

# Growth Mechanism, Kinetics and Morphology of Gas Hydrates of Carbon Dioxide, Methane and their Mixtures

Camilo Martinez, Juan F. Rueda, Nathalia Ortiz, Sebastian Ovalle, Juan G. Beltran

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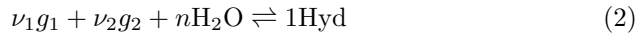
## Supporting Information

### Modified model for binary mixtures

In order to extend Kishimoto's model to mixtures, it is necessary to modify the equilibrium expression as follows:

$$x_{i,eq,LV} = y_i \frac{f_i(T, P)}{H_i} \quad (1)$$

Where  $x_{i,eq,LV}$  is the liquid-phase mole fraction of the component  $i$ ,  $f_i$  is the fugacity of the guest molecule  $i$  at the pressure and temperature of the system,  $H_i$  is Henry's constant and  $y_i$  is the vapor phase composition of the  $i$  component. Ideal solution and infinite dilution in the liquid phase were assumed. In addition, it is necessary to account for the presence of two guests as follows:



Where  $g$  are the hydrate guests,  $n$  is the hydration number and  $\nu$  are the stoichiometric coefficients of each guest. This coefficient is found through the hydrate phase composition. The Herriot Watt University HWPVT software was used to establish the stoichiometric coefficients and hydration number for the two mixtures. Volumetric growth rate of the hydrate film is then expressed as:

$$v_h = \frac{\dot{m}_g(\nu_1 M_{g_1} + \nu_2 M_{g_2} + n M_W)}{\rho_h} \quad (3)$$

In this case  $\dot{m}_g$  is the molar flux of both guests into the hydrate phase. This equivalence can be expressed with the stoichiometric coefficient of one guest.

$$\dot{m}_g = \frac{\dot{m}_{g_1}}{\nu_1} \quad (4)$$

Where  $\dot{m}_{g_1}$  is the molar flux of guest 1 at the surface of the growing hydrate, expressed as:

$$\dot{m}_{g_1} = h_{m,g_1} \rho_l \Delta x_{g_1} \quad (5)$$

Where  $h_{m,g_1}$  is the mass transfer coefficient for guest 1,  $\rho_l$  is the molar density of water and  $\Delta x_{g_1}$  is the difference in liquid mole fraction of guest 1 between HLV and experimental conditions. Density of the hydrate is defined by:

$$\rho_h = \frac{(N_w/n)(\nu_1 M_{G_1} + \nu_2 M_{G_2} + n M_W)}{A a^3} \quad (6)$$

Where A is the Avogadro number,  $N_w$  is the number of water molecules in each unit cell and a is the lattice constant of the hydrate. Substituting  $\dot{m}_{g_1}$  and  $\rho_h$  in the volumetric growth rate equation:

$$\dot{v}_h = h_{m,g_1} \left( \frac{a^3 \rho_l A}{N_w} \right) n \frac{\Delta x_{g_1}}{\nu_1} \quad (7)$$

[?] assumed  $h_{m,g}$  is proportional to  $D_{g,w}$ , the diffusion coefficient of the guest in water and variations of  $D_{g,w}$  are deemed insignificant compared to  $\Delta x_g$ . This results in the following correlation:

$$\dot{v}_h \propto \frac{n \Delta x_{g_1}}{\nu_1} \quad (8)$$

## Video

**Supporting video S1.** Growth of CH<sub>4</sub> hydrate film at a uniform temperature setting. Several instances of partial dissociation are observed throughout growth.  $\Delta T_{sub} = 0.3$  K.  $P_{exp} = 4.00$  MPa.  $n \Delta x_g = 0.95$ .

**Supporting video S2.** Growth of CO<sub>2</sub> hydrate film at a uniform temperature setting. One instance of partial dissociation is observed throughout growth.  $\Delta T_{sub} = 0.5$  K.  $P_{exp} = 2.10$  MPa.  $n \Delta x_g = 22$ .