Production of Methane from Hydrate and CO2 Zero-Emission Concept

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Abstract.

We have evaluated enthalpies of formation, or dissociation, for hydrates of CO_2 and CH_4. The exothermic heat released when a CO_2 hydrate is formed could be 9 - 10 kJ/mol of guest molecule more than the heat required to dissociate a CH_4 hydrate to methane gas and liquid water. The implication is that the heat released is available for dissociating the surrounding CH_4 hydrate to CH_4 gas and liquid water. In addition to the free pore water additional free water will become available for new CO_2 hydrate to form in place of the original CH_4 hydrate. The released CH_4 will migrate upwards due to buoyancy. The pressure–temperature projection is not what is essential to replace in situ methane hydrate with carbon dioxide. The difference in free energy of the two hydrates (CO_2 and CH_4 hydrates) and the heat of crystallization of CO_2 hydrate relative to the heat of dissociation (or formation) of the CH_4 hydrate is what is vital. This is based on the combined first and second laws of thermodynamics. Carbon dioxide hydrate is thermodynamically more stable than methane hydrate in respect of free energy. The free energy of CO_2 hydrate may be 1.8 - 2.0 kJ/mol lower than that of CH_4 hydrate.

Keywords: Hydrate, CO2, methane.

1 Introduction

There is a huge amount of natural occurring methane hydrates distributed all over the world in the permafrost and in the oceans [1]. This could serve as a huge source of cleaner energy [2]] for the world and at the same time it could provide a safe long-term CO_2 storage possibility [3].

Natural gas hydrates are non-stoichiometric crystalline inclusion compounds (ice-like substances) formed when hydrogen-bonded water molecules form threedimensional 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). Some of the guest molecules that can form hydrate in their pure form are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), isobutane (iC_4H_{10}), carbon dioxide (CO_2), and hydrogen sulphide (H_2S).

Research interest in natural gas hydrates as a source of energy has significantly increased in recent decades. Even with the high amount of available literature in this field, the thermodynamics of these natural gas hydrate systems, which are very complex systems are still poorly understood [1, 4]. Any technique that will be applied to produce CH_4 gas from CH_4 gas hydrates will involve heat transfer. The major focus has been on reducing the pressure [5] below hydrate stability. Even though this addresses the thermodynamic driving force, heat is still required to be supplied from the surroundings or added in some other ways. A number of very short pilot tests have been carried out in Alaska [6]. Two tests were performed offshore Japan some years ago [3]. In the first test, they encountered a problem of production of sand and water, together with freezing down as a result of inadequate heat supply capacity from the surroundings [3], thus, they stopped after six days. The second test which was originally designed and planned to last for six months continuous production was shut down after 24 days also because of freezing down problems. Thermal stimulation [2], for example by means of steam or hot water, is also a possibility, it is however considered too costly as the only means. A more novel technique is to inject carbon dioxide into the methane hydrate deposits. A solid-state process has been demonstrated by Lee et al. [7] and Falenty et al. [8] for the ice region of water. This work is aimed at evaluating the enthalpies of CO_2 and CH_4 hydrate formation or dissociation, and their free energies.

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:

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

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:

$$\mu_{H_2O}(T,P,\vec{x}) = \mu^{pure,H_2O}_{H_2O}(T,P) + R.T ln\left(x_{H_2O}.\gamma_{H_2O}(T,P,\vec{x})\right) \approx \mu^{pure,H_2O}_{H_2O}(T,P) + R.T ln\left(x_{H_2O}\right) \qquad (2)$$

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

The focus here is to illustrate the complexity of multiple hydrate formation in systems of water and CO_2 we use 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 CH_4 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]:

$$\mu^{H}_{H_2O} = \mu^{O,H}_{H_2O} - \sum_{k=1,2} RTv_k \ln\left(1+\sum_i h_{ij}\right) \qquad (3)$$

in which *H* denote hydrate and *0* 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 CO_2 as only guest *i* is 1 in the sum over canonical partition functions for small and large cavities.

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

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

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

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).

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

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:

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

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

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

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

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

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

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:

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

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.

$$z_{ki} = \frac{PV_{ki}}{k_B T} \tag{12}$$

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:

$$\left[\frac{\partial \mu_{ki}}{\partial T}\right]_{P\vec{N}} = \frac{\mu_{ki} - H_{ki}}{T} \tag{13}$$

Equation (31) can then be rearranged into:

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

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

$$H_{ki}^{R}=-RT^{2}\sum_{i}y_{i}\left[\frac{\partial\ln\phi_{i}^{gas}}{\partial T}\right]_{P,y_{j\neq i}} \tag{15}$$

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

3 Results and discussion

Estimates of hydrate equilibrium temperatures and pressures for CH_4 and CO_2 hydrates with our modelling scheme are presented in Fig. 1, Fig. 2 and Fig. 3. In Fig. 1 and Fig. 2, we compared our estimates with literature/experimental data [15-18]. Fig. 1. has estimates for pure CH_4 (…. line) and a mixture of CH_4 and 5.9 mole per cent of methanol (CH_3OH) (solid line). The equilibrium curves of CH_4 and CO_2 are plotted on the same figure for comparison purpose. The jump at around 283 K in both Fig. 2 and Fig. 3 show transition to higher density for CO_2 due to phase split. This also occurs for propane at around 278.5 K [19]. In some literature the curve for these components are straightened out at these points (this is wrong, it is not the true representation of reality), while some others do not go beyond the phase split point. This is not intended to criticise the experimental groups or other researchers. Discussion on this is beyond the scope of this work but it is important to mention it.

In recent years, much focus has been given to the study of exchange of CH_4 hydrate with CO_2 [3], that is forming CO_2 hydrate in place of the CH_4 hydrate, thereby storing the CO_2 gas in form of CO_2 hydrate and releasing or producing CH_4 as a clean energy. Several experimental groups in different parts of the world have been carrying out experiments on this exchange of CH_4 hydrate with CO_2 gas. The common inferences are that the process is overly slow. Some of them add nitrogen or other gases, with this, the conversion of the CH_4 hydrate to CO_2 usually becomes much slower due to the reduction of the thermodynamic driving forces for the critical parts of the mechanism. Two mechanisms have been demonstrated for the conversion: the first is the solid-state conversion mechanism which has merely been confirmed in the ice-region much below 273.15 K (0 °C), and the second mechanism has to do with injection of CO_2 gas into the natural gas (CH_4) hydrate reservoir resulting in forming a new hydrate (CO_2 hydrate) thereby releasing the CH_4 gas-this has be confirmed by state-of-the-art theoretical methods [3].

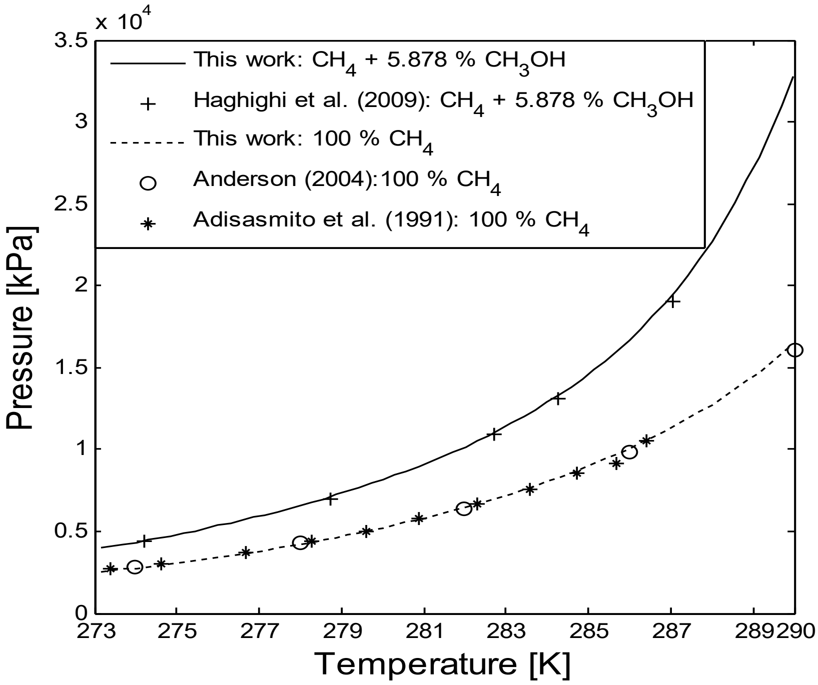

Fig. 1. Estimates of CH_4 hydrate equilibrium pressures compared with literature [15-17]

We have evaluated enthalpies of hydrate formation/dissociation using residual thermodynamics. With residual thermodynamics, there is no limitations in respect of the phases water and hydrate formers come from. As can be observed in Fig. 4, the exothermic heat liberated when a CO_2 hydrate is formed could be around ‘nine to ten’ kilojoule per mole (9 - 10 kJ/mol) of guest molecule more than when a CH_4 hydrate is formed. Or better stated that the heat released when a CO_2 hydrate is formed is around 9 to 10 kJ/mol of guest molecule more than the heat required to dissociate a CH_4 hydrate to methane gas and liquid water. The implication is that this heat can help as supplied heat to dissociate the surrounding CH_4 hydrate to CH_4 gas and liquid water, that means providing more free water for formation of new CO_2 hydrate in place of the original CH_4 hydrate.

It is imperative to state here that it is not really the pressure–temperature projection that is necessary to replace in situ methane hydrate with carbon dioxide. It is the difference in free energy of the two hydrates (CO_2 and CH_4 hydrates) and the heat of crystallization of CO_2 hydrate relative to the heat of dissociation (or formation) of the CH_4 hydrate. The process with the most negative free energy is favoured to occur because thermodynamic processes tend to the least free energy [20] based on the combined first and second laws of thermodynamics. Methane hydrate and CO_2 hydrates free energies along the equilibrium curve are plotted together in Fig. 5.

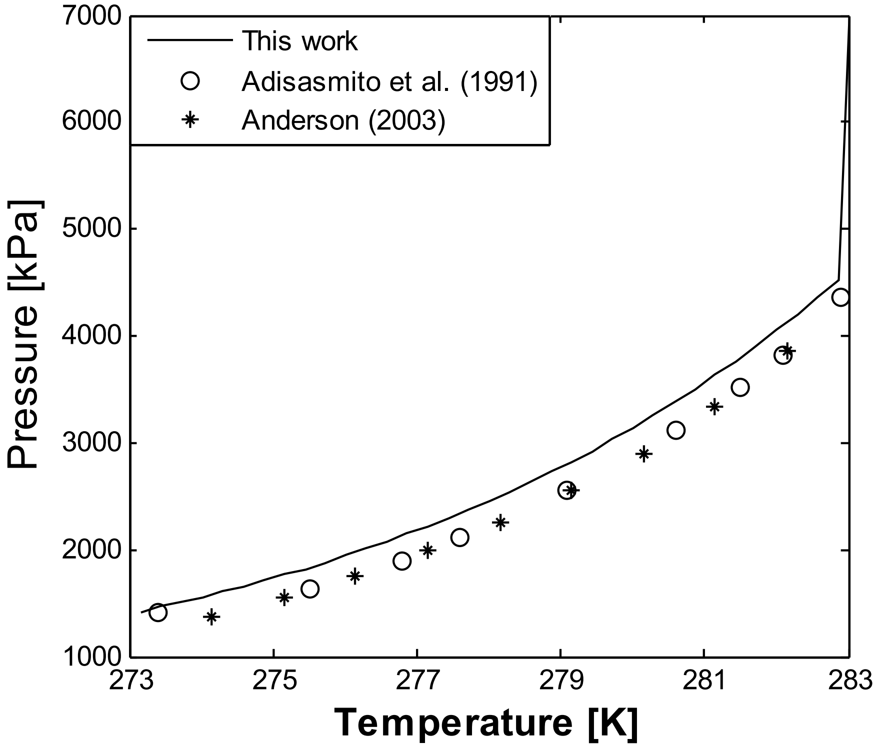

Fig. 2. Estimates of CO_2 hydrate equilibrium pressures compared with literature [17, 18]

Fig. 5 shows that carbon dioxide hydrate is thermodynamically more stable than methane hydrate in respect of free energy for the temperature range of 273.15 K (0 °C) to 283.15 K (15 °C). Fig. 5 reveals that the free energy of CO_2 could be about 1.8 to 2.0 kJ/mol more negative or lower than that of CH_4. These free energies are comparable because every component and every phase is based on residual thermodynamic descriptions, therefore, they are consistent. Using residual thermodynamics as well for water as liquid, ice or in empty hydrate of sI and II makes it possible to evaluate thermodynamic properties associated with hydrate phase transitions in a consistent way because the reference state for every component, in the different phases is the same. Utilizing model molecules and Molecular Dynamics (MD) simulations give residual properties directly through samplings in configurational space [9]. Average properties of ideal gas are also obtainable through samplings in momentum space [9]. For rigid molecules like those used in this project, it is trivial to obtain ideal gas properties from atomic masses and moments of inertia [9].

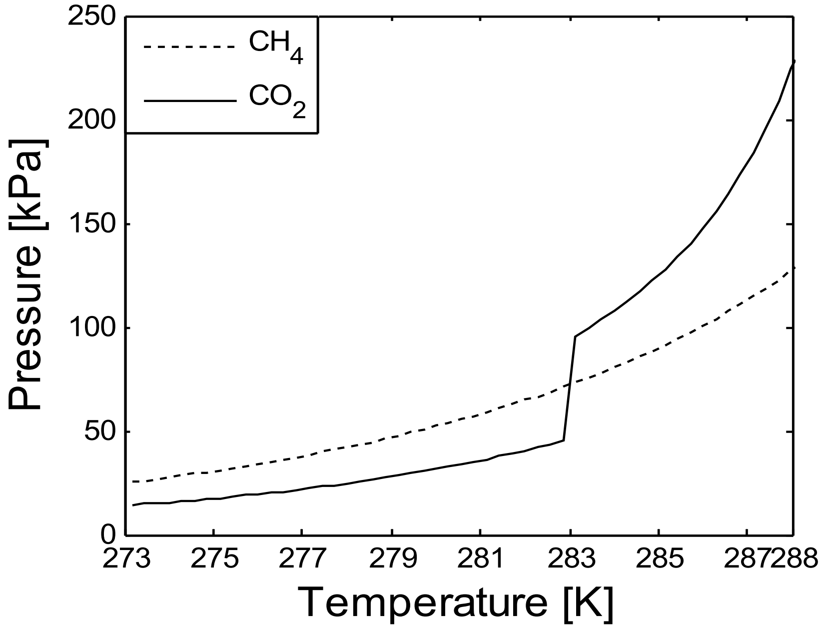

Fig. 3. Estimates of CH_4 and CO_2 hydrate equilibrium pressures compared with literature

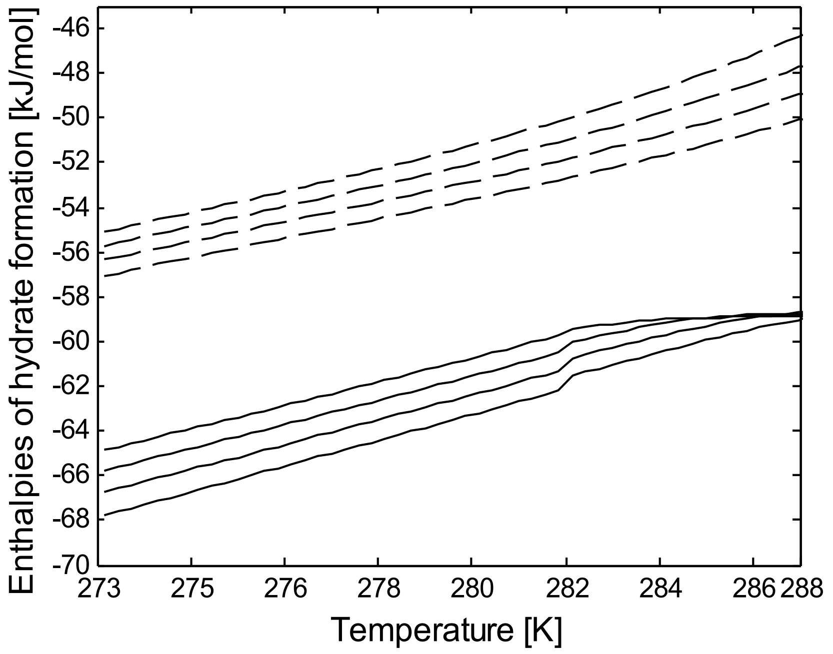

Fig. 4. Enthalpies of hydrate formation. Bottom four solid lines (–) from bottom to top are for pure CO_2, CO_2 and 2.5 mole % of methanol, CO_2 and 5.0 mole % of methanol and CO_2 and 7.5 mole % of methanol. Top four dash-dash lines (--) from bottom to top are for pure CH_4, CH_4 and 2.5 mole % of methanol, CH_4 and 5.0 mole % of methanol and CH_4 and 7.5 mole % of methanol.

In this study we applied this method and evaluated results for different properties towards experimental data from open literature. Hydrate formation enthalpies along the pressure-temperature equilibrium curve will certainly have the same values (but with opposite sign) as enthalpies of dissociation for the same conditions. Hydrate formation enthalpies are negative while enthalpies of hydrate dissociation are positive. We introduced 2.5, 5.0 and 7.5 mole per cents of methanol to both CO_2 and CH_4 hydrate formation enthalpies and free energies calculations (See Fig. 4 and Fig. 5) and 5.9 mole per cent in the equilibrium curve for CH_4 hydrate to show methanol's inhibition impacts. Based on our earlier work involving addition of small quantities of alcohols or surfactants, we suggested the addition of these types of chemicals instead adding nitrogen or other gases that could cause the system to be less probable to create new hydrate.

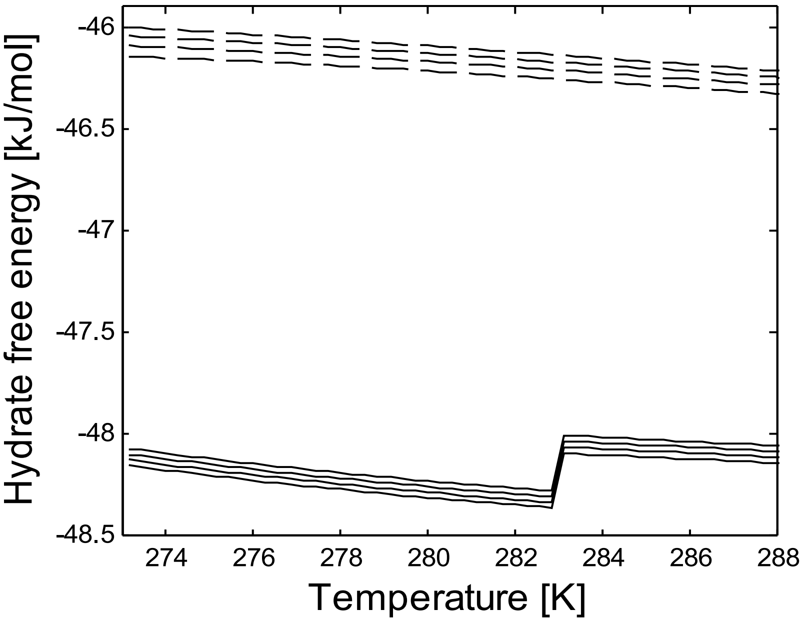

Fig. 5. Hydrate free energy. Bottom four solid lines (–) from bottom to top are for pure CO_2, CO_2 and 2.5 mole % of methanol, CO_2 and 5.0 mole % of methanol and CO_2 and 7.5 mole % of methanol. Top four dash-dash lines (--) from bottom to top are for pure CH_4, CH_4 and 2.5 mole % of methanol, CH_4 and 5.0 mole % of methanol and CH_4 and 7.5 mole % of methanol.

3 Conclusion

There is much research focus on unconventional source of energy like naturally occurring gas hydrate. The typical approach for production of the methane stored in these vast natural gas hydrates distributed over the world has been on pressure reduction below the stability region for hydrates. While this addresses the thermodynamic driving force, yet heat must be supplied from the surroundings or added in some other ways. Any technology that will successfully achieve production of the methane required supply of heat to dissociate the hydrate to methane gas and liquid water. Thermal stimulation by means of steam or hot water is a possibility, the drawback is that it is extremely costly. The more innovative technology is to inject carbon dioxide into the methane hydrate deposits. By this, methane will be produced for energy needs and simultaneously CO_2 will be stored in form of hydrate.

We used residual thermodynamics to calculate the heat of CO_2 and CH_4 hydrate formation/dissociation. This approach does not have limitations regarding the phases water and hydrate formers come from. The exothermic heat released during CO_2 hydrate formation may be 9 - 10 kJ/mol of guest molecule more than the heat required to dissociate a CH_4 hydrate to methane gas and liquid water. What this means is that this heat release available for dissociating the surrounding CH_4 hydrate to CH_4 gas and liquid water, making more free water available for formation of new CO_2 hydrate in place of the original CH_4 hydrate and liberating CH_4. We showed that the pressure–temperature projection is not what is necessary to replace in situ methane hydrate with carbon dioxide. The difference in free energy of the two hydrates (CO_2 and CH_4 hydrates) and the heat of crystallization of CO_2 hydrate relative to the heat of dissociation (or formation) of the CH_4 hydrate is what is important. This is based on the combined first and second laws of thermodynamics. Carbon dioxide hydrate is thermodynamically more stable than methane hydrate in respect of free energy for the temperature range of 273.15 K (0 °C) to 283.15 K (15 °C). The free energy of CO_2 may be 1.8 to 2.0 kJ/mol lower than that of CH_4.

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