A Comparison of Variable Reference Potential Models for Gas Hydrates

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Gas hydrates are non-stoichiometric, crystalline molecular complexes formed from water and low molecular weight gases. The water molecules form a lattice structure and the gas molecules occupy the interstitial vacant cavities or cages of the lattice. Interest in gas hydrates began in 1930s when it was discovered that gas hydrates were responsible for the plugging of natural gas process and transportation lines. This interest grew recently, particularly due to the discovery of large hydrate deposits that could be the potential energy source (Kvenvolden 2000; Kerr 2004) and the possible means of sequestrating CO_2, a way to mitigate the buildup of greenhouse gas in the atmosphere(Handa 1990; Ormerod 1996; Ormerod 1996a; Wong 1997; Johnston 1999). For many applications of hydrate research, it is necessary to have a thermodynamic model that could give predict gas hydrate formation pressures.

All common natural gas hydrates belong to the three crystal structures: cubic I (sI), cubic structure II (sII), and hexagonal structure (sH). Structure I is formed with gas molecules smaller than 6 $\mathring{A}$, such as methane, ethane, carbon dioxide and hydrogen sulfide. Structure II is formed with gas molecules somewhat lager (6 $\mathring{A} < d < 7 \mathring{A}$), such as propane or iso-butane. Still larger molecules (7 $\mathring{A} < d < 9 \mathring{A}$), such as iso-pentane or neo-hexane can form structure H when accompanied by smaller molecules such as methane, hydrogen sulfide or nitrogen. (Sloan 1998)

With the knowledge of the crystal structure of hydrates, which was discovered by von Stackelberg and co-workers via X-ray diffraction in the early 1950s, a statistical thermodynamic model was proposed by van der Waals and Platteeuw (vdWP model)(Van der Waals 1959). In this model, the chemical potential of water in the hydrate phase was developed using a Langmuir adsorption model. Saito (Saito 1964) first used the vdWP model to systematically predict hydrate formation temperatures and pressures. Their approach was extended by Parrish and Prausnitz (Parrish 1972), and later substantially simplified by John and Holder (John 1981). The vdWP model coupled with simplified Parrish and Prausnitz algorithm has been used widely during the last 30 years.(Sloan 1998; Sparks 1999; Zele 1999; Klauda 2000; Balloard 2002; Klauda 2002; Lee 2002; Klauda 2003; Sloan 2003; Sloan 2003a)

Since the original vdWP model thermodynamic models for gas hydrates generally treat the reference properties of the empty hydrate lattice as fixed or independent of the guest that occupies the hydrate. Since 1989, Holder and co-workers(Hwang 1993; Zele 1999; Lee 2002) have proposed that the correct empty lattice to use in the model is dependent upon the guest that occupies that lattice and thus the reference properties should vary from guest to guest. A number of models developed by many investigators have overtly or more subtly used the variable reference models to predict and/or correlate experimental vapor pressures.

In the series of papers published by Klauda, J and Sandler, S (Klauda 2000; Klauda 2002; Klauda 2003), they proposed a fugacity model for gas hydrate phase equilibria. Instead of using $\mu_w^H = \mu_w^\pi$ or $\Delta\mu_w^H = \Delta\mu_w^\pi$ (where $\Delta\mu_w^H = \mu_w^\beta - \mu_w^H$, and $\Delta\mu_w^\pi = \mu_w^\beta - \mu_w^\pi$, μ_w^β is the chemical potential of water in a hypothetical empty hydrate lattice), which applies that chemical potential of water in hydrate phase is equal to that in water or ice phase (π phase) at equilibrium, they proposed to use $f_w^H(T,P) = f_w^\pi(T,P)$, where

$$f_w^H(T,P) = f_w^\beta(T,P)\exp\left(\frac{-\Delta\mu_w^H(T,P)}{RT}\right) \qquad (1)$$

$$f_w^\beta(T,P) = P_w^{sat,\beta}(T,P)\exp\left(\frac{V_w^\beta(T,P)(P - P_w^{sat,\beta}(T))}{RT}\right) \qquad (2)$$

$$f_w^\alpha(T,P) = P_w^{sat,\alpha}(T,P)\phi_w^{sat,\alpha}(T)\exp\left(\frac{V_w^\alpha(T,P)(P - P_w^{sat,\alpha}(T))}{RT}\right) \quad \text{(ice phase)} \qquad (3)$$

$$f_w^L(T,P) = x_w(T,P)\gamma_w(x_w,T)P_w^{sat,L}(T,P)\phi_w^{sat,L}(T)\exp\left(\frac{V_w^L(T,P)(P - P_w^{sat,L}(T))}{RT}\right) \quad \text{(water phase)} \qquad (4)$$

In order to obtain $P^{sat,\beta}$ for each guest, the experimental data of I-H-V and a few data points in the L-H-V region of each guest hydrate were fitted to the quasi-polynomial form:

$$\ln(P^{sat,\beta}[Pa]) = A\ln(T) + \frac{B}{T} + C + DT \qquad (5)$$

In their model, “the assumption of a constant crystal lattice for different guests within a structure, which is not in agreement with quantum chemistry calculations is removed.”(Klauda 2000) However, in order to avoid a large number of parameters in their model, “the shell radii were kept constant even though there is a different degree of lattice distortion for each guest”. (Klauda 2000) This was compensated by obtaining $P^{sat,\beta}$ for each guest from its experimental data. As Klauda and Sandler also agreed, the fugacity of hypothetical empty hydrate lattice depends upon the guest that occupied the lattice and the guest also distorts the lattice; in another words, the hydrogen bonds of hypothetical empty hydrate lattice are stretched according to different guests. This means that chemical potential of hypothetical empty hydrate lattice at zero temperature and pressure, $\Delta\mu_w^0$, which is taken as a reference state, is dependent upon guest molecules. Basically, the models based on the fugacity of hypothetical empty hydrate lattice are the same as those based on variable reference chemical potential.

When water is present, at equilibrium,

$$f_w^H(T,P) = f_w^L(T,P) \qquad (6)$$

We calculated $\Delta\mu_w^0$ by using equation (1), (2), (5), (6) and the value of A, B, C, D of different guest molecules provided in Table 6 of the paper of Klauda, J and Sandler, S. in 2000. The fugacity of water at zero pressure and different temperatures was obtained from the Steam Table (Rocchetti) as the pressure is zero at the reference state and the fugacity coefficient of water is considered to be unity. We also use the variable potential model described in Lee and Holder's paper (Lee 2002) to calculate $\Delta\mu_w^0$. Note that it seems to us that there were some mistakes in the values reported in Lee's paper (Lee 2002). All the experimental data used in this work were cited from Lee, S. Y.'s PhD dissertation (Lee 1999) and were in the V-L-H region. Table 1 and 2 are the summaries of our calculation results of $\Delta\mu_w^0$ in comparison with the values obtained from the paper by Klauda and Sandler in 2000.(Klauda 2000)

Table 1. The comparison of the results of $\Delta\mu_w^0$ of structure I gas hydrates

Gas Molecule	Values calculated from Klauda and Sandler *(J/mol)*	this work *(J/mol)*
CH_4	1931.2	1160.7
C_2H_6	1939.0	1963.6
c-C_3H_6	555.0	1957.1
H_2S	2637.1	2127.6
CO_2	3639.5	2642.1

Table 2. The comparison of the results $\Delta\mu_w^0$ of structure II gas hydrates

Gas Molecule	Values calculated from Klauda and Sandler *(J/mol)*	this work *(J/mol)*
C_3H_8	1671.4	1701.8
Ar	NA	1102.4
c-C_3H_6	1958.4	1453.7
i-C_4H_{10}	444.1	2114.5

From the basic thermodynamic relations, there is $\frac{d(\frac{\Delta\mu_w}{T})}{dT} = -\frac{\Delta h_w}{T^2}$. We plot $\frac{\Delta\mu_w}{T}$ vs. Temperature, where $\frac{\Delta\mu_w}{T}$ was obtained by using the values calculated from the paper of Klauda and Sandler in 2000 (Klauda 2000), and the slope is $-\frac{\Delta h_w}{T^2}$. At the reference temperature (T_0=273.15 K), $\Delta h_w = \Delta h_w^0$.

We also calculate Δh_w^0 using the method that is described in the following:

$$\frac{\Delta\mu_w^L}{RT} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T} \frac{\Delta h_w}{RT^2} dT + \int_0^P \frac{\Delta V_w}{RT_F} dP - \ln \gamma_w x_w$$

$$\frac{\Delta\mu_w^L}{RT} - \frac{\Delta\mu_w^0}{RT_0} - \int_0^P \frac{\Delta V_w}{RT} dP + \ln \gamma_w x_w = -\int_{T_0}^{T} \frac{\Delta h_w}{RT^2} dT$$

As $\Delta\mu_w^H = \Delta\mu_w^L$, we can obtain $\frac{\partial}{\partial T}\left(\frac{\Delta\mu_w^H}{RT} - \frac{\Delta\mu_w^0}{RT_0} - \int_0^P \frac{\Delta V_w}{RT} dP + \ln \gamma_w x_w\right) = -\frac{\Delta h_w}{RT^2}$. Because $\frac{\Delta\mu_w^0}{RT_0}$ is a constant for a given gas hydrate, the equation can be further simplified as the following:

$$\frac{\partial}{\partial T}\left(\frac{\Delta\mu_w^H}{RT} - \int_0^P \frac{\Delta V_w}{RT} dP + \ln \gamma_w x_w\right) = -\frac{\Delta h_w}{RT^2}$$

The slope of ΔU vs. T is $-\frac{\Delta h_w}{RT^2}$, where $\Delta U = \frac{\Delta\mu_w^H}{RT} - \int_0^P \frac{\Delta V_w}{RT} dP + \ln \gamma_w x_w$. We define $a = -\frac{\Delta h_w}{RT^2}$. Once we have a, Δh_w^0 can be calculated as $\Delta h_w^0 = -aRT_0{}^2$,

Figure 1. shows ΔU vs. T for CH_4 gas hydrates with the data from the temperatures above T_0. This plot shows that $-\frac{\Delta h_w}{RT^2}$ is constant since the slope is constant. Similar linearity was found for other gases. These mean that the integral: $-\int_{T_0}^{T} \frac{\Delta h_w}{RT^2} dT = a(T - T_0)$, is a simpler, but more accurate method of calculating the contributions of the temperature difference. Previous models use heat capacities, ΔC_{pw}^0, of somewhat dubious accuracy; but the experimental data show that the heat capacity is not needed here (Although it could be calculated as $-2aRT$). Note that for temperatures above 0 ^{o}C, a value of 6010 J/mol, the latent heat of converting water to ice (Holder 1984), needs to be added to Δh_w^0 (T>0 ^{o}C) to obtain Δh_w^0 (T<0 ^{o}C). Thus, what appears as a negative value of Δh_w^0 from Figure 1, gives a positive value for Δh_w^0 T<0 ^{o}C as expected.

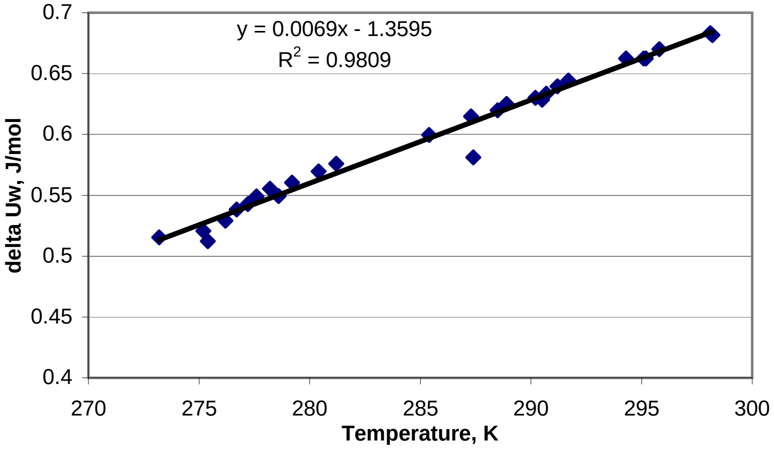

Figure 1 ΔU vs. Temperature of CH_4 gas hydrates

Table 3 and 4 are the comparison of our results and the values calculated from Klauda and Sandler. In Table 3 and 4, we calculated data below and above T_0 and converted all the values obtained above T_0 to their corresponding values that are below T_0.

Table 3. Comparison of our results of Δh_w^0 of structure I gas hydrates and values calculated from Klauda and Sandler (Klauda 2000).

Gas Molecule	Values calculated from Klauda and Sandler (J/mol)	This work obtained from $T>T_0$ (J/mol)	This work obtained from $T<T_0$ (J/mol)
CH_4	2194.1	1729.8	2047.0
C_2H_6	2164.3	1543.7	2171.1
c-C_3H_6	830.0	1667.8	2233.1
H_2S	3013.9	1853.9	2481.3
CO_2	3863.5	1605.8	4032.0

Table 4. Comparison of our results of Δh_w^0 of structure II gas hydrates and values calculated from Klauda and Sandler (Klauda 2000)

Gas Molecule	Values calculated from Klauda and Sandler (J/mol)	This work obtained from $T>T_0$ (J/mol)	This work obtained from $T<T_0$ (J/mol)
C_3H_8	2186.7	1295.6	1736.9
Ar	NA	1978.0	3163.6
c-C_3H_6	2522.0	799.4	1426.7
i-C_4H_{10}	681.1	2536.2	2109.1

Note that $\Delta \mu_w^0$ is a constant and does not have any impact on obtaining the value of Δh_w^0. Δh_w^0 is not a constant for different guests. The values reported are at T_0. For most guest molecules, there are much more experimental data above 273.15 K than those below, which leads us believe that the results from above 273.15 K are more accurate than below. Also, because the data below 273 K represents equilibria between two solid phases, it is more likely to have some error involved and the values of Δh_w^0 below 273 K are more likely to be in error.

There are two important observations that should be made about these results. First, when aberrant values of $\Delta \mu_w^0$ and/or Δh_w^0 are obtained for one species in comparison to most others, for example cyclo-propane and i-C_4H_{10}, then the data for that species may be suspect, either because of incorrect temperatures and pressures or an incorrect structure. Second, when the values of Δh_w^0 above and below the ice point are radically different, the data may also be suspect. (For example, CO_2 and Argon) Finally, the difference in reference values between the present work and Klauda and Sandler's is due to the difference in Langmuir constants that are obtained.

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