

Driving Force for Nucleation of Multi-Component Gas Hydrate

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ABSTRACT: *Based on driving force for crystallization of one-component gas hydrate, in this report an expression for the supersaturation for crystallization of multicomponent gas hydrate is derived. Expressions for the supersaturation are obtained in isothermal and isobaric regimes. The results obtained are applied to the crystallization of hydrates of mixtures of methane plus ethane and can apply to other mixtures.*

KEY WORDS: *Driving force, Crystallization, Kinetics of hydrate formation, Gas hydrate.*

INTRODUCTION

Gas hydrates are crystalline compounds that can be formed when light gases, such as methane come into contact with water at a temperature close to freezing point of water and at high pressure. The light gases may enter into the lattice of water molecules and stabilize it, resulting in a three dimensional framework containing large and small cavities. Such cavities can be occupied by certain gas molecules whose diameters are less than the cavity diameter. Time-dependent hydrate phenomena are substantially more challenging than time-independent hydrate phenomena such as structure and thermodynamics. Today, gas hydrates have drawn much attention, not only as a new natural energy source [1, 2], but also as a new means for natural gas storage and transportation [3, 4]. Moreover, new ideas have been offered in order to avoid hydrate formation by controlling

the parameters that have an effect on the rate of hydrate formation. Therefore, considering these developments, it is necessary to pay specific attention to hydrate formation kinetics and its effective parameters.

One of the effective parameters in gas hydrate formation is the driving force, which is also known as supersaturation [5,6]. The driving force necessary for hydrate crystallization is the difference between the *Gibbs* free energies of the solution and crystal phases. On this basis, a number of driving forces for the nucleation and growth process of hydrate crystallization have been introduced in the literature [7-10]. In the present report, the driving force for crystallization of one-component gas hydrate [11] is extended to gas mixtures and the driving force is obtained based on the difference between the *Gibbs* free energies of the solution and crystal phases.

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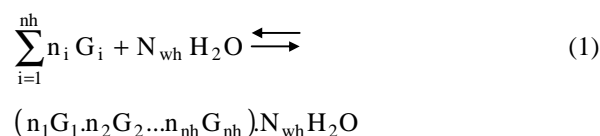
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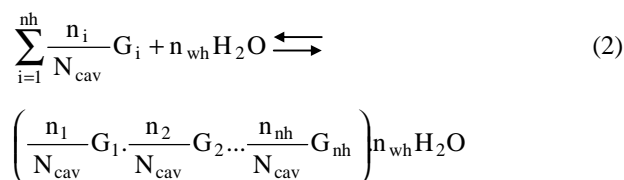
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GENERAL ANALYSIS

Let's consider a three-phase system consisting of: (i) a multicomponent gas, (ii) an aqueous solution of the gases, and (iii) a solid crystalline hydrate composed of water and the guest gases (Fig. 1). The gas phase is considered to be water-free because the partial pressure of water vapor in it is often negligible at the hydrate crystallization temperatures. The system is held at conditions of fixed pressure P , temperature T and composition \underline{z} . The hydrate phase is formed as a result of the following precipitation "reaction" occurring in the solution [2]:



In this equation, n_i is the number of gas molecules that occupy the cavities. N_{wh} is the number of water molecules in the sI and sII hydrate unit cells (i.e., 46 and 136, respectively). By dividing the above equation by N_{cav} , the number of cavities that can be occupied by the guest gas molecules in the hydrate unit cell, this newly developed equation becomes:



where n_{wh} is the number of water molecules per cavity number that can be occupied by the guest molecules. In one-component gas hydrate, we have one molecule of dissolved gas, and n_w water molecules of the solution which form one building unit of the hydrate crystal [11].

In this work, $\sum_{i=1}^{nh} n_i / N_{cav}$ molecules of the dissolved gases, and n_{wh} water molecules of the solution, form one building unit $((n_1 / N_{cav}) G_1 \cdot (n_2 / N_{cav}) G_2 \dots (n_{nh} / N_{cav}) G_{nh}) \cdot n_{wh} H_2O$ of the hydrate crystal. For a stoichiometric hydrate crystal we have $\sum_{i=1}^{nh} n_i / N_{cav} = 1$.

Although, the number and types of cavities in the hydrate structure is known and determined, different

molecules occupy different cavities. Thus, for different hydrate structures and components N_{cav} will vary. For example: (i) in a mixture of methane and ethane that form sI structure, $N_{cav} = 8$ (i.e.: $2+6=8$), (ii) in a mixture of propane and methane that form sII, $N_{cav} = 24$ (i.e.: $16+8=24$), and (iii) in a mixture of propane and ethane that form sII, $N_{cav} = 8$ (i.e.: $0+8=8$).

For the reaction shown in Eq. (2), applying the constraint of chemical equilibrium [12], we derive the following expression for the chemical potential μ_{hs} of a hydrate building unit in the solution:

$$\mu_{hs} = \sum_{i=1}^{nh} \frac{n_i}{N_{cav}} \mu_{gs_i} + n_{wh} \mu_w \quad (3)$$

where μ_{gs_i} and μ_w are the chemical potentials of the gas and water molecules in the aqueous solution, respectively.

Having determined the chemical potential of a hydrate building unit in the solution, the driving force for crystallization, which is the difference between the chemical potential of the given substance in the solution and in the crystal, is derived. The driving force for crystallization, also called supersaturation, is commonly denoted by $\Delta\mu$ and is obtained from the following equation [5, 6]:

$$\Delta\mu = \mu_{hs} - \mu_h \quad (4)$$

where, μ_h is the chemical potential of a building unit $(\sum_{i=1}^{nh} n_i / N_{cav}$ gas molecules and n_{wh} water molecules) in the hydrate crystal. Substituting Eq. (3) in Eq. (4), we obtain:

$$\Delta\mu = \sum_{i=1}^{nh} \frac{n_i}{N_{cav}} \mu_{gs_i} + n_{wh} \mu_w - \mu_h \quad (5)$$

Nucleation and/or growth of hydrate crystals are possible only when the solution is supersaturated (i.e., $\Delta\mu > 0$).

By using the definitions that were considered in Ref. [11], and recalling that n_i is a function of P and T [2], we can express $\Delta\mu$ in terms of the actual concentration $C_i [m^{-3}]$ of dissolved gases in the aqueous solution as:

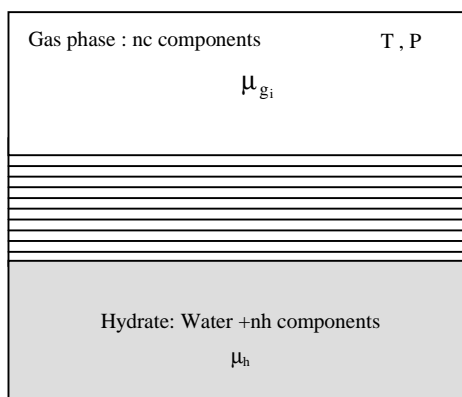


Fig. 1: Three-phase system of multicomponent gas, aqueous solution of the gases and gas hydrate.

$$\Delta\mu = \quad (6)$$

$$\sum_{i=1}^{nh} \frac{n_i(T,P)}{N_{cav}} \left[\mu_{gs_i}^*(T,P) + kT \ln[\gamma_i(T,P,C_i) C_i v_w] \right] + n_{wh} \mu_w(T,P) - \mu_h(T,P,\underline{x})$$

This general equation gives the dependence of $\Delta\mu$ on C_i in crystallization of gas hydrates in aqueous solutions of multicomponent gas.

Chemical equilibrium between solution and gas phases

In this case, the aqueous and gas phases must be in contact with each other for a long time in order for the system to reach equilibrium. The equilibrium concentration C_i is then determined by the following condition:

$$\mu_{gs_i} = \mu_{gg_i} \quad (7)$$

where $\mu_{gg_i}(T,P,\underline{y})$ is the chemical potential of a gas molecule in the gas phase (Fig. 1). Eq. (7) implies that in the case of solution/gas equilibrium, we can replace μ_{gs_i} in Eq. (5), or the first two summands on the right-hand side of Eq. (6), by μ_{gg_i} . Hence, we can eliminate the gas concentration C_i and obtain $\Delta\mu$ in the form:

$$\Delta\mu = \sum_{i=1}^{nh} \frac{n_i(T,P)}{N_{cav}} \mu_{gg_i}(T,P,\underline{y}) + n_{wh} \mu_w(T,P) - \mu_h(T,P,\underline{x}) \quad (8)$$

This general formula reveals that in the case of solution/gas chemical equilibrium, supersaturation ($\Delta\mu$)

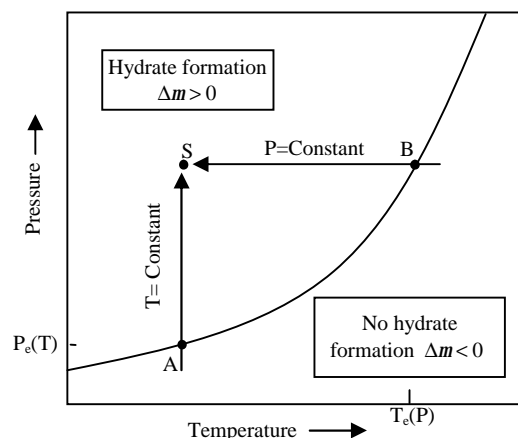


Fig. 2: Three-phase equilibrium curve for gas, solution and hydrate.

depends on P , T , the gas phase composition \underline{y} , and the hydrate phase composition \underline{x} . Eq. (8) allows determination of the supersaturation in an arbitrary regime of variation of P , T and \underline{y} . We shall now consider the two important regimes of isothermal and isobaric variation of $\Delta\mu$.

Isothermal regime

This regime is illustrated in Fig. 2 by a vertical line from point A to point S. In this regime, $\Delta\mu$ is varied by changing P at constant T and \underline{y} . As known from thermodynamics [13], for this regime we can write:

$$\mu_{gg_i}(T,P,\underline{y}) = \mu_{gg_i,0}(T) + kT \ln[\phi_i(T,P,\underline{y}) y_i P] \quad (9)$$

$$\mu_w(T,P) = \mu_{w,0}(T) + \int_0^P v_w(T,P') dP' \quad (10)$$

$$\mu_h(T,P,\underline{x}) = \mu_{h,0}(T) + \int_0^P v_h(T,P',\underline{x}) dP' \quad (11)$$

where ϕ_i is the fugacity coefficient of component i in the gas phase, v_w [m^3] is the volume of a water molecule in the solution, and v_h [m^3] is the volume of a building unit in the hydrate crystal. $\mu_{gg_i,0}$, $\mu_{w,0}$ and $\mu_{h,0}$ are reference chemical potentials depending only on T . Substitution of the above equations in Eq. (8) yields:

$$\Delta\mu = kT \sum_{i=1}^{nh} \frac{n_i(T,P)}{N_{cav}} \ln[\phi_i(T,P,\underline{y}) y_i P] + \quad (12)$$

$$\sum_{i=1}^{nh} \frac{n_i(T,P)}{N_{cav}} \mu_{gg,i,0}(T) + n_{wh} \mu_{w,0}(T) - \mu_{h,0}(T) + n_{wh} \int_0^P v_w(T,P') dP' - \int_0^P v_h(T,P',\underline{x}) dP'$$

As we know, the phase equilibrium between solution and hydrate is characterized by $\Delta\mu = 0$. At the chosen temperature T , there is an equilibrium pressure $P_e(T)$, corresponding to point A in Fig. 2, point at which the supersaturation becomes zero. The $P_e(T)$ function can be obtained from the expression:

$$0 = kT \sum_{i=1}^{nh} \frac{n_i(T,P_e)}{N_{cav}} \ln[\phi_i(T,P_e,\underline{y}) y_i P_e] + \sum_{i=1}^{nh} \frac{n_i(T,P_e)}{N_{cav}} \mu_{gg,i,0}(T) + n_{wh} \mu_{w,0}(T) - \mu_{h,0}(T) + n_{wh} \int_0^{P_e} v_w(T,P') dP' - \int_0^{P_e} v_h(T,P',\underline{x}) dP' \quad (13)$$

This expression allows elimination of the reference chemical potentials $n_{wh} \mu_{w,0}(T)$ and $\mu_{h,0}(T)$ in Eq. (12) and representation of $\Delta\mu$ in the form of:

$$\Delta\mu = \sum_{i=1}^{nh} \left[\frac{n_i(T,P)}{N_{cav}} - \frac{n_i(T,P_e)}{N_{cav}} \right] \mu_{gg,i,0}(T) + kT \sum_{i=1}^{nh} \frac{n_i(T,P)}{N_{cav}} \ln[\phi_i(T,P,\underline{y}) y_i P] - kT \sum_{i=1}^{nh} \frac{n_i(T,P_e)}{N_{cav}} \ln[\phi_i(T,P_e,\underline{y}) y_i P_e] + n_{wh} \left[\int_0^P v_w(T,P') dP' - \int_0^{P_e} v_w(T,P') dP' \right] - \int_0^P v_h(T,P',\underline{x}) dP' + \int_0^{P_e} v_h(T,P',\underline{x}) dP' \quad (14)$$

This is the general formula for $\Delta\mu$ in isothermal regime provided that the solution is in equilibrium with the gas phase. It can be simplified with the help of the following approximations:

$$n_i(T,P) \approx n_i(T,P_e), \quad v_h \approx v_h(T,P_e,\underline{x}) \approx v_h(T,P_e) \quad \text{and} \quad v_w \approx v_w(T,P_e)$$

For P close enough to P_e , the above relations imply negligible pressure dependence of: (i) the number of gas molecules that occupy the cavities; (ii) the compressibility of the aqueous phase; and, (iii) the compressibility of the hydrate phase. Their use in Eq. (14) results in:

$$\Delta\mu = kT \sum_{i=1}^{nh} \frac{n_i(T,P_e)}{N_{cav}} \ln \left[\frac{\phi_i(T,P,\underline{y}) P}{\phi_i(T,P_e,\underline{y}) P_e} \right] + \Delta v_e(P - P_e) \quad (15)$$

where:

$$\Delta v_e(T) = n_{wh} v_w(T,P_e) - v_h(T,P_e) \quad (16)$$

and $n_i(T,P_e)/N_{cav}$ is the total fractional occupation of cavities by molecule i .

The fractional occupation of a cavity of type j by a molecule of type i , is obtained [2]:

$$\theta_{ij} = \frac{C_{ij} f_i}{1 + \sum_{k=1}^{nh} C_{kj} f_k} \quad (17)$$

where C_{ij} is the *Langmuir* constant of molecule i in cavity of type j and f_i is the fugacity of component i . By using this equation, we can calculate total fractional occupation of cavities as:

$$\frac{n_i(T,P_e)}{N_{cav}} = \frac{\theta_{i,1} N_{cav,1} + \theta_{i,2} N_{cav,2}}{N_{cav}} \quad (18)$$

where 1 and 2 are the types of cavities (i.e., small and large cavities in sI and sII).

In the case when N_{cav} is the number of cavities that can be occupied by gas molecule in unit cell of the hydrate crystal lattice, which its volume is v_{cell} , we can calculate v_h by using the relation:

$$v_h = \frac{v_{cell}}{N_{cav}} \quad (19)$$

combining Eqs. (16) and (19), leads to:

$$\Delta v_e = n_{wh} v_w - \frac{v_{cell}}{N_{cav}} \quad (20)$$

Eq. (15) differs from that of *Gnanendran et al.* [14] in which they used the water free mole fraction of gaseous components in hydrate phase, x_m^h , while in this work, the total fractional occupation of cavities by molecule i , was considered.

Isobaric regime

In this regime $\Delta\mu$ is varied by changing T at constant P and \underline{y} . This is shown in Fig. 2 by a horizontal arrow

from point B to point S. From thermodynamics [13], in isobaric regime μ_{gg_i} , μ_w and μ_h are given by:

$$\mu_{gg_i}(T, P, \underline{y}) = \mu_{gg_i}^*(P) - \int_{T^*}^T s_{gg_i}(T', P, \underline{y}) dT' \quad (21)$$

$$\mu_w(T, P) = \mu_w^*(P) - \int_{T^*}^T s_w(T', P) dT' \quad (22)$$

$$\mu_h(T, P, \underline{x}) = \mu_h^*(P) - \int_{T^*}^T s_h(T', P, \underline{x}) dT' \quad (23)$$

Here, s_{gg_i} , s_w and s_h are the entropies per gas molecule in the gas phase, per water molecule in the solution and per hydrate building unit in the hydrate crystal, respectively. $\mu_{gg_i}^*$, μ_w^* and μ_h^* are reference chemical potentials depending only on P, and T^* is a reference temperature. Using the above equations in the general expression for $\Delta\mu$, Eq. (8), results in:

$$\begin{aligned} \Delta\mu = & \sum_{i=1}^{nh} \frac{n_i(T, P)}{N_{cav}} \mu_{gg_i}^*(P) + n_{wh} \mu_w^*(P) - \\ & \sum_{i=1}^{nh} \frac{n_i(T, P)}{N_{cav}} \int_{T^*}^T s_{gg_i}(T', P, \underline{y}) dT' - \\ & n_{wh} \int_{T^*}^T s_w(T', P) dT' - \mu_h^*(P) + \\ & \int_{T^*}^T s_h(T', P, \underline{x}) dT' \end{aligned} \quad (24)$$

At the chosen pressure P, there exists an equilibrium temperature $T_e(P)$ at which the solution and the hydrate phase can coexist. It corresponds to point B in Fig. 2 and is the solution of the following equation:

$$\begin{aligned} 0 = & \sum_{i=1}^{nh} \frac{n_i(T_e, P)}{N_{cav}} \mu_{gg_i}^*(P) + n_{wh} \mu_w^*(P) - \\ & \sum_{i=1}^{nh} \frac{n_i(T_e, P)}{N_{cav}} \int_{T^*}^{T_e} s_{gg_i}(T', P, \underline{y}) dT' - \\ & n_{wh} \int_{T^*}^{T_e} s_w(T', P) dT' - \mu_h^*(P) + \\ & \int_{T^*}^{T_e} s_h(T', P, \underline{x}) dT' \end{aligned} \quad (25)$$

Employing Eq. (25) to eliminate $n_{wh} \mu_w^*(P)$ and $\mu_h^*(P)$ from Eq. (24), we get:

$$\begin{aligned} \Delta\mu = & \sum_{i=1}^{nh} \left(\frac{n_i(T, P)}{N_{cav}} - \frac{n_i(T_e, P)}{N_{cav}} \right) \mu_{gg_i}^*(P) - \\ & \sum_{i=1}^{nh} \frac{n_i(T, P)}{N_{cav}} \int_{T^*}^T s_{gg_i}(T', P, \underline{y}) dT' + \\ & \sum_{i=1}^{nh} \frac{n_i(T_e, P)}{N_{cav}} \int_{T^*}^{T_e} s_{gg_i}(T', P, \underline{y}) dT' - \\ & n_{wh} \int_{T^*}^T s_w(T', P) dT' + n_{wh} \int_{T^*}^{T_e} s_w(T', P) dT' + \\ & \int_{T^*}^T s_h(T', P, \underline{x}) dT' - \int_{T^*}^{T_e} s_h(T', P, \underline{x}) dT' \end{aligned} \quad (26)$$

This is the general formula for $\Delta\mu$ in isobaric regime when there exists equilibrium between the solution and the gas phases. It can be simplified by means of the following two approximations:

(i) Approximation $n_i(T, P) \approx n_i(T_e, P)$: This approximation ignores the temperature dependence of the number of gas molecules that occupy the cavities for T close enough to T_e and results in elimination of $\mu_{gg_i}^*$ and T^* from Eq. (26). This equation thus becomes:

$$\Delta\mu = \int_{T^*}^{T_e} \Delta s(T', P, \underline{z}) dT' \quad (27)$$

where:

$$\begin{aligned} \Delta s(T, P, \underline{z}) = & \sum_{i=1}^{nh} \frac{n_i(T_e, P)}{N_{cav}} s_{gg_i}(T, P, \underline{y}) + \\ & n_{wh} s_w(T, P) - s_h(T, P, \underline{x}) \end{aligned} \quad (28)$$

And Δs is the hydrate dissociation entropy per hydrate building unit at the given P and T. That is, the entropy changes due to the transfer of $\sum_{i=1}^{nh} n_i/N_{cav}$ gas molecules from the hydrate crystal into the gas phase and transfer of n_{wh} water molecules from the hydrate crystal to the solution.

(ii) Approximation resulting from Taylor series truncation: According to thermodynamics [12], the entropy s and the heat capacity c_p at constant pressure are related by $ds = (c_p/T)dT$. For that reason $\Delta\mu$ from Eq. (27) can be expanded in the following Taylor series about $T=T_e$ [5]:

Table 1: Hydrate crystal structure and values of water molecules per cavities that can be occupied by gas molecules, number of cavities that can be occupied by gas molecules per unit cell of hydrate crystal, volume of hydrate building unit* u_h , volume difference Δu_e .

Gas	Hydrate Structure	n_{wh}	N_{cav}	u_h (nm ³)	Δu_e (nm ³)
CH ₄	sI	23/4	8	0.216	-0.0435
C ₂ H ₆	sI	23/3	6	0.288	-0.058
c-C ₃ H ₄	sI	23/3	6	0.288	-0.058
C ₃ H ₈	sII	17	8	0.647	-0.137
i-C ₄ H ₁₀	sII	17	8	0.647	-0.137
CH ₄ + C ₂ H ₆	sI	23/4	8	0.216	-0.0435
CH ₄ + C ₂ H ₆	sII	17/3	24	0.216	-0.046
CH ₄ + C ₃ H ₈	sII	17/3	24	0.216	-0.046
C ₂ H ₆ + C ₃ H ₈	sII	17	8	0.647	-0.137
C ₃ H ₈ + i-C ₄ H ₁₀	sII	17	8	0.647	-0.137

$$\Delta\mu = -\Delta s_e (T - T_e) - \left(\frac{\Delta c_{p,e}}{2T_e} \right) (T - T_e)^2 - \left[\frac{T_e \Delta c'_{p,e} - \Delta c_{p,e}}{6T_e^2} \right] (T - T_e)^3 - \dots \quad (29)$$

where Δs_e and $\Delta c_{p,e}$ are the differences between the entropies and the heat capacities of the old and the new phases, respectively, at $T=T_e$; and, $\Delta c'_{p,e} = dc_p/dT$, at $T=T_e$. Since the second and the third terms have negligible contribution in Eq. (29) [11], we can ignore them. Then we can write:

$$\Delta\mu = \Delta s_e \Delta T \quad (30)$$

here ΔT (K), is defined as:

$$\Delta T = T_e - T \quad (31)$$

and the quantity Δs_e (J/K), is given by:

$$\Delta s_e (T, P, z) = \sum_{i=1}^{nh} \frac{n_i(T_e, P)}{N_{cav}} s_{gg_i}(T_e, P, y) + n_{wh} s_w(T_e, P) - s_h(T_e, P, x) \quad (32)$$

From basic thermodynamic relations [13], $T_e \Delta s_e = \Delta h_e$, where Δh_e is the enthalpy or latent heat (per hydrate building unit) of dissociation of the hydrate crystal into gaseous phase and liquid water at $T=T_e$.

CALCULATIONS AND RESULTS

Table 1, shows the number of water molecules per cavity that can be occupied by the guest molecules and the number of cavities that can be occupied by the guest molecules in the cubic structures of hydrate crystal, sI and sII [1, 2]. The values of u_h and Δu_e calculated from Eqs. (19) and (20) for a number of gas hydrates are listed in table 1.

The calculations are based on $v_{cell} = d_0^3 = 1.73$ and 5.18 nm^3 for the cubic structures I and II, respectively, $v_w = 0.03 \text{ nm}^3$ and the N_{cav} and n_{wh} values listed in table 1 ($d_0 = 1.2$ and 1.73 nm is the lattice parameter of the sI and sII hydrate crystals [2]).

The curves in Figs. 3 and 4 depict the $\Delta\mu(P, y)$ (Eq. (15)) for three different mixtures of methane and ethane hydrates at $T=275.15 \text{ K}$, the compositions of which are 25 %, 50 % and 75 % methane (mole fraction), respectively. Mixtures of methane and ethane can form sI and sII hydrate.

In this work, the mixture containing 25 % and 50 % methane forms sI and the mixture containing 75 % methane forms sII hydrate, at $T=275.15 \text{ K}$. The curves were drawn with the aid of $P_e = 0.7, 0.88$ and 1.27 MPa for mixtures containing 25 %, 50 % and 75 % methane, respectively. For mixtures containing 25 % and 50 % methane, the fractional occupation of cavities by methane is 0.0990475 and 0.1981975, for ethane is 0.7149675

and 0.668775, and total fractional occupation is 0.814015 and 0.8669725, respectively. For a mixture containing 75 % methane, the fractional occupation of cavities by methane is 0.433447, for ethane is 0.31482, and total fractional occupation is 0.748267. These equilibrium pressures and the fractional occupation of cavities have been determined using the model of *van der Waals* and *Platteeuw* [15] with *Kihara* parameters obtained by *Sloan* [16]. The parameters that were considered in these calculations included, Δv_e from table 1 (represented by curve 1, in Figs. 3 and 4), $\Delta v_e = 0$ (represented by curve 2, in Figs. 3 and 4), and ϕ_i values which were obtained by using the *Peng-Robinson* equation of state [17], with $k_{ij} = 0.0026$. The difference between curves 1 and 2 illustrates the appreciable contribution of the Δv_e term, in Eq. (15), to the supersaturation at high pressure.

The isobaric $\Delta\mu(T, y)$ given by Eq. (30) is illustrated in Fig. 5 for mixtures of methane and ethane containing 75 % and 25 % methane at $P = 7.89$ and $P = 4.55$ Pa, respectively. For both mixtures the equilibrium temperature is 290.0 K. The enthalpy of dissociation has been calculated by Clapeyron equation. The equilibrium temperature and pressure for these mixtures have been determined using the model of *van der Waals* and *Platteeuw* [15] with *Kihara* parameters obtained by *Sloan* [16]. At $T_e = 290.0$ K, for mixtures containing 75 % and 25 % methane, the enthalpies of dissociation are 80083.0 and 76239.0 J/mol which yielded $\Delta s_e = 33.2$ k and $\Delta s_e = 31.6$ k, respectively.

CONCLUSIONS

In this work we have derived a general expression for the supersaturation for nucleation of multicomponent gas hydrates. We have assumed that the number of gas molecules that occupy the cavities is a function of temperature and pressure. Consequently, this analysis provides two formulas at isothermal and isobaric regimes for driving force for nucleation of hydrates of multicomponent gas in aqueous solutions (Eqs.(14, 26)).

In isothermal regime, the general formula for supersaturation was simplified (Eq. (15)), by ignoring the effect of pressure on: (i) the number of molecules that occupy the cavities, (ii) compressibility of aqueous, and (iii) compressibility of hydrate phase for pressure close to equilibrium pressure.

In isobaric regime, the general formula for

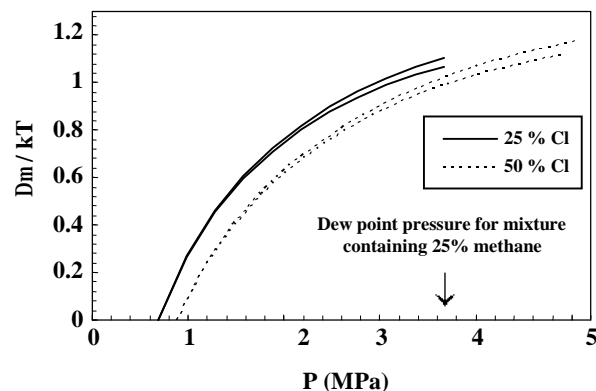


Fig. 3: Pressure dependence of the supersaturation for crystallization of 25 % and 50 % methane mixtures at $T = 275.15$ K. Curve 1 and 2 Eq. (15) with $Du_e = -0.0435 \text{ nm}^3$ and $Du_e = 0$, respectively.

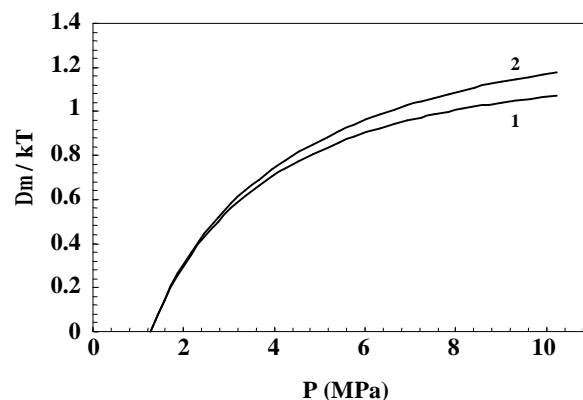


Fig. 4: Pressure dependence of the supersaturation for crystallization of 75 % methane and 25 % ethane mixture at $T = 275.15$ K. curve 1 and 2 Eq. (15) with $Du_e = -0.046 \text{ nm}^3$ and $Du_e = 0$, respectively.

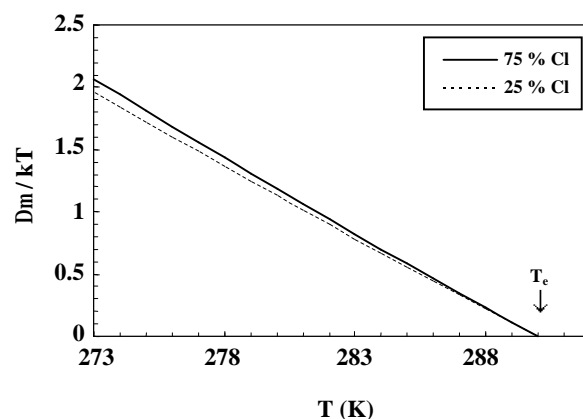


Fig. 5: Temperature dependence of the supersaturation for crystallization of mixtures of methane and ethane. Solid line is for mixture containing 75% methane at $P = 7.89 \text{ MPa}$, and dashed line is for mixture containing 25 % methane at $P = 4.55 \text{ MPa}$.

supersaturation was also simplified, (Eq. (30)) assuming the effect of temperature on the number of molecules that occupy the cavities is negligible for temperature close to equilibrium temperature.

Nomenclatures

C	Concentration
c_p	Heat capacity
C_{ij}	Langmuir constant of molecule i in cavity of type j
f	Fugacity
G	Gas molecule
H	Enthalpy or latent heat of dissociation
k	Boltzmann's constant
n	Number of gas molecules that occupy the cavities
n_c	Number of component
n_h	Number of hydrate former component
n_{wh}	Number of water molecules per occupied cavities in hydrate crystal unit
N_{cav}	Number of cavities that can occupy by gas molecules in cubic structure of hydrate crystal
N_{wh}	Number of water molecules in the unit structure of hydrate crystal
P	Pressure
s	Entropy
T	Absolute temperature
V	Volume of solution
v	Volume of molecule or building unit of hydrate crystal
\underline{x}	Vector of hydrate phase mole fraction
\underline{y}	Vector of gas phase mole fraction
\underline{z}	Vector of composition

Greek letters

φ	Gas phase fugacity coefficient
γ	Activity coefficient
μ	Chemical potential
θ_{ij}	Fractional occupation of cavity of type j by molecule i

Subscripts

0	Reference property
e	Equilibrium condition
gg	Gas phase
gs	Aqueous solution of gas
h	Hydrate phase
hs	Aqueous solution of hydrate

i	Gaseous component
j	Type of cavity
w	Water

Superscripts

*	Reference property
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REFERENCES

- [1] Makogon, Y. F., "Hydrates of Hydrocarbons", Pennwell, Tulsa, (1997).
- [2] Sloan, E.D., "Clathrate Hydrates of Natural Gases", Dekker, New York, (1998).
- [3] Gudmundsson, J.S., Anderson, V., Levik, O.I., Parlaktuna, M., *SPE Paper 50598*, (1998).
- [4] Fitzgerald, M. Taylor, *SPE Paper 71805*, (2001).
- [5] Kashchiev, "Nucleation; Basic Theory with Applications", Butterworth-Heinemann, Oxford, (2000).
- [6] Mullin, J.W., "Crystallization", Third edition, Butterworth-Heinemann, Oxford, (1993).
- [7] Visniauskas, A., Bishnoi, P.R., *Chem. Eng. Sci.* **38**, 1061 (1983).
- [8] Englezos, P., Kalogerakis, N., Dholabhai, P.D., Bishnoi, P.R., *Chem. Eng. Sci.*, **42**, 2647 and 2659 (1987).
- [9] Natarajan, V., Bishnoi, P.R., Kalogerakis, N., *Chem. Eng. Sci.*, **49**, 2075 (1994).
- [10] Scovborg, P., Rasmussen, P., *Chem. Eng. Sci.*, **49**, 1131 (1994).
- [11] Kashchiev, D., Firoozabadi, A., *Journal of Crystal Growth*, **241**, 220 (2002).
- [12] Denbigh, K., "The Principles of Chemical Equilibrium", Cambridge University Press, Cambridge, (1971).
- [13] Firoozabadi, A., "Thermodynamics of Hydrocarbons Reservoirs", McGraw-Hill, New York, (1999).
- [14] Gnanendran, N., Amin, R., *Chem. Eng. Sci.*, **59**, 3849 (2004).
- [15] van der Waals, J.H., Platteeuw, J.C., *Adv. Chem. Phys.*, **2**, 1 (1959).
- [16] Ballard, A.L., Sloan, E.D., Proceeding of the 3rd International Conference on Gas Hydrates, Salt Lake City, Utah, p. 702, 18-22 July (2000).
- [17] Peng, D. Y., Robinson, D. B., *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).