

# Constructing Thermodynamic Equations for Ice-Hydrate Equilibria in Porous Media

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This work discusses the relationships among equilibrium pressure, temperature, and pore size for ice-gas hydrate equilibria in porous media. The goal is thermodynamic equations that are conceptually correct for expressing such equilibria. An equation has been proposed to describe the relationships. This new equation can be converted to a form nearly identical to the one for bulk ice-hydrate equilibria. Perhaps the most important evidence for this near-identity is the recent knowledge from experiments that the ice-hydrate equilibrium pressures of gas hydrates in pores are, within experimental resolution, independent of the pore size. Although the two equations for ice-hydrate equilibria, one for bulk hydrate and one for pore hydrate, are approximately equal to each other quantitatively, it is necessary to distinguish their physical and thermodynamic differences.

## 1 Introduction

Gas hydrates are crystalline clathrate compounds (Sloan, 1997). Water molecules form the clathrate cages via hydrogen bonds, and individual gas molecules are enclosed in these cages. It is estimated that nearly 2/3 of the earth's carbon is stored in the form of gas hydrates, with most of these hydrates being methane hydrates (Kvenvolden, 1993). Natural gas hydrates are stable in low-temperature and high-pressure conditions. They have been found in permafrost and on the ocean bottoms of most outer continental shelves. They may become the most important source of hydrocarbon energy in the future. On the other hand, the potential impact of gas hydrates on our environment has been a major concern. Hydrate dissociation from these locations may be a huge threat to the earth's atmosphere. In the past, applied research on hydrates has focused on their formation in gas/oil transmission lines, since such formation can block pipelines and cause huge industrial losses or accidents (Sloan, 1997; Kvenvolden, 1993; Hammerschmidt, 1934).

In order to explore the natural gas hydrate resource, to predict hydrate stability, and to prevent hydrate formation in gas/oil transmission, it is important to understand hydrate phase equilibria. Natural gas hydrates often are dispersed in porous media such as rock, sand, or mud. Due to surface tension effects, the equilibrium pressures of natural gas hydrate-liquid water systems in small pores is higher than that of such systems in bulk (Henry, 1999; Uchida, 1999; Seshadri, 2001; Clarke, 1999; Wilder, 2001). Thermodynamically, this is different from the addition of inhibitors to decrease the activity of water and increase the equilibrium pressures (Anderson, 1986; Munck, 1998).

Thermodynamic equations that relate equilibrium pressure to equilibrium temperature have been developed for gas hydrates in limited spaces. One such equation is as follows [see Appendix]:

$$\begin{aligned}
 - \sum_i \nu_i \ln(1 - \sum_k y_{ki}) \Big|_{pore} &= \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta h_w^{liq}}{RT^2} dT \\
 + \int_{P_0}^{P_f} \frac{2\sigma_{H-w} \cos\theta}{r} \frac{\Delta v_w^{liq}}{RT_f} dP - \ln(\gamma_w X_w) & \\
 + \frac{2\sigma_{H-w} V_l}{rRT_f} \cos\theta & \\
 (T_f \geq T_q) & \quad (1)
 \end{aligned}$$

The solution of the above equation gives a different pore-size-dependent pressure vs temperature profile ( $P$ - $T$  profile) for the hydrate-liquid water equilibrium in each different size pore. Since virtually all porous media have pores of many different sizes, each size pore has a different  $P$ - $T$  profile at temperatures above its quadruple point. As discussed below, for bulk hydrate-ice equilibria at lower temperatures, the terms that contain surface tension and the term that contain water activity vanish, the parameters relating to liquid water should be replaced with those related to ice, and the equation becomes,

$$\begin{aligned}
 - \sum_i \nu_i \ln(1 - \sum_k y_{ki}) \Big|_{bulk} &= \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta h_w^{sol}}{RT^2} dT \\
 + \int_{P_0}^{P_g} \frac{\Delta v_w^{sol}}{RT_f} dP & \quad (2)
 \end{aligned}$$

Equation 2, however, can only be applied to ice-bulk

hydrate equilibria, as indicated by the subscript of the term on the left of the equation. The standard state chemical potential  $\Delta\mu_w^0$  is for the standard state temperature  $T_0 = 273.15$  K, which is the quadruple point temperature of a bulk hydrate. (Above this temperature the hydrate is in equilibrium with liquid water, and below this temperature the hydrate is in equilibrium with ice.)

When the hydrate is finely dispersed, hydrate, gas, liquid water and ice reach their four-phase equilibrium at a temperature lower than 273.15 K; the amount of quadruple point lowering depends on the pore size. Between the pore quadruple point temperature,  $T_q$ , and the normal ice melting point temperature of 273.15 K, hydrate in pores will coexist with pore water, and surface tension effects will be operative. Equation (2), therefore, does not apply between  $T_q$  and  $T_0$ ; instead equation (1) is still applicable. For hydrates in pores below the quadruple point temperature of the pore hydrate,  $T_q$ , neither of the above equations is applicable. Equation (1) only applies to liquid water-hydrate equilibria. Equation (2) is no longer correct, because the path of the integral for the temperature and pressure corrections has to cover both the liquid water-hydrate and ice-hydrate equilibria. This paper proposes a solution to this problem.

## 2 Analysis and Solution

Since the thermodynamic properties of water change dramatically at the ice-water transition point, it is necessary to split all the relevant terms into two sections, *i.e.* for liquid and solid water regions respectively and deal with them separately.

The chemical-potential difference between an empty hydrate cavity and ice at any given temperature can be obtained by adding a term of correction to that measured at a standard condition,  $(T_0, P_0)$ . The correction is expressed as an integral over a certain path along which temperature and pressure change. Here we choose the path from A to B to C where A is at the standard reference point  $(T_0, P_0)$ , B is the quadruple point of hydrate in pore of radius  $r$ ,  $(T_q, P_q)$ , and C is the final state of interest. State C is at the formation or equilibrium condition  $(T_f, P_f = P_g)$ , where  $P_g$  denotes the gas pressure at the equilibrium.

Since the first integral is within the region of liquid water-hydrate equilibrium, it can be expressed as

$$\begin{aligned} \left. \left( \frac{\Delta\mu_w}{RT} \right)_{pore} \right|_{A-B} &= \frac{(\Delta\mu_w^q)}{RT_q} \\ &= \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_q} \frac{\Delta h_w^{liq}}{RT^2} dT + \int_{P_0}^{P_i=P_q} \frac{2\sigma_{H-w} \cos \theta}{r} \frac{\Delta v_w^{liq}}{RT_q} dP \\ &\quad - \ln(\gamma_w X_w) \Big|_{T \rightarrow T_0} + \frac{2\sigma_{H-w} V_l}{rRT_q} \cos \theta \end{aligned} \quad (3)$$

$(T_0 > T > T_q)$

Note that  $P_l$  here is the pressure on the liquid, aqueous phase.

In the attempt to find an expression for the second half of the integration, it is appropriate to hypothesize that the term for interfacial tension between two solids, the ice and the hydrate, should approximately disappear—this follows from the hypotheses that (1) the operative interface is between hydrate and water and (2) the tension between liquid water and hydrate is approximately equal to the tension between liquid water, so that (3) the tension between ice and hydrate is very small. For hydrocarbon guests the term representing the effect of solubility on the potential energy usually is, and can be, similarly ignored. One therefore can write

$$\begin{aligned} \left. \left( \frac{\Delta\mu_w}{RT} \right)_{pore} \right|_{B-C} &= \int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP + \int_{P_0}^{P_i=P_q} \frac{\Delta v_w^{ice}}{RT_f} dP \\ &\quad - \int_{T_q}^{T_f} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_q}^{P_f=P_i} \frac{\Delta v_w^{ice}}{RT_f} dP \\ &= \int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP - \int_{T_q}^{T_f} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_g} \frac{\Delta v_w^{ice}}{RT_f} dP \end{aligned} \quad (4)$$

$(T < T_q)$

Here  $P_i$  is the pressure on the ice phase, and the second and the fourth terms in the first line on the right of the previous equation have been combined and become the third term in the last line.

In the last line of equation (4), the first term accounts for the dimensionless energy change from state  $(T_q, P_q)$  to  $(T_q, P_0)$ , with  $T$  being constant and equal to  $T_q$ ; the second term is from  $(T_q, P_0)$  to  $(T_f, P_0)$ , the pressure being the reference pressure,  $P_0$ ; and the third term is from  $(T_f, P_0)$  to  $(T_f, P_g)$ , at the temperature at which the system reaches the hydrate-ice equilibrium.

The total of the integral then becomes

$$\begin{aligned}
\left(\frac{\Delta\mu_w}{RT_f}\right) &= \left(\frac{\Delta\mu_w}{RT}\right)_{pore} \Big|_{A-B} + \left(\frac{\Delta\mu_w}{RT}\right)_{pore} \Big|_{B-C} \\
&= \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_q} \frac{\Delta h_w^{liq}}{RT^2} dT + \int_{P_0}^{P_i=P_q} \frac{2\sigma_{H-w} \cos \theta}{r} \frac{\Delta v_w^{liq}}{RT_q} dP \\
&\quad - \ln(\gamma_w X_w) \Big|_{T_q} + \frac{2\sigma_{H-w} V_l}{rRT_q} \cos \theta \\
&\quad + \int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP - \int_{T_q}^{T_f} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_g} \frac{\Delta v_w^{ice}}{RT_f} dP
\end{aligned}
\tag{5}$$

At equilibrium,

$$\Delta\mu_H = \Delta\mu_w \tag{6}$$

Introducing equation a-(4) (Appendix) and equation (5) into (6), one has

$$\begin{aligned}
& - \sum_i v_i \ln(1 - \sum_k y_{ki}) \Big|_{pore} \\
&= \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_q} \frac{\Delta h_w^{liq}}{RT^2} dT + \int_{P_0}^{P_i=P_q} \frac{2\sigma_{H-w} \cos \theta}{r} \frac{\Delta v_w^{liq}}{RT_q} dP \\
&\quad - \ln(\gamma_w X_w) \Big|_{T_q} + \frac{2\sigma_{H-w} V_l}{rRT_q} \cos \theta \\
&\quad + \int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP - \int_{T_q}^{T_f} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_g} \frac{\Delta v_w^{ice}}{RT_f} dP
\end{aligned}
\tag{7}$$

or, by further combing equation (3), one arrives at

$$\begin{aligned}
& - \sum_i v_i \ln(1 - \sum_k y_{ki}) \Big|_{pore} = \left(\frac{\Delta\mu_w^q}{RT_q}\right) + \\
& \int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP - \int_{T_q}^{T_f} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_g} \frac{\Delta v_w^{ice}}{RT_f} dP
\end{aligned}$$

Both equation (7) and (8) can be used to determine the equilibrium pressure of hydrate in any size pore below the quadruple point temperature of that size of pore.

In comparison with equation (2) there are a number of

extra terms in equation (7). In particular,

Term  $\int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP$  compensates for the energy

difference caused by the change of temperature from  $T_q$  to  $T_f$ . More importantly, the solution for the equilibrium pressure in equation (7) will be independent to the pore size, although the equation appears to contain the terms affected by surface tension and therefore by pore size. The proof of this point is as follows.

### 3 Pore Size Independence of the Equilibrium Pressure of Hydrate-ice System

Experiments have shown that below  $T_q$  the equilibrium pressure of a hydrate in pores of any size is the same (within experimental resolution) regardless of the size of the pores (Zhang,2002). Secondly, below the ice melting point, the effective concentration and activity of water is always one. Hence, the chemical potential of the water on the equilibrium  $P$ - $T$  line is only a function of temperature.

At  $T < T_q$ , the right hand side of equation (2) can be expanded and rearranged into the following equation:

$$\begin{aligned}
& - \sum_i v_i \ln(1 - \sum_k y_{ki}) \Big|_{bulk} = \\
& \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_q} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_q} \frac{\Delta v_w^{ice}}{RT_q} dP + \int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP \\
& - \int_{T_q}^{T_f} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_g} \frac{\Delta v_w^{ice}}{RT_f} dP
\end{aligned}
\tag{9}$$

Apparently, the sum of the first three terms in the last line

of equation (9) is equal to  $\left(\frac{\Delta\mu_w^q}{RT_q}\right)$ , since this sum is

equivalent to a integral from  $(T_0, P_0)$  to  $(T_q, P_q)$  along the ice-hydrate equilibrium line for the bulk condition; *i.e.*,

$$\left(\frac{\Delta\mu_w}{RT}\right)_{bulk} \Big|_{A-B} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_q} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_q} \frac{\Delta v_w^{ice}}{RT_q} dP$$

T

(10)

Now we need to prove that

$$\left(\frac{\Delta\mu_w}{RT}\right)_{bulk} \Big|_{A-B} = \left(\frac{\Delta\mu_w}{RT}\right)_{pore} \Big|_{A-B} \quad (11)$$

Experiments (Zhang,2002) have indicated that the quadruple points of ice-water-hydrate-gas equilibria in pores of different pore size should all fall on the equilibrium  $P$ - $T$  line of the bulk hydrate. In other words, the state of  $(T_q, P_q)$  is reachable along the ice-hydrate equilibrium line of the bulk condition. Equation (11) is therefore true for any pore size, because both sides are the chemical potential difference between the same start and end states; *i.e.*, both are from  $(T_o, P_o)$  to  $(T_q, P_q)$ .

On the other hand, though different integration paths were taken, the results from both paths turn out to be the unit energy difference between the standard reference point and the quadruple point of hydrate in pores of radius  $r$ ; therefore,

$$\left(\frac{\Delta\mu_w}{RT}\right)_{bulk} \Big|_{A-B} = \left(\frac{\Delta\mu_w}{RT}\right)_{pore} \Big|_{A-B} = \frac{\Delta\mu_w^q}{RT_q} \quad (12)$$

Introducing (10-12) into equation (9), one has

$$\begin{aligned} & -\sum_i \nu_i \ln(1 - \sum_k y_{ki}) \Big|_{bulk} \\ & = \frac{\Delta\mu_w^q}{RT_q} - \int_{T_q}^{T_f} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_g} \frac{\Delta v_w^{ice}}{RT_f} dP + \int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP \end{aligned} \quad (13)$$

$(T < T_q)$

Comparing equation (13) with equation (8) for pore hydrate, one is clear that the formulas on the right-hand sides of the two equations are identical. Equations (13) and (8) are a pair of mathematical expressions indicating that the ice-hydrate equilibrium pressure for pore hydrate is the same as that of bulk hydrates, if they are at the same temperature.

#### 4 Discussion

Evidence for the approximate equality of the equations of ice-hydrate equilibria for the bulk and porous condition rests on the experimental evidence; *i.e.*, experiments indicate that the pressures for ice-hydrate equilibria in pores are essentially independent of pore size from the smallest pores studied (about 2 nm radius) up to pores of “infinite radius” (bulk hydrate). Below the quadruple point temperature, therefore, the chemical potential

difference between an empty hydrate cavity and pore ice is the same as the chemical potential difference between the empty cavity and bulk ice, *i.e.*

$$\Delta\mu_{ice,pore} \Big|_{T_f < T_q} = \Delta\mu_{ice,bulk} \Big|_{T_f < T_q} .$$

For numerical purposes, equation (2) for the hydrate-ice equilibrium of a bulk hydrate can thus be employed to determine the equilibrium pressures of this (chemically) same hydrate in pores below their (pore-size dependent) quadruple points.

The quadruple point temperature is the highest temperature for which the equilibrium pressure of a pore hydrate is essentially independent of its pore size. A

dimensionless chemical potential difference,  $\left(\frac{\Delta\mu_w}{RT_f}\right)$ ,

between an empty cavity and ice at an equilibrium condition  $(T_f, P_f)$  can be referenced to the corresponding

term  $\left(\frac{\Delta\mu_w^q}{RT_q}\right)$  for a different reference point  $(T_q, P_q)$ . The

difference between  $\left(\frac{\Delta\mu_w}{RT_f}\right)$  and  $\left(\frac{\Delta\mu_w^q}{RT_q}\right)$  should only be

due to the effects of temperature and pressure that are described by the sum of the last three terms of equations (8) or (13), *i.e.*,

$$\int_{P_i=P_q}^{P_0} \frac{\Delta v_w^{ice}}{RT_q} dP - \int_{T_q}^{T_f} \frac{\Delta h_w^{ice}}{RT^2} dT + \int_{P_0}^{P_i=P_g} \frac{\Delta v_w^{ice}}{RT_f} dP .$$

These integrals, which account for the effects of solubility and interfacial tension, should become negligible for hydrates with small guest solubilities in water in all but the very smallest pores.

Although the thermodynamic equation for ice-hydrate equilibria of pore hydrates can be approximated by a form that is mathematically identical to the equation for the bulk ice-hydrate equilibrium, this is a physical as well as mathematical approximation. If this is unclear, mistakes may lead to conflicting results. For example, one might carelessly use equation (2) for pore hydrate with the upper temperature of integration falling between the normal ice melting point of 273.15 K and the quadruple point of a pore hydrate, a condition that fails equation (2). Being aware that an integral path is going to pass the ice-water transition point at  $T_q$  and therefore different thermodynamic properties should apply to each side of the ice-water transition point, one may become confused if equation (2) for the bulk hydrate is still employed for the calculation of equilibrium pressure for a pore hydrate.

#### 5 Conclusion

A thermodynamic equation has been developed for

ice-hydrate equilibria in porous media. This equation takes into account the difference in the properties of water below and above the melting point of pore ice (*i.e.*, the quadruple point of a pore hydrate). Experiments indicate that at temperatures below the quadruple point of a pore hydrate the equilibrium pressure of the hydrate is independent of the pore size. Hence, it is concluded that the equation for the ice-hydrate equilibrium in pores can be converted into a form which is approximately identical to the equation for the bulk ice-hydrate equilibrium. Therefore, numerically, the equilibrium pressure of a pore hydrate at below quadruple point can be calculated via the use of the thermodynamic equation for bulk hydrate. However, conceptually one needs to realize that although the equations are approximately the same, the bulk- and pore-hydrate equilibria are physically and thermodynamically distinct.

## Appendix

The method for predicting the hydrate-water- gas equilibrium is based on the criterion that at equilibrium, the chemical potential of hydrate,  $\mu_H$ , is the same as that of water,  $\mu_w$ , in either the water rich phase or ice phase (Saito,1964;Holder,1988).

$$\mu_w = \mu_H \quad (a-1)$$

With an imaginary state of empty hydrate cage of a chemical potential,  $\mu_\beta$ , either side of above equation can be replaced by their difference from the chemical potential of an unoccupied hydrate lattice and that of the water phase and hydrate phase.

$$\Delta\mu_w = \mu_\beta - \mu_w \quad (a-2)$$

$$\Delta\mu_H = \mu_\beta - \mu_H \quad (a-3)$$

Following the van der Waals and Platteeuw equation (1959) one has

$$(\Delta\mu_H) = -RT \sum_i v_i \ln(1 - \sum_k y_{ki}) \quad (a-4)$$

where  $y_{ki}$  is the fractional occupation of cavity type  $i$ , and

$$y_{ki} = \frac{C_{ki} f_k}{1 + \sum_j C_{ji} f_j} \quad (a-5)$$

In above equation,  $f_k$ , is the fugacity of gas  $k$ . A

modified Redlich-Kwong equation of state can be employed to calculate the fugacity (Peng, 1976).  $C_{ki}$  is the Langmuir constant for gas  $k$  in cavity  $i$ . Two methods have been used to calculate the Langmuir constants. One is a parameter fitting method as suggested by Munck (1998). The other involves the calculation of potential wells (Sloan,97; McKoy, 1963).

For an ideal solution of water, the following relationship obtains (Holder,1988):

$$\Delta\mu_w = \Delta\mu_w'(X_w = 1.0) - RT \ln(\gamma_w X_w) \quad (a-6)$$

Here  $X_w$  is the mole fraction and  $\gamma_w$  is the activity coefficient of water in the water-rich phase;  $\Delta\mu_w'$  is a function of pressure and temperature only and can be written as

$$d\left(\frac{\Delta\mu_w'}{RT}\right) = -\left(\frac{\Delta h_w'}{RT^2}\right)dT + \left(\frac{\Delta V_w'}{RT}\right)dP \quad (a-7)$$

where  $\Delta h_w'$  is the molar enthalpy and  $\Delta V_w'$  the mole-volume difference between the empty hydrate and pure ice( $T < T_0$ ) or liquid water ( $T > T_0$ ) phases.

Integration of equation (a-7) and combining it with equation (a-2) and (a-6) gives,

$$\frac{(\Delta\mu_w)}{RT_f} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta h_w}{RT^2} dT + \int_{P_0}^{P_f} \frac{\Delta v_w}{RT_f} dP - \ln(\gamma_w X_w) \quad (a-8)$$

For the study of hydrate formation in pores, Clarke (1999), Henry (1999), and Clennell (1999), and Wilder(2001) have considered that an additional term should be added to above equation to reflect the effect of surface energy on the chemical potential change. Equation (a-8) is therefore corrected to the form,

$$\frac{(\Delta\mu_w)}{RT_f} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta h_w^{liq}}{RT^2} dT + \int_{P_0}^{P_f} \frac{\Delta v_w}{RT_f} dP - \ln(\gamma_w X_w) + \frac{2\sigma V_l}{rRT_f} \cos \theta \quad (a-9)$$

Here  $V_l$  is the mole volume of water ( $V_l = 18.016$  m<sup>3</sup>/mole),  $\sigma$  the surface tension, and  $\theta$ , the contact angle. It is assumed that  $\theta = 0$ . The upper limit of intergration for the third term on the right is related to the total gas pressure by the Young-Laplace equation of the form,

$$P_l = P_g - \frac{2\sigma}{r} \cos \theta \quad (\text{a-10})$$

Henry(1999) and Clennell (1999) suggested that for the liquid water-hydrate equilibrium in porous media, the operating surface tension,  $\sigma$ , should be the interfacial tension between liquid water and hydrate. Combining equation (a-1), (a-2), (a-3), (a-4) and equation (a-9), therefore, one arrives at

$$\begin{aligned} - \sum_i v_i \ln(1 - \sum_k y_{ki}) \Big|_{\text{pore}} &= \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta h_w^{\text{liq}}}{RT^2} dT \\ + \int_{P_0}^{P_l = P_g - \frac{2\sigma_{H-w}}{r} \cos \theta} \frac{\Delta V_w}{RT_f} dP - \ln(\gamma_w X_w) & \\ + \frac{2\sigma_{H-w} V_l}{rRT_f} \cos \theta & \\ (T_f \geq T_q), & \quad (\text{a-11}) \end{aligned}$$

where the subscript of the term on the left hand side of the equation indicates the term is for pore hydrate. The variable,  $\sigma_{H-w}$ , in the last term on the right denotes the interfacial tension between hydrate and liquid water.

## Nomenclature

$\Delta\mu_w$	Difference in chemical potential between empty hydrate cage and ice or aqueous phase in equilibrium with hydrate, and $\Delta\mu_w^0$ , the one at standard state.
$\Delta V_w$	Difference in mole volume between empty hydrate and the $\alpha$ phase, the phase in equilibrium with hydrate, which can be ice, water or aqueous solutions.
$\Delta h_w$	Difference in enthalpies between empty hydrate and the $\alpha$ phase.
$V_i$	Number of type $i$ cavities per water molecule.
$V_w$	Mole volume of water, $V_w = 18.016 \text{ m}^3/\text{mole}$ .
$\gamma_w$	Activity coefficient of liquid water
$X_w$	Molar fraction of water
$\sigma_{H-w}$	Surface tension (surface energy per unit area) of hydrate-water interface
$\theta$	Porous host-water contact angle.
$r$	Pore radii.
$R$	Gas Constant.
$y_{ki}$	The fractional occupation of cavity type $i$ , and
$C_{ki}$	Langmuir constants of the cavity $i$ for gas $k$ .
$T$	Temperature( $T_p$ , $T$ at formation, $T_0$ , $T$ at Standard Condition, and $T_q$ , $T$ at quadruple

point.

$P$  Pressure( $P_l$ ,  $P$  on liquid phase;  $P_g$ ,  $P$  on gas phase;  $P_i$ ,  $P$  on ice phase, and  $P_0$ ,  $P$  at standard condition,  $P_q$ ,  $P$  at quadruple point, etc..

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