Thermodynamic and Kinetic Modeling of CH4/CO2 Hydrates Phase transitions

B. Kvamme[1], K. Baig, M. Qasim and J. Bauman

Abstract—Natural gas hydrates in reservoirs are thermodynamically unstable due to exposure to mineral surfaces and possibly undersaturated phases of water and hydrate formers. Changes in global temperatures also alter the stability regions of the accumulations of gas hydrates worldwide. The fact that hydrates in porous media never can reach equilibrium, and formation can occur from different phases, as well as dissociate according to different thermodynamic driving forces imposes very complex phase transition dynamics. These phase transitions dynamics are solutions to coupled differential equations of mass transport, heat transport and phase transition kinetics. The availability of free energy as functions of temperature, pressure and the composition of all components in all phases in states outside of equilibrium is therefore necessary in kinetic theories based on minimisation of free energy. For this purpose we have applied an extended adsorption theory for hydrate, SRK equation of state for methane/CO2 gas and solubilities of these components in water for the limit of water thermodynamics. The thermodynamic model is developed for calculation of free energy of super saturated phase along all different gradients (mole fractions, pressure and temperature) of super saturation.

Keywords—Gas hydrates, Kinetic modeling, Phase transitions, Thermodynamics.

I. INTRODUCTION

GAS as hydrates are crystalline solids which occur when water molecules form a cage like structure around a non-polar or slightly polar (eg. CO2, H2S) molecule. These enclathrated molecules are called guest molecules and obviously have to fit into the cavities in terms of volume. In this work we focus on two specific guest molecules; carbon dioxide (CO2) and methane (CH4). Processing, transport and storage of carbon dioxide and potential hydrate formation is a

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timely issue. Natural gas is dominated by methane and processing as well as transport of methane involves conditions of hydrate stability in terms of temperature and pressure. In addition to methane from conventional hydrocarbon reservoirs huge amounts of methane is trapped inside water in the form of hydrates. Both of these guest molecules form structure I hydrate with water. Macroscopically, hydrates are similar in appearance to ice or snow. At sufficiently high pressure, hydrates are also stable at temperatures where ice cannot form. The encaged guest molecules are able to stabilize the hydrate through their interactions with the water molecules making up the cavity walls.

The description of hydrate phase thermodynamics typically follows the approach pioneered by van der Waal & Platteeuw [1]. A disadvantage of this simplified semi grand canonical ensemble result is that the empty clathrate were considered as rigid and unaffected by the inclusion of guest molecules. Another disadvantage in the typical engineering use of this is the lack of values for empty clathrate which have led to the use of chemical potential of liquid water (or ice) minus that of empty clathrate. This involves that a number of fundamental thermodynamic properties have been fitted empirically. An alternative form was derived by Kvamme & Tanaka [2] and examined using molecular dynamics simulations and two models for estimation of cavity partition function. The first was the classical integration over the Boltzmann factor for the cavity partition function using a rigid water lattice and the second one was a harmonic oscillator approach with full dynamics of all molecules and sampling of frequencies for displacements. An advantage of the latter approach is the sampling of frequencies that interferes with water lattice movements and reduces the stabilization of the cavity, which leads to approximately 1 kJ/mole difference in chemical potential of hydrate water at 0 °C compared to the classical rigid cavity integration for CO2. In contrast a small molecule like for instance methane does not significantly affect the water movements [2]. Empirical corrections are often introduced to correct for these effects as well as other shortcomings in the original van der Waal & Platteeuw formulation. An example of this is due to John & Holder [3]. The thermodynamic model is enhanced to calculate free energy of hydrate by inclusion of free energy gradient with respect to mole fraction, pressure and temperature. The use of these gradients will describe the phase transition kinetics in terms of the phase field theory (PFT) in presence of ice.

Carbon dioxide hydrate is more stable than methane hydrate

over a large range of conditions. Furthermore - the filling of methane in small cavities makes this mixed hydrate more stable at all conditions (fig.1).
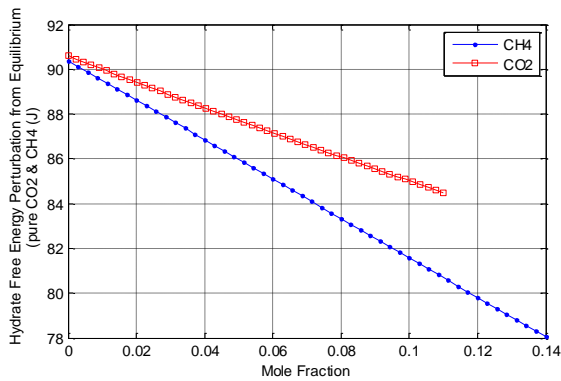

Figure 1: Perturbation due to pressure, temperature and composition gradients in CH4 and CO2 hydrate free energy from equilibrium.

This opens up for a novel technique for exploitation of methane form hydrates by injection of carbon dioxide. This is a win-win situation that also ensures long term storage of carbon dioxide as hydrate. And since pure carbon dioxide and pure methane both forms structure I it is straightforward to evaluate the changes in free energy as function of pressure and temperature in order to evaluate the thermodynamic control mechanisms.
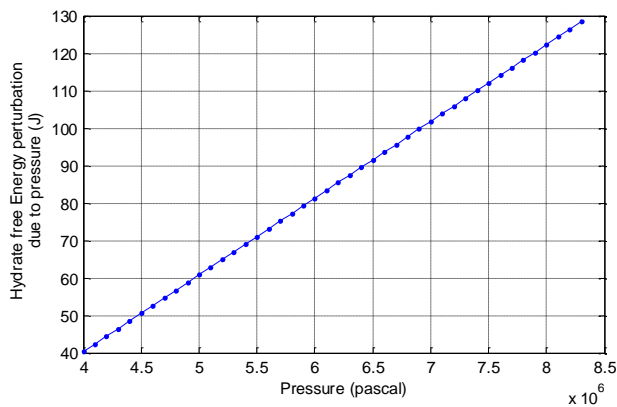

Figure 2: Perturbation in hydrate free energy from equilibrium due to pressure gradient term at constant temperature and composition.

Figure 2 shows the calculated free energy changes for mixed hydrate at constant temperature and constant mole fraction at different pressures in between 40 bar and 83 bar, this perturbation from equilibrium due to pressure gradient is increasing   by   increasing   pressure.
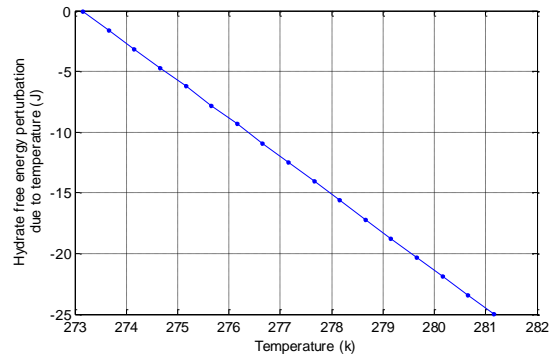

Figure 3: Perturbation in hydrate free energy from equilibrium due to temperature gradient at constant pressure of 20 bar and constant mole fraction.

Figure 3 shows the Free energy perturbation away from equilibrium is decreasing due to increase in temperature at constant pressure. Figure 4 is given to see the effect of temperature gradient on the free energy with variation in mole fractions at constant temperature and pressure.
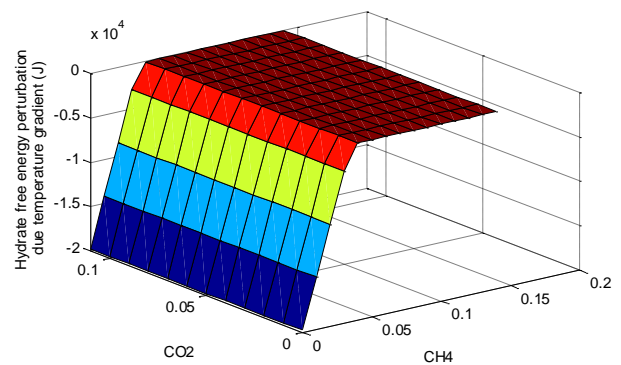

Figure 4: Perturbation in hydrate free energy perturbation from equilibrium with variation in compositions at constant temperature and pressure.

II. HYDRATE THERMODYNAMICS

The Gibbs free energy of the hydrate phase is written as a sum of the chemical potentials of each component [4].

$$G_H = \sum_{r=CO2,CH4,water} x_r \mu_r^H \qquad (1)$$

where μ_r^H and x_r is chemical potential and mole fraction of component r respectively. G_H is the free energy of hydrate. In the earlier work due to Svandal et al. [4] a simple interpolation in mole-fractions was used between pure CH4 hydrate and pure CO2 hydrate, which was considered as sufficient to theoretically illustrate the exchange concept under phase field theory. This will of course not reproduce the absolute minimum in free energy for a mixed hydrate in which CH4 occupies portions of the small cavities and increases stability over pure CO2 hydrate. The expression for free energy

gradients with respect to mole fraction, pressure and temperature is:

$$G_H^{EXP} = G^{EQ} + \sum_r \frac{\partial G_H}{\partial x_r}\Bigg|_{P,V,T,x_{i \neq r}} (x_r^{act} - x_r^{EQ})$$
$$+ \frac{\partial G_H}{\partial P}\Bigg|_{T,V,\vec{x}} (P^{act} - P^{EQ}) \qquad (2)$$
$$+ \frac{\partial G_H}{\partial T}\Bigg|_{P,V,\vec{x}} (T^{act} - T^{EQ})$$

Here G_H^{EXP} is the free of hydrate away from equilibrium. G^{EQ} is free energy at equilibrium. In the earlier work [6] the mass balance of a hydrate is given by:

$$x_w + x_c + x_m = 1 \qquad (3)$$

Which is of course being conserved inside the integration of the free energy functional but in the contour maps of the free energy of supersaturation with respect to concentrations different levels of concentration supersaturations in different directions (water, CO2, CH4) is not conserved and has to be evaluated as orthonormal gradient effects outside of equilibrium. In simple terms that means:

$$\left(\frac{\partial x_z}{\partial x_r}\right) \begin{cases} 0, z \neq r \\ 1, z = r \end{cases} \qquad (4)$$

Where z and r both represent any of the components of the hydrate: water, methane, and carbon dioxide. This is just means that the mole fractions are all independent. Using equation (1) we simply take the derivative with respect to one of the mole fractions ($r = m, c,$ or w):

$$\frac{\partial G_H}{\partial x_r} = x_c \frac{\partial \mu_c^H}{\partial x_r} + x_m \frac{\partial \mu_m^H}{\partial x_r} + x_w \frac{\partial \mu_w^H}{\partial x_r} + \mu_c \frac{\partial x_c}{\partial x_r} + \mu_m \frac{\partial x_m}{\partial x_r}$$
$$+ \mu_w \frac{\partial x_w}{\partial x_r},$$

The mole fraction derivatives in above equation simply collapse by using equation (4) for mole fraction independence to get:

$$\frac{\partial G_H}{\partial x_r} = x_c \frac{\partial \mu_c^H}{\partial x_r} + x_m \frac{\partial \mu_m^H}{\partial x_r} + x_w \frac{\partial \mu_w^H}{\partial x_r} + \mu_r \frac{\partial x_r}{\partial x_r} \qquad (5)$$

It was previously shown [4] that the chemical potential of a guest molecule can be approximated to a high degree of accuracy and in gradient terms:

$$\mu_k^H = A \ln(x_k) + B, \quad \frac{\partial \mu_k^H}{\partial x_r} = \{0, r \neq k\} \qquad (6)$$

Where k and r both represents any of the components of the hydrate (CO2, CH4 & water). For the gradient due to a guest molecule, these simplifications lead to:

$$\frac{\partial G^H}{\partial x_k} = x_k \frac{\partial \mu_k^H}{\partial x_k} + \mu_k^H \qquad (7)$$

For water, the form has two more terms:

$$\frac{\partial G_H}{\partial x_w} = \sum_{r=m,w,c} x_r \frac{\partial \mu_r^H}{\partial x_w} + \mu_w^H \qquad (8)$$

The chemical potential of a guest in the hydrate μ_k^H from [2] is:

$$\mu_k^H = \Delta g_{kj}^{inc} + RT \ln(h_{kj}) \qquad (9)$$

Where Δg_{kj}^{inc} is the Gibbs free energy of inclusion of guest molecule k in cavity j, h_{kj} the cavity partition function of component k in cavity j, the universal gas constant is R and T is temperature. The derivative of equation (9) with respect to an arbitrary molecule r is:

$$\frac{\partial \mu_k^H}{\partial x_k^H} = \frac{\partial \Delta g_{kj}^{inc}}{\partial x_r^H} + \frac{\partial \left(RT \ln(h_{kj})\right)}{\partial x_r^H} \qquad (10)$$

The first term of equation (10), the stabilization energy is either evaluated as the Langmuir constant or using harmonic oscillator approach [2]. In either case it is assumed to be approximately of temperature and pressure. Omitting the first term of (10) and approximating impacts of guest-guest interactions to be zero we arrive at:

$$\frac{\partial \mu_k^H}{\partial x_k^H} = \frac{RT}{h_{kj}} \frac{\partial h_{kj}}{\partial x_r^H} \qquad (11)$$

The validity of omitting guest-guest interactions may be questionable for some systems even though it is omitted in most hydrate equilibrium codes or empirically corrected for. Extensions for corrections to this can be implemented at a later stage.

The chemical potential of water:

$$\mu_w^H(T, P, \vec{\theta}) = \mu_w^{0,H}(T, P_0)$$
$$- \sum_j RT v_j \ln\left(1 + \sum_k h_{kj}\right) \qquad (12)$$

Where $\mu_w^{0,H}$ is the chemical potential of water in an empty hydrate structure, the first sum is taken over both small and large cavities, the second sum are over the components k in the cavity j. Here v_j is the number of type-j cavities per water molecule. Hydrate structure I contains 3 large cavities and 1 small cavity per 23 water molecules, $v_l = 3/23$ and $v_s = 1/23$. The paper by Kvamme & Tanaka [3] provides the empty hydrate chemical potential as polynomials in inverse temperature, the Gibbs free energies of inclusion, and

chemical potential of pure water, $\mu_w^{pure}(T)$. The derivative for the above equation with respect to an arbitrary molecule r results in:

$$\frac{\partial \mu_w^H}{\partial x_r} = \frac{\partial \mu_w^{0,H}}{\partial x_r} - \frac{\partial}{\partial x_r}\left(\sum_j RT v_j \ln\left(1 + \sum_k h_{kj}\right)\right)$$

$$\frac{\partial \mu_w^H}{\partial x_r} = -RT \sum_j v_j \frac{\partial}{\partial x_r}\left(\ln\left(1 + \sum_k h_{kj}\right)\right)$$

$$\frac{\partial \mu_w^H}{\partial x_r} = -RT \sum_j v_j \left[\frac{\sum_k \frac{\partial h_{kj}}{\partial x_r}}{(1 + \sum_k h_{kj})}\right] \qquad (13)$$

From equations (11) and (13), the derivative of the partition function can be evaluated from the equation that relates the filling fraction to the partition function:

$$h_{kj} = \frac{\theta_{kj}}{1 - \sum_i \theta_{kj}} \qquad (14)$$

Where θ_{kj} is the filling fraction of the components k in the cavity j. But it is easiest to recast everything in terms of mole fraction because of the basic assumption of mole fraction independence:

$$\theta_{kj} = \frac{x_{kj}}{v_j x_w} \qquad (15)$$

Since mass conservation is not used, the usual form of $1 - x_T$ is not considered. This is substituted into equation (16) and we get:

$$h_{kj} = \frac{\frac{x_{kj}}{v_j x_w}}{1 - \sum_i \frac{x_{ij}}{v_j x_w}}$$

$$h_{kj} = \frac{x_{kj}}{x_w v_j - \sum_i x_{kj}} \qquad (16)$$

Now we can take the derivative with respect to an arbitrary component r and then equation (16) is used to eliminate the sums, we get:

$$\frac{h_{kj}}{\partial x_r} = \frac{1}{x_w v_j - \sum_i x_{ij}} \frac{\partial x_{kj}}{\partial x_r}$$

$$- \frac{x_{kj}}{\left(x_w v_j - \sum_i x_{ij}\right)^2}\left(v_j \frac{\partial x_w}{\partial x_r} - \sum_i \frac{\partial x_{ij}}{\partial x_r}\right)$$

$$\frac{h_{kj}}{\partial x_r} = \frac{h_{kj}}{x_{kj}}\frac{\partial x_{kj}}{\partial x_r} - \frac{h_{kj}^2}{x_{kj}}\left(v_j \frac{\partial x_w}{\partial x_r} - \sum_i \frac{\partial x_{ij}}{\partial x_r}\right) \qquad (17)$$

The first thing that must be dealt with the cavity mole fractions as a function of total mole fraction of a component:

$$x_k = \sum_j x_{kj} \qquad (18)$$

Since the derivative of one mole fraction with respect to another is independent, the mole fraction in the cavity is also independent:

$$\frac{\partial x_{kj}}{\partial x_r}\begin{cases}0, k \neq r \text{ or } r = w \\ 1, k = r\end{cases} \qquad (19)$$

If $r = w$, then the derivative has to be zero because the mole fraction of the guest are independent of the mole fraction of water. Now equation (17) is simplified by using equation (18) and equation (19):

$$\frac{h_{kj}}{\partial x_w} = \frac{h_{kj}}{x_{kj}}\frac{\partial x_{kj}}{\partial x_w} - \frac{h_{kj}^2}{x_{kj}}\left(v_j \frac{\partial x_w}{\partial x_w} - \sum_i \frac{\partial x_{ij}}{\partial x_w}\right)$$

$$\frac{h_{kj}}{\partial x_w} = -\frac{h_{kj}^2 v_j}{x_{kj}} \qquad (20)$$

$$\frac{h_{kj}}{\partial x_p} = \frac{h_{kj}}{x_{kj}}\frac{\partial x_{kj}}{\partial x_p} - \frac{h_{kj}^2}{x_{kj}}\left(v_j \frac{\partial x_w}{\partial x_p} - \sum_i \frac{\partial x_{ij}}{\partial x_p}\right)$$

$$\frac{h_{kj}}{\partial x_p} = \frac{h_{kj}}{x_{kj}}\frac{\partial x_{kj}}{\partial x_p} + \frac{h_{kj}^2}{x_{kj}}\frac{\partial x_{pj}}{\partial x_p} \qquad (21)$$

Where p is an arbitrary guest molecule, k is also a guest molecule. These can be the same or different. If k and p are the same molecule, this gradient still exist and the "cross terms" are still able to be found even if there is independency in the mole fractions. $\frac{dx_{kj}}{dx_k}$ is calculated by starting with the equation (18) which is the basic definition of the mole fraction of the cavities and how they relate to the total mole fraction of the component. The total methane mole fraction x_m, is the sum of the mole fraction in the large cavities x_{ml}, and the mole fraction in the small cavities x_{ms}:

$$x_m = x_{ml} + x_{ms} \qquad (22)$$

From discussions it is assumed that there is a constant ratio between the partition functions and between different cavities of the same component. This is defined as A:

$$A \equiv \frac{h_{ml}}{h_{ms}} \quad (23)$$

The partition function can be written in terms of the filling fraction as shown in equation (14). Using equation (14), equation (15), equation (23) and assuming that the filling fraction of CO2 in large cavities is zero we get:

$$A = \frac{\dfrac{\theta_{ml}}{1 - \theta_{ml} - \theta_{cl}}}{\dfrac{\theta_{ms}}{1 - \theta_{ms}}} = \frac{\theta_{ml}}{\theta_{ms}} \left(\frac{1 - \theta_{ms}}{1 - \theta_{ml} - \theta_{cl}} \right)$$

$$A = \frac{\dfrac{x_{ml}}{v_l x_w}}{\dfrac{x_{ms}}{v_s x_w}} \left(\frac{1 - \dfrac{x_{ms}}{v_s x_w}}{1 - \dfrac{x_{ml}}{v_l x_w} - \dfrac{x_{cl}}{v_l x_w}} \right) \quad (24)$$

This Simplifies to:

$$A = \frac{x_{ml}}{x_{ms}} \left(\frac{v_s x_w - x_{ms}}{1 - \dfrac{x_{ml}}{v_l x_w} - \dfrac{x_{cl}}{v_l x_w}} \right)$$

$$x_{ml}[-v_l x_w] + x_{ms}[A v_l x_w - A x_{cl}] + x_{ms} x_{ml}[1 - A] = 0 \quad (25)$$

Taking derivative of above equation with respect to total methane mole fraction:

$$[-v_s x_w] \frac{\partial x_{ml}}{\partial x_m} + [A v_l x_w - A x_{cl}] \frac{\partial x_{ms}}{\partial x_m} + x_{ml}[1 - A] \frac{\partial x_{ms}}{\partial x_m} + x_{ms}[1 - A] \frac{\partial x_{ml}}{\partial x_m} = 0$$

$$[x_{ms}[1 - A] - v_s x_w] \frac{\partial x_{ml}}{\partial x_m} + [A v_l x_w - A x_{cl} + x_{ml}[1 - A]] \frac{\partial x_{ms}}{\partial x_m} \quad (26)$$

Substitutions were made to simplify the above equation and get it into a simpler form:

$$X = x_{ms}(1 - A) - v_s x_w$$

$$Y = A v_l x_w - A x_{cl} + x_{ml}(1 - A)$$

$$X \frac{\partial x_{ml}}{\partial x_m} + Y \frac{\partial x_{ms}}{\partial x_m} = 0 \quad (27)$$

Taking the derivative of equation (22) with respect to the

total mole fraction of methane and simplification results in:

$$\frac{\partial x_{ml}}{\partial x_m} + \frac{\partial x_{ms}}{\partial x_m} = \frac{\partial x_m}{\partial x_m} = 1$$

$$\frac{\partial x_{ml}}{\partial x_m} = -\frac{Y}{X - Y}$$
$$\frac{\partial x_{ms}}{\partial x_m} = \frac{X}{X - Y} \quad (28)$$

Substituting the values of X and Y gives the final answer:

$$\frac{\partial x_{ml}}{\partial x_m}$$
$$= \frac{A v_i x_w - A x_{cl} + x_{ml}(1 - A)}{x_{ml}(1 - A) + x_{ms}(1 - A) - v_s x_w - A v_l x_w - A x_{cl}} \quad (29)$$
$$\frac{\partial x_{ml}}{\partial x_m}$$
$$= \frac{x_{ms}(1 - A) - v_s x_w}{x_{ml}(1 - A) + x_{ms}(1 - A) - v_s x_w - A v_l x_w - A x_{cl}}$$

$\partial G / \partial P$ is calculated by taking derivative of equation (1) with respect to pressure:

$$\frac{\partial G_H}{\partial P} = x_c \frac{\partial \mu_c^H}{\partial P} + x_m \frac{\partial \mu_m^H}{\partial P} + x_w \frac{\partial \mu_w^H}{\partial P} + \mu_c \frac{\partial x_c}{\partial P} + \mu_m \frac{\partial x_m}{\partial P} + \mu_w \frac{\partial x_w}{\partial P} \quad (30)$$

The chemical potential gradients with respect to pressure can be given by:

$$\frac{\partial \mu_r^H}{\partial P} = \bar{V}_r$$

Thus equation (30) can be written as:

$$\frac{\partial G_H}{\partial P} = x_c \bar{V}_c + x_m \bar{V}_m + x_w \bar{V}_w + \mu_c^H \frac{\partial x_c}{\partial P} + \mu_m^H \frac{\partial x_m}{\partial P} + \mu_w^H \frac{\partial x_w}{\partial P} \quad (31)$$

The sum of the molar volumes $(\bar{V}_c, \bar{V}_m, \bar{V}_w)$ is in fact the total clathrate molar volume:

$$\bar{V}^{clath} = x_c . \bar{V}_c + x_m . \bar{V}_m + x_w . \bar{V}_w \quad (32)$$

Using the above value of $\bar{V}^{clath}$ simplifies the equation (31) to:

$$\frac{\partial G}{\partial P} = \bar{V}^{clath} + \mu_c^H \frac{\partial x_c}{\partial P} + \mu_m^H \frac{\partial x_m}{\partial P} + \mu_w^H \frac{\partial x_w}{\partial P} \quad (33)$$

The mole fraction derivatives can be calculated from

equation of state but there is no change under this derivative so equation (33) rewritten as:

$$\left(\frac{\partial G}{\partial P}\right)_{T,V,\bar{x}} = \overline{V}^{clath} \tag{34}$$

The free energy gradient with respect to temperature comes from the same fundamental relationship as used for the chemical potential gradient:

$$\frac{\partial\left(\frac{G}{RT}\right)}{\partial T} = -\frac{\overline{H}}{RT^2} \tag{35}$$

As before this can be differentiated and solved for the gradient:

$$\frac{\partial\left(\frac{G}{RT}\right)}{\partial T} = -RT^2 \int_{T_0}^{T}\left[\frac{H_0(T_0,P) + \int_{T_0}^{\theta} C_{p_i} d\eta}{R\theta^2}\right] d\theta \tag{36}$$

The Gibbs free energy for the hydrate as a function of mole fractions is shown in fig. 5. The CO2 only enters the large cavities, at least under moderate condition, and CH4 will occupy portion of the small cavities. As hydrate can never be fully occupied, the surface is restricted by the full filling of the large cavities $xc + xm < 4/24$ and $xm < 1/27$ is for small cavities. In this figure, the large cavities are less occupied by carbon dioxide and the small cavities are fully occupied by methane.
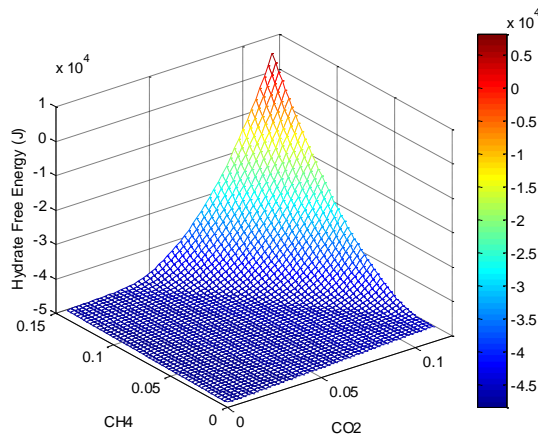

Figure 5: Hydrate free energy of mixed hydrate at 3°C and 40 bars.

The perturbation due to pressure temperature and composition gradients from equilibrium in hydrate Gibbs free energy is plotted in fig. 6.
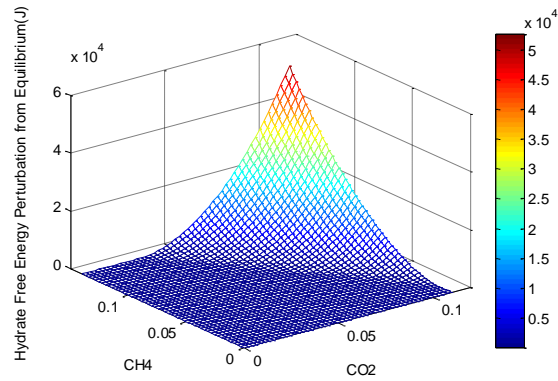

Figure 6: Perturbation due to pressure, temperature and composition gradients in hydrate free energy from equilibrium at 3°C and 40 bars.

III. FLUID THERMODYNAMICS

The free energy of the fluid phase is assumed to have:

$$G_L^{Fluid} = \sum_{r=c,m,w} x_r \mu_r^{Fluid} \tag{37}$$

where μ_r^{Fluid} is the chemical potential of the fluid phase. The lower concentration of water in the fluid phase and its corresponding minor importance for the thermodynamics results in the following form of water chemical potential with some approximation of fugacity and activity coefficient:

$$\mu_w^{Fluid} = \mu_w^{ideal\ gas}(T,P) + RT\ln(y_w) \tag{38}$$

Where $\mu_w^{ideal\ gas}(T,P)$ chemical potential of water in ideal gas and y_w is the mole fraction of water in the fluid phase and can be calculated as:

$$y_w = \frac{x_w \gamma_w(T,P,\bar{x}) P_w^{sat}(T)}{\varphi_w(T,P,\bar{y})} \tag{39}$$

The vapour pressure can be calculated using many available correlations but one of the simplest is given in [6] as a fit to the simple equation:

$$\ln(P) = V_A - \frac{V_B}{T + V_C} \tag{40}$$

The temperature of the system is obviously available and $V_A = 52.703$, $V_B = -3146.64$ and $V_C = 5.572$. Further, the fugacity and the activity coefficient are approximated to unity merely because of the very low water content in fluid phase and its corresponding minor importance for the thermodynamics of the system. Hydrate formation directly from water in gas is not considered as significant within the systems discussed in this work. The water phase is close to unity in water mole fraction. Raoult's law is therefore accurate enough for our purpose. The chemical potential for the mixed fluid states considered as:

$$\mu_i^{Fluid} = \mu_i^{id.gas,pure} + RT\ln(y_i) + RT\ln\varphi_i(T,P,\bar{y}) \tag{41}$$

Where i represents CH4 or CO2. The fugacity coefficients of component i in the mixture is calculated using the classical SRK equation of state (EOS), [5]

$$\ln \varphi_i = (BB)_i(Z - 1) \\ - \ln(Z - B) \\ - \frac{A}{B}((AA)_i - (BB)_i) \ln\left[1 + \frac{B}{Z}\right] \qquad (42)$$

Where Z is the compressibility factor of the phase and is calculated using the following cubic SRK EOS:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \qquad (43)$$

Where,

$$A = \frac{\alpha a P}{R^2 T^2}$$

$$B = \frac{bP}{RT}$$

$$a = 0.427480 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.086640 \frac{RT_c}{P_c}$$

$$\alpha = \left[1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)\left(1 - \sqrt{T_r}\right)\right]^2$$

Where ω is the accentric factor of components. For mixture, the mixing rule with modification proposed by Soave [5] is used using the following formulations:

$$(\alpha a)_m = \sum\sum y_i y_j (\alpha a)_{ij} \; ; \; (\alpha a)_{ij} \\ = \sqrt{(\alpha a)_i (\alpha a)_j}(1 - k_{ij}) \qquad (44)$$

Where k_{ij} is the binary interaction parameter. Coutinho et al. [7] has proposed number of values for k_{ij} for CO2/CH4 system. Here we selected an average value $k_{ij} = k_{ji} = 0.098$ for unlike pairs of molecules and it is zero for alike pairs of molecules.

$$b_m = \sum_i y_i b_i \qquad (45)$$

$(AA)_i$ and $(BB)_i$ in equation (42) are calculated as:

$$(AA)_i = \frac{2}{(a\alpha)_m}\left[\sum_j (a\alpha)_{ij}\right] \qquad (46)$$

$$(BB)_i = \frac{b_i}{b_m} \qquad (47)$$

IV. AQUEOUS THERMODYNAMICS

The free energy of the aqueous phase can be written as:

$$G_L^{aqueous} = \sum_{r=c,m,w} x_r \mu_r^{aqueous} \qquad (48)$$

The chemical potential $\mu_r^{aqueous}$ for components c (carbon dioxide) and m (methane) dissolved into the aqueous phase is described by nonsymmetric excess thermodynamics:

$$\mu_i = \mu_i^\infty(T) + RT \ln(x_i \gamma_i^\infty) + v_i^\infty(P - P_o) \qquad (49)$$

μ_i^∞ is the chemical potential of component i in water at infinite dilution, γ_i^∞ is the activity coefficient of component i in the aqueous solution and v_i^∞ is the partial molar volume of the component i at infinite dilution. The chemical potentials at infinite dilution as a function of temperature are found by assuming equilibrium between fluid and aqueous phases $\mu_i^{Fluid} = \mu_i^{aqueous}$. This is done at varying low pressures where the solubility is very low and the gas phase is close to ideal gas using experimental values for the solubility and extrapolating the chemical potential down to a corresponding value for zero concentration. The Henry's constants k_H are calculated for CH4 and CO2 using the expression proposed by Sander.[8]

$$k_H(T) = k_H^\ominus e^{\left(\frac{-\Delta_{soln}H}{R}\left(\frac{1}{T} - \frac{1}{T^\ominus}\right)\right)} \qquad (50)$$

Where $T^\ominus$ is the reference temperature, which is equal to 298.15K. $\Delta_{soln}H$ is the enthalpy of dissolution and it is represented by the Clausius-Clapeyron equation[9] as:

$$\frac{d \ln k_H}{d(1/T)} = \frac{-\Delta_{soln}H}{R} \qquad (51)$$

The values of $-(d \ln[\![k\_H]\!])/d(1/T)$ and $k_H^\ominus$ are given by Zheng et al.[10] and by Kavanaugh et al.[11] for CO2 and CH4 respectively which is shown in Table 1.

Table 1: Values of parameters.

Constants	CO2	CH4
$k_H^\ominus$ (M/atm)	0.036	0.0013
$-(d \ln[\![k\_H]\!])/d(1/T)$ (K)	2200	1800

The activity coefficient at infinite dilution γ_i^∞ is calculated as:

$$\gamma_i^\infty = \frac{f_i^\infty}{k_H(T)} \qquad (52)$$

Where,

$$f_i^\infty = e^{(-\beta\mu_i^\infty)} \qquad (53)$$

Where f_i^∞ is the fugacity of component i, while μ_i^∞ is calculated from [4]. The activity coefficient can be regressed by using the model for equilibrium to fit experimental solubility data. The chemical potential of water can be written as:

$$\mu_w = \mu_w^{pure\ liquid}(T) + RT\ln(1-x)\gamma_w \\ + v_w(P - P_o) \qquad (54)$$

where $\mu_w^{pure\ liquid}$ is pure water chemical potential and v_w is the molar volume of water. The strategy for calculating activity coefficient is given by Svandal et al.[4]. The Gibbs free energy for the liquid phase as function of mole fraction is shown in fig.7.
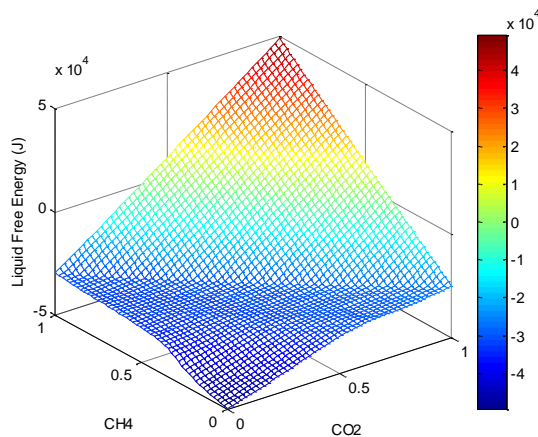

Figure 7: Liquid Gibbs free energy (J) as a function of the mole fraction of CH4 and CO2 at 3°C and 40 bars.

The aqueous and fluid phases are treated as a single common phase in the phase field theory approach. The smooth Gibbs free energy have constructed over the whole mole fraction domain of both CO2 and CH4 for this purpose.

V. CONCLUSION

Formulations of super saturation or undersaturation of hydrate in pressure, temperature and concentrations have been derived for a three component system of water, CO2 and CH4. Unlike earlier published approximations for mixed hydrate super saturation or sub saturation the expansions are rigorous to first order Taylor expansion and will as such also capture the total free energy minimum in mixed hydrate of CO2 and CH4. The results are implemented in Phase Field Theory model for the same system of three components and all possible surrounding fluid phases of these.

The Previously published results on absolute thermodynamics of hydrate also been used to illustrate the impact of molecular size on destabilization of the water clathrate. In particular it is demonstrated that a molecule like CO2 will stabilize the hydrate cages well but due to its size it will interfere with the movements of the water molecules constituting the cavity and cause a destabilization effect in the order of 1 kJ/mole at zero Celsius.

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