressure and temperature conditions of the CH_4 -hydrate-water equilibrium curve for the pure CH_4 -oxic seawater system. For equivalent salinity solutions, the $\ln a_w$ of a NaCl solution is significantly less than that of oxic seawater (in part because of SO_4^{2-} ion interaction in seawater). Thus CH_4 hydrate is significantly less stable in NaCl solutions than in equivalent salinity seawater (as observed in experimental data and noted in Dickens and Quinby-Hunt [1994]).

Recent investigations concerning in situ pressures and temperatures [Brown and Bangs, 1995; Davis *et al.*, 1995] have shown that the BSR is at a depth approximately coincident with that expected from pressure-temperature conditions of the CH_4 -hydrate-water equilibrium curve for the pure CH_4 -seawater system [Dickens and Quinby-Hunt, 1994]. Thus Brown and Bangs [1995] and Davis *et al.* [1995] have suggested that the CH_4 -hydrate-seawater equilibrium curve is appropriate for understanding the sedimentary zone of CH_4 hydrate and the depth of BSRs in the marine environment. Implicit in this suggestion is that the a_w of pore water is similar to that of seawater in all marine sediment that contains CH_4 hydrate. Although this supposition may be correct, it cannot be rigorously evaluated at present because in situ pore water compositions have not yet been determined in sediment with CH_4 hydrate. Likewise, it is unclear if (and how) capillary forces and variations in sediment composition affect pressure-temperature conditions of CH_4 -hydrate-water equilibrium curves [cf. Cha *et al.*, 1988; Ouar *et al.*, 1992; Clennell *et al.*, 1995].

Conclusion

The reciprocal temperature offset of CH_4 hydrate dissociation, $1/T_d^0$ minus $1/T_d$, is linearly related to $\ln a_w$ at a given pressure for all electrolyte solutions examined to date. The "slope" of this relationship is equivalent to $\Delta H_{\text{DIS}}/nR$. These expectations are predicted from classical thermodynamics and provide a simple approach for determining stability conditions along a CH_4 -hydrate-water equilibrium curve in any given pore water. This approach (Appendix 2) can be used to estimate CH_4 hydrate stability conditions in hypothetical pore waters and to evaluate how various processes affect CH_4 hydrate stability conditions in the marine environment.

Appendix 1: Calculation of the Logarithm of the Activity of Water

The logarithm of the activity of water ($\ln a_w$) in this paper was calculated according to the techniques of Pitzer [1991] and Patwardhan and Kumar [1986]. They have thoroughly discussed these techniques that are summarized here for the benefit of the reader. Note that $\ln a_w$ for a given solution also can be determined via relatively accessible computer programs (e.g., SOLMINEQ.88 [Kharaka *et al.*, 1988]) or freezing point information (see equation (6)).

The a_w of a solution is defined in equations (1) and (2) (see text). However, for purposes of calculation it is customary to rearrange these equations and introduce a new parameter, the molal osmotic coefficient (ϕ), that contains thermodynamic

expressions for chemical potentials [e.g., *Pitzer*, 1991]. Thus the $\ln a_w$ for single-electrolyte solutions is often rewritten as

$$\ln a_w = \frac{-18vm}{1000} \phi, \quad (8)$$

where v is the number of ions in the electrolyte formula and m is the molality of the electrolyte solution. For an electrolyte MX with v_M positive ions of charge z_M and v_X negative ions of charge z_X the molal osmotic coefficient is

$$\phi = 1 + |z_M z_X| f^\phi + m(2v_M v_X / v) B_{MX}^\phi + m^2 \left[2(v_M v_X)^{3/2} / v \right] C_{MX}^\phi, \quad (9)$$

where f^ϕ is an extended Debye-Hückel term and B_{MX}^ϕ and C_{MX}^ϕ are virial coefficients. The extended Debye-Hückel term is

$$f^\phi = -A_\phi I^{1/2} / (1 + bI^{1/2}), \quad (10)$$

where A_ϕ is the Debye-Hückel parameter, I is the ionic strength of the solution, and b is a constant. Values for A_ϕ depend on temperature and are given by *Pitzer* [1991]. The value for b is $1.2 \text{ kg}^{1/2}/\text{mol}^{1/2}$.

Virial coefficients C_{MX}^ϕ are tabulated by *Pitzer* [1991]; virial coefficients B_{MX}^ϕ are calculated as follows. For all electrolytes MX except 2-2 salts,

$$B_{MX}^\phi = B_{MX}^{(0)} + B_{MX}^{(1)} \exp(-\alpha I^{1/2}), \quad (11)$$

where $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ are parameters specific to a given electrolyte, and α has a value of $2.0 \text{ kg}^{1/2}/\text{mol}^{1/2}$ (at 25°C). For 2-2 salts (e.g., MgSO_4),

$$B_{MX}^\phi = B_{MX}^{(0)} + B_{MX}^{(1)} \exp(-\alpha_1 I^{1/2}) + B_{MX}^{(2)} \exp(-\alpha_2 I^{1/2}), \quad (12)$$

where $B_{MX}^{(0)}$, $B_{MX}^{(1)}$, and $B_{MX}^{(2)}$ are parameters specific to a given 2-2 electrolyte and α_1 and α_2 have values of $1.4 \text{ kg}^{1/2}/\text{mol}^{1/2}$ and $12 \text{ kg}^{1/2}/\text{mol}^{1/2}$, respectively (at 25°C). Note that virial coefficient parameters depend on temperature [*Pitzer*, 1991]. In calculations for this paper, virial coefficient parameters at 25°C were used for all calculations of $\ln a_w$ because these parameters have been tabulated for 25°C , because the approach for correcting the parameters to temperatures other than 25°C is relatively involved, and because the corrections are relatively minor for the temperature range of interest.

The $\ln a_w$ for mixed electrolyte solutions was determined according to the *Patwardhan and Kumar* [1986] approximation:

$$\ln a_w = \sum_k^N \left(\frac{m_k}{m_k^o} \right) \ln a_{w,k}^o, \quad (13)$$

where m_k is the molality of electrolyte k in the mixed electrolyte solution and m_k^o and $a_{w,k}^o$ are the molality and activity of water (as calculated above) of a solution containing only electrolyte k , which has the same ionic strength as that of the mixed electrolyte solution.

Appendix 2: Conditions of Methane Hydrate Stability in Seawater

In this appendix we demonstrate how the approach detailed in this paper can be used to determine a CH_4 -hydrate-water equilibrium curve for a pore water of given ionic distribution. The primary objective therefore is to calculate $\ln a_w$ of the pore water. Once $\ln a_w$ has been calculated, the CH_4 -hydrate-water equilibrium curve of the pore water system can be easily determined from that of the pure water system (e.g., equations (4) and (5)). The example presented here is oxic seawater with a salinity of 30‰.

Concentrations of dissolved ions in pore water typically are presented in units of molarity. These concentrations are converted to units of molality. This conversion is shown in Table 3 for seawater with a salinity of 30‰.

The component neutral salts that can be combined to give the total molality of each ion are then determined. For most water in the marine environment a relatively small number of component salts (<12) can characterize >99% of the total ionic distribution. Concentrations of component neutral salts in seawater with a salinity of 30‰ are given in Table 3.

The *Patwardhan and Kumar* [1986] approximation for mixed electrolyte solutions (equation (13)) requires that $\ln a_w$ of each component neutral salt be calculated at the same ionic strength (I) as that of the given pore water. For the component neutral salts in seawater with a salinity of 30‰ (Table 3), I is 0.6196. The $\ln a_w$ of each salt at this value then can be calculated using equations (8) through (10) and either equation (11) or (12) (Appendix 1). In the example presented here, consider the component salts NaCl and CaCl_2 . Tabulated values (at 25°C) for $B_{\text{NaCl}}^{(0)}$, $B_{\text{NaCl}}^{(1)}$, $B_{\text{CaCl}_2}^{(0)}$, and $B_{\text{CaCl}_2}^{(1)}$ are 0.0765, 0.2664, 0.4071, and 2.278, respectively [*Pitzer*, 1991]. Thus, at $I = 0.6196$, the virial coefficients B_{NaCl}^ϕ and $B_{\text{CaCl}_2}^\phi$ (with $\alpha = 2.0 \text{ kg}^{1/2}/\text{mol}^{1/2}$) are 0.1317 and 0.8790, respectively (equation (11)). The Debye-Hückel parameter, A_ϕ , is 0.3915 at 25°C [*Pitzer*, 1991]. The extended Debye-Hückel term f^ϕ (with $b = 1.2 \text{ kg}^{1/2}/\text{mol}^{1/2}$) is therefore -0.1585 (equation (10)). Tabulated values (at 25°C) for C_{NaCl}^ϕ and $C_{\text{CaCl}_2}^\phi$ are 0.00127 and -0.00064, respectively [*Pitzer*, 1991]. Thus, at $I = 0.6196$, the osmotic coefficient (ϕ) of NaCl ($v_M, z_M, v_X, z_X = 1$) is 0.9236 (equation (9)), and the $\ln a_w$ of NaCl is -0.0206 (equation (8)). Likewise, ϕ of CaCl_2 ($v_M, z_M, v_X, z_X = 1; z_M, v_X = 2$) is 0.8646, and the $\ln a_w$ of CaCl_2 is -0.0096. Using the same procedure, the $\ln a_w$ of other component neutral salts in seawater (Table 3) at $I = 0.6196$ are as follows: $\text{Na}_2\text{SO}_4 = -0.0084$; $\text{NaHCO}_3 = -0.0193$; $\text{NaF} = -0.0197$; $\text{KCl} = -0.0200$; $\text{KBr} = -0.0202$; $\text{MgCl}_2 = -0.0098$; and $\text{SrCl}_2 = -0.0095$.

The contribution of each component neutral salt to the total $\ln a_w$ of the mixed electrolyte solution is calculated according to equation (13). In the example presented here, consider again the component salts NaCl and CaCl_2 . Concentrations of NaCl and CaCl_2 in seawater with a salinity of 30‰ are 0.36369 and 0.00918 mol/kg, respectively (Table 3). Concentrations of NaCl and CaCl_2 in solutions containing only these salts at an ionic strength ($I = 0.6196$) equivalent to that of seawater with a salinity of 30‰ are 0.6196 and 0.2065 mol/kg, respectively. Thus the contributions of NaCl and CaCl_2 to the total $\ln a_w$ of the example solution are -0.0121 and -0.0004, respectively (above and equation (13)). The contribution of other component neutral salts (Table 3) to the total $\ln a_w$ of seawater with a salinity of 30‰ are as follows: $\text{Na}_2\text{SO}_4 = -0.0010$; $\text{NaHCO}_3 = -0.00006$; $\text{NaF} = -0.000002$; $\text{KCl} = -0.0003$; $\text{KBr} = -0.00002$; $\text{MgCl}_2 = -0.0022$; and $\text{SrCl}_2 =$

-0.000004. The $\ln a_w$ of seawater with a salinity of 30‰ is therefore -0.0161 (equation (13)).

The temperature offset between the CH_4 -hydrate-water equilibrium curve of seawater with a salinity of 30‰ and that of the pure water system can be estimated from this calculated $\ln a_w$. Using equations (4) and (5), the temperature offset for a solution with an $\ln a_w$ of -0.0161 is approximately -1.1°C to -1.2°C at a given pressure. For comparison, laboratory results indicate that the temperature offset between the CH_4 -hydrate-water equilibrium curve of actual seawater with a salinity of 33.5‰ and that of the pure water system is -1.1°C [Dickens and Quinby-Hunt, 1994].

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