

## Thermopack hydrate model

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### 1 Introduction

The current memo introduces the Thermopack hydrate model, which applies the van der Waals and Platteeuw method to determine the onset of hydrate formation. The approach is similar to the model described by Chapoy et al. [2]. It is important to note that only CO<sub>2</sub> is considered as a guest molecule in the hydrate cages. Hydrates formed with other guest molecules, such as CH<sub>4</sub> or H<sub>2</sub>S, are not accounted for, even if these species are present in the mixture. This limitation arises both from the absence of necessary parameterization and the fact that the numerical methods are not configured to handle hydrates formed with different guest molecules.

### 2 Hydrate model

The main equations of the hydrate model are given in this section.

The equilibrium condition of hydrate formation is equality between the chemical potentials of water in the hydrate phase  $\mu_W^H$ , and water in the fluid mixture,  $\mu_W^M$ ,

$$\mu_W^H = \mu_W^M. \quad (1)$$

Equation (1) can be split into three separate contributions, where each contribution represent a hypothetical sub-process of the hydrate formation Sloan and Koh [9]:

$$\mu_W^H - \mu_W^M = \left( \mu_W^{\text{ice/liq}} - \mu_W^M \right) + \left( \mu_W^\beta - \mu_W^{\text{ice/liq}} \right) + \left( \mu_W^H - \mu_W^\beta \right) = 0. \quad (2)$$

- **Term 1**  $\left( \mu_W^{\text{ice/liq}} - \mu_W^M \right)$ : Formation of pure and free water (ice or liquid) from the VLLE mixture.
- **Term 2**  $\left( \mu_W^\beta - \mu_W^{\text{ice/liq}} \right)$ : Formation of an empty hydrate lattice from pure water.
- **Term 3**  $\left( \mu_W^H - \mu_W^\beta \right)$ : Formation of the hydrate-clathrate from the empty hydrate lattice.

It should be noted that since we are looking at the difference between chemical potentials, all three terms can be modelled separately. The three pairs must individually have the same reference state. Since the reference states cancel, the pairs can have different reference states.



If we choose to look at the fugacity directly, the equilibrium condition becomes,

$$f_W^M = f_W^H, \quad (3)$$

with the hydrate fugacity

$$f_W^H = f_W^{\text{ice/liq}} e^{\left(\frac{\mu_W^H - \mu_W^\beta}{RT}\right)} e^{\left(\frac{\mu_W^\beta - \mu_W^{\text{ice/liq}}}{RT}\right)}. \quad (4)$$

## 2.1 Term 1 - Formation of free water

The fugacity of free water can be modeled from an suitable Equation of State (EoS) available in Thermopack.

$$f_W^{\text{ice/liq}} = \min(f_W^{\text{liq}}, f_W^{\text{ice}}) \quad (5)$$

Here  $R$  is the universal gas constant, and  $T$  is the temperature,  $f$  is the fugacity.

To calculate the ice fugacity, the EoS by Feistel and Wagner [3] have been used, while the fluid fugacity can be calculated from multiple EoSs.

## 2.2 Poynting correction

To account for ice, the Poynting correction given in the PhD-thesis by Haghighi [4] can also be used. The Poynting correction uses the Wagner et al. [10] sublimation correlation to predict the fugacity change of the assumed incompressible solid phase. It is important to note that the predicted saturation pressure at 273.16°C for pure water, depends on the choice of EoS. It is therefore necessary to calculate the saturation pressure at 273.16°C from the EoS and apply this in the ice model. Otherwise there will be a discontinuity in the fugacity over the melting line.

## 2.3 Term 2 - Formation of an empty hydrate lattice from pure water

The change in chemical potential associated with the formation of an empty hydrate lattice from pure water is modeled as follows:

$$\frac{\mu_W^\beta - \mu_W^{\text{ice/liq}}}{RT} = \frac{\Delta\mu_W^{\beta-\text{ice}_0/\text{liq}_0}}{RT_0} - \int_{T_0}^T \frac{\Delta h_W^{\beta-\text{ice/liq}}}{RT^2} dT + \int_{P_0}^P \frac{\Delta v_W^{\beta-\text{ice/liq}}}{RT} dP. \quad (6)$$

Here  $h$  is the molar enthalpy,  $v$  is the molar volume, and the reference state  $(T_0, P_0)$  is the triple point of water. The enthalpy difference is modeled as,

$$\Delta h_W^{\beta-\text{ice/liq}} = \Delta h_W^{\beta_0-\text{ice}_0/\text{liq}_0} + \int_{T_0}^T \Delta C p_W^{\beta-\text{ice/liq}} dT. \quad (7)$$

The heat capacity difference,  $\Delta C p_W^{\beta-\text{ice/liq}}$ , is modeled as linear function in temperature [5]

$$\Delta C p_W^{\beta-\text{ice/liq}} = A_{Cp} + B_{Cp}(T - T_0). \quad (8)$$



Table 1: Reference properties for empty hydrate lattice from ice or water [4]

	ice	water
$\Delta\mu_W^{\beta_0-\text{ice}_0/\text{liq}_0}(\text{J/mol})$	1297	1297
$\Delta h_W^{\beta_0-\text{ice}_0/\text{liq}_0}(\text{J/mol})$	1389	-4620.5
$\Delta v_W^{\beta-\text{ice}/\text{liq}}(\text{cm}^3/\text{mol})$	3.0	4.601
$A_{Cp}(\text{J/mol})$	0.565	-37.32
$B_{Cp}(\text{J}/(\text{molK}))$	0.002	0.179

The parameters used for the integration is found in Table 1. The triple point temperature is set to  $T_0 = 273.16$  K. The triple point pressure is calculated as the saturation pressure at the triple temperature, and will be close to the experimental value of  $P_0 = 611.73$  Pa.

It should be noted that the discontinuous value of  $\Delta v_W$  will give a small discontinuity in the hydrate fugacity.

## 2.4 Term 3 - Formation of the hydrate-clathrate from the empty hydrate lattice

The change in chemical potential for the formation of the hydrate-clathrate from the empty hydrate lattice is derived from statistical thermodynamics:

$$\Delta\mu_W^{\beta-H} = -RT \sum_i v_i \ln \left( 1 - \sum_j \theta_{i,j} \right). \quad (9)$$

The first sum is over small and larger cavities, and  $v_i$  is here the number of type  $i$  cavities per water molecule, which is 1/23 for small cavities and 3/23 for large cavities in structure I hydrates. The fractional filling of cavity  $i$  by component  $j$  is given by an Langmuir adsorption isotherm:

$$\theta_{i,j} = \frac{C_{i,j} f_j}{1 + \sum_k C_{i,k} f_k} \quad (10)$$

The Kihara potential model is used to calculate the Langmuir parameters  $C_{i,j}$ . See McKoy and Sinanoğlu [8] and Sloan and Koh [9, Sec. 5.1.4]. Kihara potential parameters are taken from multiple sources Sloan and Koh [9], Avlonitis [1], Kalorazi [7], Jäger et al. [6].

## 3 Isopleth hydrate appearance curve

In order to map the hydrate appearance curve given an overall composition, intersections with the fluid phase diagram are determined and appearance curves are mapped from these intersections. Examples of such plots are given in `thermopack/addon/pyExamples/hydrate_curves.py`. See Figures 1 for a pure CO<sub>2</sub> example and Figure 2 for example of a binary mixture.

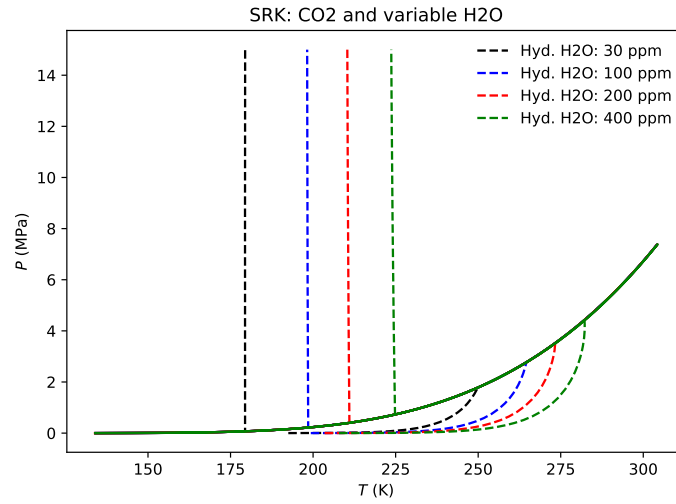


Figure 1: Hydrate appearance curves in pure  $\text{CO}_2$ . Four hydrate curves are plotted for the water content 30 ppm, 100 ppm, 200 ppm and 400 ppm

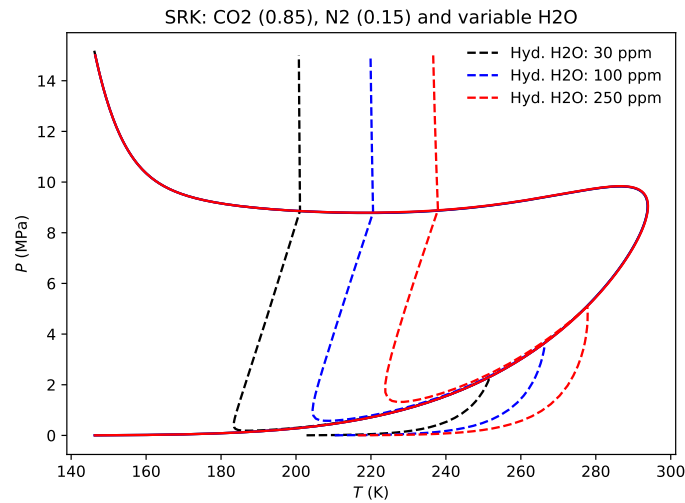


Figure 2: Illustration of hydrate appearance in a binary  $\text{CO}_2$ - $\text{N}_2$  mixture. The mole fraction vector of the mixture is  $[0.85, 0.15]$ . Three hydrate curves are plotted for the water content 30 ppm, 100 ppm and 250 ppm.



### References

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