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Abstract.

The available experimental data in literature for enthalpies of hydrate formation and dissociation are limited and often lacks relevant information required for interpretation. Commonly missing information include hydrate composition, hydration number, temperature and/or pressure data, and degree of super heating during dissociation of hydrate. Clausius-Clapeyron equations used with measured or calculated hydrate formation pressure-temperature equilibrium data is the simplest indirect methods used for evaluating enthalpy change involved in phase transition during hydrate formation or dissociation. However, this approach involves over-simplifications. These over simplifications make all the data based on Clausius-Clapeyron to be unreliable. And old data using Clapeyron do not have appropriate volume corrections. We therefore propose a thermodynamic scheme (residual thermodynamics approach) without these limitations. This method is based on residual thermodynamics for all properties like equilibrium (pressure-temperature) curves, free energy change as thermodynamic driving force in kinetic theories and enthalpies of hydrate formation and dissociation.

Keywords: Residual thermodynamics, hydrate, dissociation.

1 Introduction

Natural gas hydrates are non-stoichiometric crystalline inclusion compounds (ice-like substances) formed when hydrogen-bonded water molecules form three-dimensional solid cage-like structures with cavities which entrap suitably small sized molecules of certain gases and volatile liquids known as guest molecules, under the condition of high

pressure and low temperature. Unlike ice, they exist above 273.15 K (0 °C). Lighter hydrocarbon components [1-3] and some inorganic gases are guest molecules that can form hydrate in their pure form. A vast amount of natural occurring methane hydrates are distributed all over the world in the permafrost and in the oceans [4]. This huge amount of methane gas trapped in the naturally existing hydrate could be a potential source of unconventional energy. And to produce this methane, any method that could be used will require supply of heat [5] to dissociate the methane hydrate. The amount of heat required for dissociation of the hydrate is the same amount that is released when the hydrate is form. The difference in representation is in the sign, negative for formation and positive for dissociation.

Hydrate formation is a complex exothermic process that involves competing phase transition mechanisms and routes where kinetics and thermodynamics play important role. The exothermic heat released (enthalpy of formation) during the phase transition is one of the most significant thermodynamic properties that we need for proper understanding of the phase transition process. This heat is either measured directly [6] by experiment or indirectly using Clausius-Clapeyron [7] or Clapeyron [8] modelling approaches. These approaches have some limitations; therefore, we proposed a consistent thermodynamic approach for evaluating enthalpies of hydrate formation or dissociation, the residual thermodynamics approach.

2 Modelling of hydrate dissociation with residual thermodynamics

The full modelling can be found in [9, 10]. It is however summarised here. The free energy change for a specific hydrate phase transition can expressed as:

$$\Delta G^{(H_1)} = x_{H_2O}^H \left(\mu_{H_2O}^H (T, P, \vec{x}^H) - \mu_{H_2O}^{water} (T, P, \vec{x}) \right) + \sum_j x_j^H \left(\mu_j^H (T, P, \vec{x}^H) - \mu_j^{gas} (T, P, \vec{y}^{gas}) \right) \quad (1)$$

The superscript H_1 distinguishes the specific heterogeneous phase transition from other hydrate formation phase transitions. T is temperature, P is pressure. x is mole-fraction in either liquid or hydrate (denoted with a subscript H) while y is mole-fraction in gas (or liquid) hydrate former phase. j is an index for hydrate formers. Superscript water denotes water phase that is converted into hydrate. Generally, this is ice or liquid but, in this work, we only consider liquid water. μ is chemical potential. These chemical potentials are convenient in discussing other routes to hydrate formation and associated hydrate former chemical potentials since any variation in chemical potential of hydrate formers will lead to changes in hydrate compositions and hydrate free energies. This is fundamentally important since any assembly of molecules with unique density and composition is a unique phase. Liquid water chemical potential is calculated from the symmetric excess conventions as:

$$\mu_{H_2O}(T, P, \vec{x}) = \mu_{H_2O}^{pure, H_2O}(T, P) + R \cdot T \ln(x_{H_2O} \cdot \gamma_{H_2O}(T, P, \vec{x})) \approx \mu_{H_2O}^{pure, H_2O}(T, P) + R \cdot T \ln(x_{H_2O}) \quad (2)$$

$$\lim(\gamma_{H_2O}) = 1.0 \text{ when } x_{H_2O} \text{ tends to unity}$$

The focus here is to illustrate the complexity of multiple hydrate formation in systems of water and CH₄ and we have used a simpler kinetic model which is more visible in terms of the various contributions to the hydrate phase transition dynamics. As such the approximation on the right-hand side of equation (2) is accurate enough for the purpose. The solubility of CH₄ in water is small and the right-hand side will be close to pure water chemical potential. Chemical potential for water in the hydrate structure is given by [11]:

$$\mu_{H_2O}^H = \mu_{H_2O}^{O,H} - \sum_{k=1,2} RT \nu_k \ln \left(1 + \sum_i h_{ij} \right) \quad (3)$$

in which H denote hydrate phase and O in the superscript on first term on right hand side means empty clathrate. These chemical potentials are readily available from model water (TIP4P) simulations [12]. The number of cavities per water ν_k is 1/23 for small cavities of structure I and 3/23 for large cavities. With CH₄ as only guest i is 1 in the sum over canonical partition functions for small and large cavities.

$$h_{ki} = e^{\beta[\mu_{ki} - \Delta g_{ki}]} \quad (4)$$

The enthalpy change is trivially related to the corresponding free energy change by the thermodynamic relationship:

$$\frac{\partial \left[\frac{\Delta G^{Total}}{RT} \right]_{P, \vec{N}}}{\partial T} = - \left[\frac{\Delta H^{Total}}{RT^2} \right] \quad (5)$$

The superscript total is introduced to also include the penalty of pushing aside the old phases. Practically, the total free energy change will be equation (2) plus the interface free energy times contact area between water and hydrate forming phase during the nucleation stage divided by number of molecules in the specific core size. Since critical nuclei sizes are small the whole particle can be considered as covered with water due to capillary forces. Above critical core size the penalty diminishes rapidly relative to the free energy benefits from (2).

$$\frac{\partial \left[\frac{\mu_{H_2O}^H}{RT} \right]_{P,\bar{N}}}{\partial T} = \frac{\partial \left[\frac{\mu_{H_2O}^{0,H}}{RT} \right]_{P,\bar{N}}}{\partial T} - \left[\frac{\partial}{\partial T} \right]_{P,\bar{N}} \left[\sum_{k=1,2} v_k \ln \left(1 + \sum_i h_{ki} \right) \right] \quad (6)$$

For the liquid water phase in (2), as well as for the empty hydrate chemical potential on right hand side of equation (6) results are trivially obtained from [11] while the second term on right hand side is reorganized as:

$$\left[\frac{\partial}{\partial T} \right]_{P,\bar{N}} \left[\sum_{k=1,2} v_k \ln \left(1 + \sum_i h_{ki} \right) \right] = \left[\sum_{k=1,2} v_k \frac{\sum_i \left[\frac{\partial h_{ki}}{\partial T} \right]_{P,\bar{N}}}{\left(1 + \sum_i h_{ki} \right)} \right] \quad (7)$$

And the derivatives of the cavity partition functions can be written as:

$$\left[\frac{\partial h_{ki}}{\partial T} \right]_{P,\bar{N}} = h_{ki} \left[-\frac{1}{RT^2} (\mu_{ki} - \Delta g_{ki}) + \frac{1}{RT} \left(\frac{\partial \mu_{ki}}{\partial T} - \frac{\partial \Delta g_{ki}}{\partial T} \right) \right] \quad (8)$$

The partial derivatives in the last term on right hand side is numerically differentiated from the polynomial fits of [11].

$$\frac{\partial \left[\frac{\mu_{H_2O}^H}{RT} \right]_{P,\bar{N}}}{\partial T} = \frac{\partial \left[\frac{\mu_{H_2O}^{0,H}}{RT} \right]_{P,\bar{N}}}{\partial T} + \left[\sum_{k=1,2} v_k \frac{\sum_i h_{ki} \left[\frac{1}{RT^2} (\mu_{ki} - \Delta g_{ki}) - \frac{1}{RT} \left(\frac{\partial \mu_{ki}}{\partial T} - \frac{\partial \Delta g_{ki}}{\partial T} \right) \right]}{\left(1 + \sum_i h_{ki} \right)} \right] \quad (9)$$

$$H_{H_2O}^{0,H} = -RT^2 \frac{\partial \left[\frac{\mu_{H_2O}^{0,H}}{RT} \right]_{P,\bar{N}}}{\partial T} + \left[\sum_{k=1,2} v_k \frac{\sum_i h_{ki} \left[(\mu_{ki} - \Delta g_{ki}) - T \left(\frac{\partial \mu_{ki}}{\partial T} - \frac{\partial \Delta g_{ki}}{\partial T} \right) \right]}{\left(1 + \sum_i h_{ki} \right)} \right] \quad (10)$$

For liquid water, the enthalpy is even more trivially obtained by numerical differentiation of the polynomial fit of chemical potential as function of T given by [11].

In an equilibrium situation, chemical potential of the same guest in the two cavity types must be the same and these have to be equal to the chemical potential of the same molecule in the phase that it came from. For the heterogeneous case this means chemical potential of the molecule in gas (or liquid) hydrate former phase. But outside of equilibrium the gradients in chemical potentials as function of T, P and mole-fractions have to reflect how the molecule behaves in the cavity.

Enthalpies for various guest molecules in the two types of cavities can be evaluated by Monte Carlo simulations along the lines described by [13] and [14] by sampling guest water interaction energies and efficient volumes from the movements of the guest molecules. That is:

$$H_{ki}^R = U_{ki}^R + (z_{ki} - 1)RT \quad (11)$$

where U is energy and superscript R denote residual (interaction) contribution. z_{ki} is compressibility factor for the guest molecule i in cavity k . Consistent ideal gas values for the same interaction models that were applied in calculation of the residual values is trivial.

$$z_{ki} = \frac{PV_{ki}}{k_B T} \quad (12)$$

In which k_B is Boltzmann's constant and V_{ki} is the excluded volume of a molecule of type i in cavity of type k . This latter volume is calculated from the sampled volume of centre of mass movements plus the excluded volume due to water/guest occupation. Slightly more complex sampling and calculation for molecules which are not monoatomic (or approximated as monoatomic like methane) but still fairly standard (6, 7) and explicit discussion on this is not needed here. The derivative of the chemical potential of a guest molecule i in cavity type k with respect to temperature as needed in equation (9) is the negative of partial molar entropy for the same guest molecule and can be calculated according to:

$$\left[\frac{\partial \mu_{ki}}{\partial T} \right]_{P, \bar{N}} = \frac{\mu_{ki} - H_{ki}}{T} \quad (13)$$

Equation (31) can then be rearranged into:

$$H_{H_2O}^{0,H} = -RT^2 \frac{\partial \left[\frac{\mu_{H_2O}^{0,H}}{RT} \right]_{P, \bar{N}}}{\partial T} + \left[\frac{\sum_{k=1,2} v_k \sum_i h_{ki} \left[(H_{ki} - \Delta g_{ki} + T \frac{\partial \Delta g_{ki}}{\partial T}) \right]}{\left(1 + \sum_i h_{ki} \right)} \right] \quad (14)$$

Residual enthalpies for hydrate former in a separate hydrate former phase are trivially given by:

$$H_{ki}^R = -RT^2 \sum_i y_i \left[\frac{\partial \ln \phi_i^{gas}}{\partial T} \right]_{P, y_{j \neq i}} \quad (15)$$

In which the same equation of state (SRK) is utilized as the one used for calculating fugacity coefficients for the chemical potentials.

3 Methane hydrate equilibrium pressure-temperature

Hydrate equilibrium pressures for methane hydrate formation have been estimated for a temperature range of 273K to 290 K as can be seen in Fig. 1. The estimates are compared with literature [8, 14] and there is a very good agreement even though we did not fit interaction parameters-that is not the priority here. The priority is to keep the statistical mechanical model free of adjustable parameters in all terms, together also with empty hydrate chemical potentials and chemical potentials for ice and liquid water.

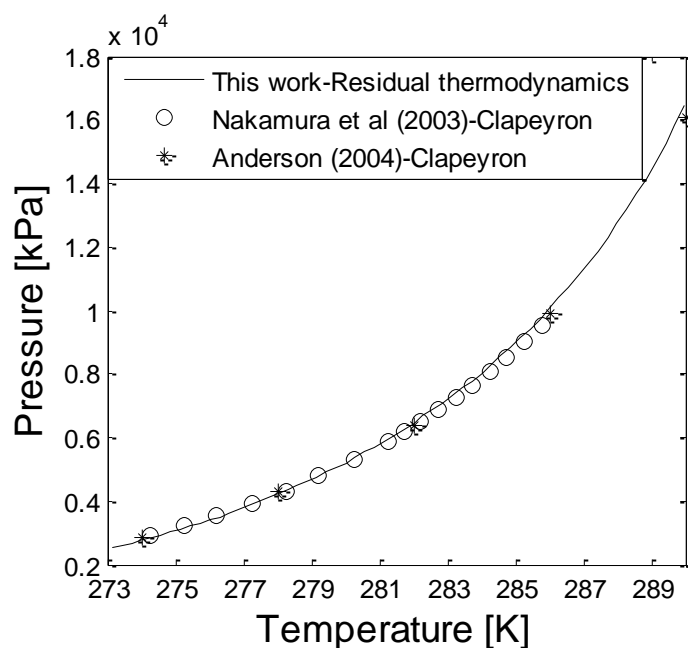


Fig. 1. Estimated methane hydrate equilibrium pressures using residual thermodynamics (this work) compared with literature [8,14].

4 Enthalpies of methane hydrate formation along equilibrium curve

The experimental data available in literature for enthalpies of hydrate formation and dissociation are limited and often lacks significant information required for interpretation. Commonly missing information include hydrate composition, hydration number, temperature and/or pressure data, and degree of super heating in the course of dissociation of hydrate. Hydrate dissociation enthalpy are measured directly or evaluated indirectly. Calorimetry, NMR, Raman, pressure drop X-ray diffraction are some of the methods used for direct measurement. And for the indirect method, Clapeyron and Clausius-Clapeyron equations are the approaches that are usually employed. The most simple indirect method is the Clausius-Clapeyron equation [7] and it is used with measured or calculated hydrate formation pressure-temperature equilibrium data. However, the simplifications in this approach limit the accuracy of results for higher pressures, therefore, more recent studies use the original Clapeyron equation with various models for the volume changes associated with the phase transitions [8]. These over simplifications make data based on Clausius-Clapeyron to be unreliable. And also, the old data using Clapeyron do not have appropriate volume corrections. The data from Anderson involves very high filling fractions of the hydrate. Some of the calculated filling fractions reported by Anderson [8] seem very high, even up to 282 K. And most calorimetry data do not have any measured filling fraction and often use a constant value which seems like guessed.

Therefore, there is a need for consistent and reliable enthalpies of hydrate formation or dissociation data, and that is why we propose the use of residual thermodynamics. This method is based on residual thermodynamics for all properties like equilibrium (pressure-temperature) curves, free energy change as thermodynamic driving force in kinetic theories and enthalpies of hydrate formation and dissociation. This scheme is also not limited to heterogeneous hydrate formation from water and a separate hydrate former phase, it can be used to evaluate associated enthalpy change in homogeneous hydrate formation from dissolved hydrate forming guest molecules in water. And even though we have applied the theory to one component (methane) because of the acceptable limit of work to be presented, there is no limitation in its application to other guest molecules and mixtures of hydrate formers (as we shall demonstrate in subsequent work), the formalism is written for mixtures. Another important advantage of this approach, unlike the Clapeyron method is that it can easily be extended to conditions outside of equilibrium as well as to other hydrate phase transitions. Applicable examples are enthalpy changes associated with hydrate forming from dissolved hydrate guest molecules in water, and the reverse process of hydrate dissociation to water under-saturated with guest molecules. Additional applicable hydrate phase transitions are nucleation of hydrate towards mineral surfaces. Our filling fractions seem realistic and also reproduce equilibrium pressures well see Fig. 1. According to Anderson [8] he used a specific code. This code is based on fitting of also the difference between chemical potential of empty hydrate and water as well as associated fitting of several related differences needed to calculate chemical potential

differences up to actual temperatures and pressures. Fitting fundamental properties like chemical potentials is by itself questionable.

Our estimates of enthalpy change for methane hydrate formation from pure methane and liquid water along the hydrate equilibrium (P, T) curve, that is three-phase coexistence conditions (liquid water, hydrate and gas simply represented as L-H-V) are presented in Fig. 2 and have been calculated using residual thermodynamics. In this figure, our intention is not to validate our scheme using these literature values. Based on all the limitations we have pointed out above, we do not expect that our result to agree perfectly with literature. Even though Nakamura et al. [14] and Anderson [8] utilized Clapeyron approach, there is a very wide difference or deviation in their results. The work of Nakamura et al. [14] even though it shows a very weak dependence on temperature till around 280 K, follows similar trend with our work, therefore, we have Table 1 for easy comparison. Table 2 gives the results from using our scheme and some literature [8, 15, 16]. In this work, hydration number was also estimated as given in Table 2 where the results from this work are compared with literature.

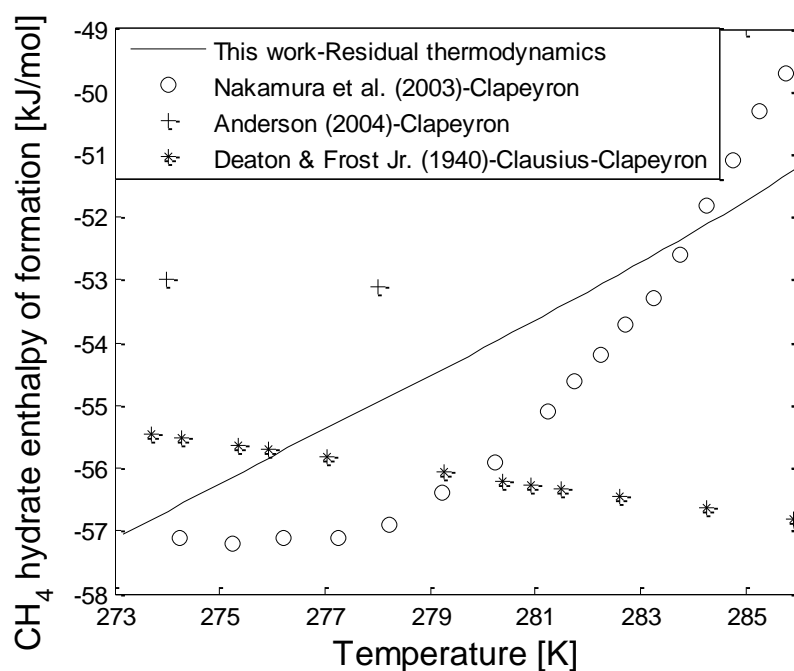


Fig. 2. Estimated enthalpies of methane hydrate formation using residual thermodynamics (this work), Clapeyron equation [8, 14], and Clausius-Clapeyron equation [7].

Table 2. Enthalpies of methane hydrate formation or dissociation [7]

Clapeyron equation (Nakamura et al. (2003))			Residual thermodynamics (This work)		
Temperature [K]	Pressure [bar]	Enthalpies of dissociation [kJ/mol]	Temperature [K]	Pressure [bar]	Enthalpies of formation [kJ/mol]
274.25	29.2	57.1	274.24	28.2	56.6
275.25	32.2	57.2	275.24	31.4	56.1
276.22	35.5	57.1	276.19	34.7	55.7
277.24	39.2	57.1	277.26	38.9	55.3
278.24	43.3	56.9	278.24	43.1	54.9
279.23	47.9	56.4	279.21	47.8	54.4

The enthalpies are in negative because hydrate formation is exothermic. The hydrate formation enthalpy is the heat of hydrate crystallization that must be transported out of the system, the system must lose this heat if the hydrate must form when every other condition favourable for hydrate to form is met. The heat transport is about 2-3 times [17] the magnitude of mass transport, that is more rapid. Heat transport limitation could lead to hydrate dissociation. These enthalpy values are the same for methane hydrate dissociation. But for hydrate dissociation, the values will be positive since heat is added to the system, or heat is required by the system for hydrate dissociation to proceed.

Table 2. Enthalpies of hydrate formation and dissociation and hydration number [8, 15, 16]

Method	Temperature [K]	Pressure [bar]	Enthalpy of formation/dissociation [kJ/mol]	Hydration number (n)
This work	273.15	25.19	-57.07	6.46
	274.1	27.82	-56.64	6.43
	278.02	42.15	-54.94	6.35
Anderson, G. K. (2004)	274	28.5	53	5.89
	278	42.8	53.1	5.79
Deaton & Frost (1946)	273.15	n/a	55.12	n/a
Kang et al. (2001)	274.15	n/a	56.84	n/a

Conclusion

We have used a consistent thermodynamic approach to evaluate the enthalpies of hydrate formation and dissociation and hydration number of methane hydrate. Besides not having the limitations of Clausius-Clapeyron and Clapeyron approaches, it has more capabilities like the ability for easy calculation of enthalpies of hydrate phase transitions for other phase transitions like for instance in case of hydrate forming from aqueous solution, and it can straightforwardly be extended to conditions outside of equilibrium as well as to other hydrate phase transitions.

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