Supplementary Materials: Mechanisms, Growth Rates and Morphologies of Gas Hydrates of Carbon Dioxide, Methane and their Mixtures

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

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:

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

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:

$$\nu_1 g_1 + \nu_2 g_2 + n\mathrm{H_2O} \rightleftharpoons 1\mathrm{Hyd} \tag{2}$$

Where g are the hydrate guests, n is the hydration number and ν 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:

$$\dot{V}_h = \frac{\dot{m}_g(\nu_1 M_{g_1} + \nu_2 M_{g_1} + nM_W)}{\rho_h} \tag{3}$$

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.

$$\dot{m}_g = \frac{\dot{m}_{g_1}}{\nu_1} \tag{4}$$

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

$$\dot{m}_{g_1} = h_{m,g_1}\rho_l \Delta x_{g_1} \tag{5}$$

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

$$\rho_h = \frac{(N_w/n)(\nu_1 M_{G_1} + \nu_2 M_{G_1} + nM_W)}{Aa^3} \tag{6}$$

Where A is the Avogrado 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 ρ_h in the volumetric growth rate equation:

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

Kishimoto and co-workers 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 Δx_g. This results in the following correlation:

$$\dot{V}_h \propto \frac{n\Delta x_{g_1}}{\nu_1} \tag{8}$$

23 *Extra Figures*

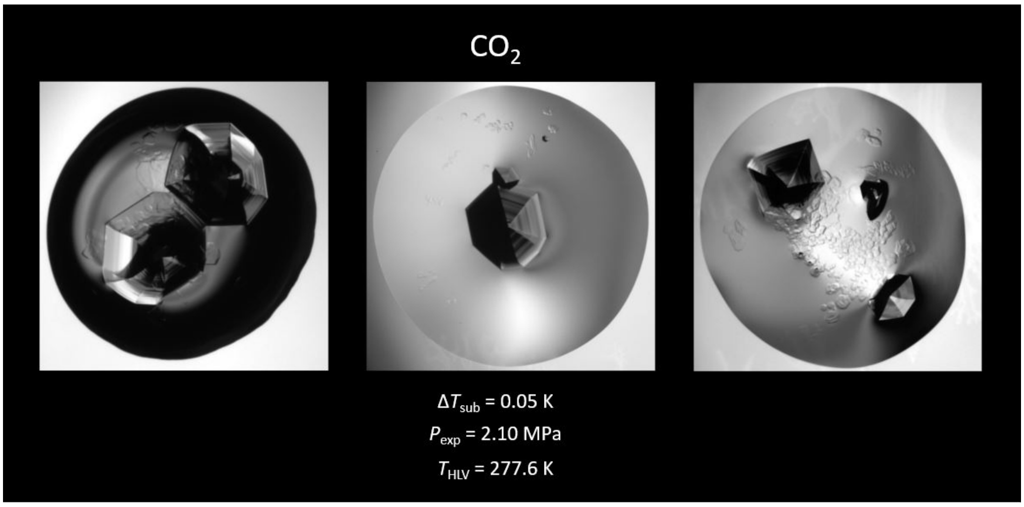

Figure S1. Morphology of pure carbon dioxide gas hydrates formed using a uniform temperature. All experiments were done using the same experimental conditions.

24 *Video*

25 **Supporting video S1.** Growth of CH_4 hydrate film at a uniform temperature setting.
26 Several instances of partial dissociation are observed throughout growth. ΔT_{sub} = 0.3 K.
27 P_{exp} = 4.00 MPa. nΔx_g = 0.95.
28 **Supporting video S2.** Growth of CO_2 hydrate film at a uniform temperature setting.
29 One instance of partial dissociation is observed throughout growth. ΔT_{sub} = 0.5 K. P_{exp}
30 = 2.10 MPa. nΔx_g = 22.