Driving force for crystallization of gas hydrates

Dimo Kashchieva, Abbas Firoozabadi

Abstract

A general expression is derived for the supersaturation for crystallization of one-component gas hydrates in aqueous solutions. The supersaturation is the driving force of the process, since it represents the difference between the chemical potentials of a hydrate building unit in the solution and in the hydrate crystal. Expressions for the supersaturation are obtained for solutions supersaturated in isothermal or isobaric regime. The results obtained are applied to the crystallization of hydrates of methane, ethane and other one-component gases.

1. Introduction

Gas hydrate crystallization and dissociation, and their inhibition or promotion are of interest to a wide range of applications, including natural gas production facilities and pipelines, deep ocean carbon dioxide sequestration, transportability of natural gases in the form of gas hydrates, use of gas hydrate deposits in the oceans and in geological formations, drilling fluids, and desalination. In these applications, two topics are of prime importance: (i) thermodynamic equilibrium, and (ii) kinetics. There has been major progress in thermodynamic modeling of gas hydrates and the associated phases since 1940 [1,2]. Studies on the kinetics of the process of gas hydrate crystallization are, however, at a relatively early stage of development despite notable work of various authors in the last three decades (see papers referred to, e.g., by Makogon [1] and Sloan [2]). Issues related to the nucleation and growth processes, including the supersaturation, the nucleation and growth rates and the induction time, have not been sufficiently clarified. For instance, there is considerable difference of opinion among various groups on what actually is the driving force for hydrate crystallization [2–6].

In this work, we define and study the driving force for the process of gas hydrate crystallization. This problem has recently been the subject of a number of papers [2,4–10], but has not been resolved yet, despite its importance for the development of a comprehensive description of...
the appearance and growth of gas hydrates under various conditions. In subsequent work we will investigate the nucleation rate and the induction time in hydrate crystallization as well as the effect of additives (surfactants, polymers, etc.) on the kinetic inhibition or promotion of the process.

2. General analysis

We consider a three-phase system of a one-component gas, an aqueous solution of the gas and a crystalline hydrate of the gas (Fig. 1). The gas phase is treated as one-component, because the partial pressure of water vapor in it is often negligible at the hydrate crystallization temperatures. The system is held at fixed pressure \( P \) and temperature \( T \), and the hydrate phase is considered as resulting from the following precipitation “reaction” occurring in the solution [2]

\[
G + n_w H_2O \rightleftharpoons G \cdot n_w H_2O. \tag{1}
\]

This relation implies that the crystallization of the hydrate in the solution is analogous to the precipitation of, e.g., inorganic salts in aqueous solutions [11]. Indeed, one molecule (G) of the dissolved gas and \( n_w \) water molecules of the solution form one building unit (\( G \cdot n_w H_2O \)) of the hydrate crystal just like, for instance, one Na and one Cl ions in an aqueous solution associate into one NaCl building unit during precipitation of crystalline sodium chloride. As seen from Table 1, for stoichiometric gas hydrates of the cubic structures sI and sII the hydration number \( n_w \) has values between \( 17/3 \approx 5.67 \) and 17 [1,2]. When the hydrate crystal is non-stoichiometric, the \( n_w \) values are higher.

Let \( \mu_{gs} \) and \( \mu_w \) be the chemical potentials of the gas and water molecules in the aqueous solution, respectively (Fig. 1). According to the thermodynamic relation between chemical potentials in reaction equilibria [12] and Eq. (1), for the chemical potential \( \mu_{hs} \) of a hydrate building unit in the solution we shall have [1]

\[
\mu_{hs} = \mu_{gs} + n_w \mu_w. \tag{2}
\]

By definition [13], the driving force for new phase formation is the difference between the chemical potentials of the old and the new phases. This difference is called supersaturation and is commonly denoted by \( \Delta \mu \). Hence, if \( \mu_{hs} \) is the chemical potential of a building unit (one gas molecule and \( n_w \) water molecules) in the hydrate crystal (Fig. 1), the supersaturation \( \Delta \mu \) in hydrate formation will be given by

\[
\Delta \mu = \mu_{gs} + n_w \mu_w - \mu_h \tag{3}
\]

because \( \mu_{hs} \) from Eq. (2) and \( \mu_h \) are the chemical potentials of the old and the new phases, respectively. Nucleation and/or growth of hydrate crystals are possible only when \( \Delta \mu > 0 \); then \( \mu_{hs} > \mu_h \) [1] and the solution is supersaturated. If \( \Delta \mu = 0 \), the solution is saturated and the system is in phase equilibrium: then \( \mu_{hs} = \mu_h \) and the dissolved and crystalline hydrate phases can coexist. When \( \Delta \mu < 0 \), the solution is undersaturated: as then \( \mu_{hs} < \mu_h \), hydrate crystals cannot nucleate in the solution, and existing ones are subject to dissolution. Thus, while \( \Delta \mu \) is the driving force for hydrate formation, \( -\Delta \mu \) is the driving force for hydrate dissolution. It must be pointed out also that replacement of “aqueous solution” (or “solution”) and “liquid water” by “ice” throughout the paper makes all expressions for \( \Delta \mu \) directly applicable to the formation of one-component gas hydrates in ice and to the decomposition of these hydrates into ice and gaseous phase.

Fig. 1. Three-phase system of one-component gas, aqueous solution of the gas and gas hydrate.
The general Eq. (3) allows expressing $\Delta \mu$ in terms of the actual concentration $C$ (m$^{-3}$) of dissolved gas in the aqueous solution. As known from thermodynamics [14]

$$\mu_{gs}(P, T, C) = \mu_{gs}^*(P, T) + kT \ln[\gamma(P, T, C)N_g/(N_g + N_w)],$$  

(4)

where $\mu_{gs}^*$, a function of $P$ and $T$ only, is a reference chemical potential, $k$ is the Boltzmann constant, $\gamma$ is the activity coefficient of dissolved gas, and $N_g$ and $N_w$ are the number of gas and water molecules in the solution, respectively. Denoting by $N$ the volume of the solution, and by $\nu$ the volume of a water molecule in it, we have $N_w \approx V/\nu_w$, because $N_w \gg N_g$. Taking into account that $N_g = CV$, we can rewrite Eq. (4) in the form

$$\mu_{gs}(P, T, C) = \mu_{gs}^*(P, T) + kT \ln[\gamma(P, T, C)\nu_w C].$$  

(5)

Employing this expression in Eq. (3), recalling that $n_w$ is a function of $P$ and $T$ [2] and accounting that $\mu_w$ and $\mu_h$ are virtually $C$-independent leads to the following formula:

$$\Delta \mu = kT \ln[\gamma(P, T, C)\nu_w C] + \mu_{gs}^*(P, T) + n_w(P, T)\mu_w(P, T) - \mu_h(P, T).$$  

(6)

This general equation gives the dependence of $\Delta \mu$ on $C$ in crystallization of gas hydrates in aqueous solutions of one-component gases. Adopting the convention [14] of gas as a solute allows using the approximation $\gamma = 1$ because of the relatively low solubility of most gases in water.

Eq. (6) shows that in the $\gamma = 1$ approximation $\Delta \mu$ increases logarithmically with $C$. This means that the concrete conditions of dissolution of the gas into the aqueous phase are of prime importance for supersaturating the system, i.e. for creating a driving force for hydrate crystallization. We shall now consider gas dissolution in two different cases which can be encountered in practice and which are characterized by different dependences of $\Delta \mu$ on $P$ and $T$.

3. Chemical equilibrium between solution and gas phase

In this case, a long enough time has elapsed after the aqueous and gas phases are in contact with each other and the system is in chemical equilibrium. This means that the concentration of dissolved gas has its equilibrium value for which we shall keep the notation $C$. The equilibrium concentration $C$ is determined by the condition for

Table 1

<table>
<thead>
<tr>
<th>Gas</th>
<th>Hydrate structure</th>
<th>$n_w$</th>
<th>$n_g$</th>
<th>$\nu_h$ (nm$^3$)</th>
<th>$-\Delta \nu$ (nm$^3$)</th>
<th>$-\nu_c$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>sII</td>
<td>17/3</td>
<td>24</td>
<td>0.216</td>
<td>0.046</td>
<td>0.034</td>
</tr>
<tr>
<td>Kr</td>
<td>sII</td>
<td>17/3</td>
<td>24</td>
<td>0.216</td>
<td>0.046</td>
<td>0.099</td>
</tr>
<tr>
<td>N$_2$</td>
<td>sII</td>
<td>17/3</td>
<td>24</td>
<td>0.216</td>
<td>0.046</td>
<td>0.019</td>
</tr>
<tr>
<td>O$_2$</td>
<td>sII</td>
<td>17/3</td>
<td>24</td>
<td>0.216</td>
<td>0.046</td>
<td>0.036</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>sI</td>
<td>23/3</td>
<td>6</td>
<td>0.216</td>
<td>0.044</td>
<td>0.086</td>
</tr>
<tr>
<td>Xe</td>
<td>sI</td>
<td>23/3</td>
<td>6</td>
<td>0.216</td>
<td>0.044</td>
<td>0.253</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>sI</td>
<td>23/3</td>
<td>6</td>
<td>0.216</td>
<td>0.044</td>
<td>0.339</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>sI</td>
<td>23/3</td>
<td>6</td>
<td>0.216</td>
<td>0.044</td>
<td>0.366</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>sI</td>
<td>17</td>
<td>8</td>
<td>0.647</td>
<td>0.137</td>
<td>0.787</td>
</tr>
<tr>
<td>Xe</td>
<td>sII</td>
<td>23/3</td>
<td>6</td>
<td>0.216</td>
<td>0.044</td>
<td>0.221</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$</td>
<td>sII</td>
<td>17</td>
<td>8</td>
<td>0.647</td>
<td>0.137</td>
<td>0.787</td>
</tr>
</tbody>
</table>

$^a$According to Ref. [2], p. 53.

$^b$Calculated from $B/v_c = 0.430 - 0.886(T_a/T) - 0.694(T_a/T)^2 - 0.0375(T_a/T)^3$ (Ref. [15], p. 126) where $T_a$ and $v_c$ are the critical temperature and volume, respectively, and $q = 0$ for Ar, Kr, N$_2$, O$_2$, CH$_4$, Xe, H$_2$S, CO$_2$ and c-C$_3$H$_4$, $q = 1$ for C$_2$H$_6$, $q = 2$ for C$_3$H$_8$ and $q = 3$ for i-C$_4$H$_{10}$. 


chemical equilibrium between the solution and the gas phase
\[ \mu_{gs} = \mu_{gg}, \]  
(7)

where \( \mu_{gg} (P, T) \) is the chemical potential of a gas molecule in the gas phase (Fig. 1). Eq. (7) implies that in the case of solution/gas chemical equilibrium the right-hand side of Eq. (4) (or (5)) is equal to \( \mu_{gg} \). Hence, in this case we can replace the first two summands on the right-hand side of Eq. (6) by \( \mu_{gg} \) in order to eliminate the gas concentration \( C \) and obtain \( \Delta \mu \) in the form

\[ \Delta \mu = \mu_{gg}(P, T) + n_w(P, T) \mu_w(P, T) - \mu_h(P, T). \]  
(8)

This general formula reveals that in the case of solution/gas chemical equilibrium \( \Delta \mu \) depends on \( P \) and \( T \) only. The reason for the disappearance of \( C \) from Eq. (8) is that \( C \) itself is a function of \( P \) and \( T \) as required by Eq. (7). Eq. (8) allows determination of the supersaturation in an arbitrary regime of variation of \( P \) and \( T \). We shall now consider the two important regimes of isothermal and isobaric variation of \( \Delta \mu \).

### 3.1. Isothermal regime

In this regime \( \Delta \mu \) is varied by changing \( P \) at constant \( T \). This is illustrated in Fig. 2 by the arrow passing through point A and ending at point S which represents the state of the system at given values of \( P \) and \( T \). From thermodynamics [14], for this regime we can write

\[ \mu_{gg}(P, T) = \mu_{gg,0}(T) + kT \ln[\varphi(P, T)P], \]  
(9)

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

\[ \mu_h(P, T) = \mu_{h,0}(T) + \int_0^P v_h(P', T) \, dP', \]  
(11)

where \( \varphi \) is the fugacity coefficient of the gas, \( v_w \) (m\(^3\)) and \( v_h \) (m\(^3\)) are the volumes of a water molecule in the solution and of a building unit in the hydrate crystal, respectively, and \( \mu_{gg,0}, \mu_{w,0}, \mu_{h,0} \) are reference chemical potentials depending only on \( T \). Substitution of the above equations in

<table>
<thead>
<tr>
<th>PRESSURE</th>
<th>TEMPERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (_e)(T)</td>
<td>T (_e)(P)</td>
</tr>
</tbody>
</table>

Eq. (8) yields

\[ \Delta \mu = kT \ln[\varphi(P_e, T)P_e] + \mu_{gg,0}(T) \]
+ \( n_w(P_e, T) \mu_{w,0}(T) - \mu_{h,0}(T) \)
+ \( n_w(P_e, T) \int_0^{P_e} v_w(P', T) \, dP' \)
\[ - \int_0^{P_e} v_h(P', T) \, dP'. \]  
(12)

As already noted, the phase equilibrium between solution and hydrate is characterized by \( \Delta \mu = 0 \).

At the chosen temperature \( T \) the supersaturation becomes zero at the so-called equilibrium (more accurately, phase equilibrium) pressure \( P_e(T) \) corresponding to point A in Fig. 2. The \( P_e(T) \) function is illustrated by the curve in this figure and can be obtained from the expression

\[ 0 = kT \ln[\varphi(P_e, T)P_e] + \mu_{gg,0}(T) \]
+ \( n_w(P_e, T) \mu_{w,0}(T) - \mu_{h,0}(T) \)
+ \( n_w(P_e, T) \int_0^{P_e} v_w(P', T) \, dP' \)
\[ - \int_0^{P_e} v_h(P', T) \, dP'. \]  
(13)
which follows from Eq. (12) at $P = P_c$. This expression allows elimination of the reference chemical potentials $\mu_{g,0}(T)$ and $\mu_{v,0}(T)$ in Eq. (12) and representation of $\Delta \mu$ in the form

$$
\Delta \mu = kT \ln[\varphi(P, T)P/\varphi(P_e, T)P_e] + [n_w(P, T) - n_w(P_e, T)]\mu_{v,0}(T) + n_w(P, T)\int_0^P v_w(P', T) \, dP' - n_w(P_e, T)\int_0^{P_e} v_w(P', T) \, dP' - \int_{P_e}^P v_h(P', T) \, dP'.
$$

(14)

This is the general formula for $\Delta \mu$ in isothermal regime provided the solution is in chemical equilibrium with the gas phase. It can be simplified and made readily applicable with the help of several successive approximations.

(i) Approximation $n_w \approx n_w(P_e, T), v_w \approx v_w(P_e, T)$ and $v_h \approx v_h(P_e, T)$: These relations imply negligible pressure dependence of the hydration number and of the compressibility of the aqueous and hydrate phases for $P$ close enough to $P_c$. Their use in Eq. (14) results in

$$
\Delta \mu = kT \ln[\varphi(P, T)P/\varphi(P_e, T)P_e] + \Delta \nu_c(P - P_c),
$$

(15)

where for brevity

$$
\Delta \nu_c(T) \equiv n_w(P_e, T)v_w(P_e, T) - v_h(P_e, T).
$$

(16)

Eq. (15) differs from those of Englezos et al. [4] and Sloan (Ref. [2], p. 100) by the definition of the quantity $\Delta \nu_c$ (for instance, the hydration number $n_w$ is missing in the $\Delta \nu_c$ expression of the latter author). Physically, $\Delta \nu_c$ in Eq. (15) is the difference between the volume of $n_w$ water molecules in the solution and the volume of a hydrate building unit in the hydrate crystal at the equilibrium pressure $P_e$. If $n_g$ is the number of gas molecules per unit cell of the hydrate crystal lattice, this cell contains $n_g$ building units (the $n_g$ value may differ from that corresponding to the stoichiometric hydrate crystal). Hence, denoting by $v_{cell}$ (m$^3$) the volume of this cell, we can calculate $v_h$ by using the relation

$$
v_h = v_{cell}/n_g.
$$

(17)

Combining Eqs. (16) and (17) thus leads to the formula

$$
\Delta \nu_c = n_wv_w - v_{cell}/n_g.
$$

(18)

The values of $v_h$ and $\Delta \nu_c$ calculated from Eqs. (17) and (18) 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 sI and sII, respectively, $v_w = 0.03$ nm$^3$ and the $n_g$ and $n_w$ values listed in the table ($d_0 = 1.2$ and 1.73 nm is the lattice parameter of the sI and sII hydrate crystals [2]). As seen from the table, $\Delta \nu_c$ is a negative quantity with a relatively high absolute value between about 0.04 and 0.14 nm$^3$. As a result, the $\Delta \nu_c$ term in Eq. (15) can contribute significantly to the value of $\Delta \mu$ when the pressure $P$ exceeds the equilibrium pressure $P_e$ by more than about 1 MPa.

The solid curves in Figs. 3 and 4 depict the $\Delta \mu(P)$ dependence from Eq. (15) for methane and ethane hydrate at $T = 273.2$ K, respectively. The curves are drawn with the aid of $P_e = 2.6$ MPa for methane hydrate and 0.53 MPa for ethane hydrate [2], $\Delta \nu_c$ from Table 1 (curves 1) or $\Delta \nu_c = 0$ (curves 2) and $\varphi$ values obtained by using the Peng–Robinson equation of state for methane and ethane. The difference between curves 1 and 2 thus illustrates the appreciable contribution of the
\[ \Delta u_e \text{ term in Eq. (15) to the supersaturation at high pressures. For methane hydrate at } P = 100 \text{ MPa, this contribution can be as high as about } 50\% \text{ (result not shown in Fig. 3). As seen from Fig. 4, since at } 273.2 \text{ K ethane is a subcritical gas, the increase of } \Delta u \text{ with increasing } P \text{ is limited by the transformation of the gas into liquid at about } 3 \text{ MPa.}
\]

(ii) Approximation \( \varphi(P, T) \approx \exp(bP/kT) \): This relation gives the fugacity coefficient \( \varphi \) in terms of the second virial coefficient \( b \) (m\(^3\)) of the gas contacting the solution \[12\]. This coefficient changes from negative to positive with increasing temperature, and setting \( b = 0 \) results in the ideal-gas approximation \( \varphi = 1 \). Values of \( b \) for some gases at \( T = 273.2 \) are presented in Table 1.

Employing the above expression for \( \varphi \) in Eq. (15) yields
\[ \Delta \mu = kT \ln(P/P_c) + v_{ef}(P - P_c), \tag{19} \]
where the effective molecular volume \( v_{ef} \) (m\(^3\)) is defined by
\[ v_{ef} = \Delta u_e + b. \tag{20} \]

Compared with Eq. (15), Eq. (19) has the advantage to give \( \Delta \mu \) as an explicit function of the pressure \( P \). While in it the logarithmic term is always positive for \( P > P_c \), depending on the sign of \( v_{ef} \), the linear term may be either positive or negative. Table 1 lists \( v_{ef} \) values for a number of gas hydrates and shows that at \( T = 273.2 \text{ K} \) they are negative. This is so, because usually \( b < -\Delta u_e \) for one-component gases at temperatures between 273 and 300 K (see Table 1).

The approximate \( \Delta \mu(P) \) dependence, Eq. (19), for methane and ethane hydrate is depicted by the dashed curves in Figs. 3 and 4, respectively. The \( T \) and \( P_c \) values are those given above, \( b \) is from Table 1, and \( \Delta u_e \) is either from Table 1 (curves 3) or equals zero (curves 4). The difference between curves 3 and 4 thus illustrates the contribution of the \( \Delta u_e \) term to \( \Delta \mu \) at high pressures. Figs. 3 and 4 show also that Eq. (19) is an acceptable approximation to Eq. (15) up to relatively high values of \( P \).

(iii) Approximation \( \varphi = 1 \): This approximation means that the hydrate-forming gas is treated as ideal, so that \( b = 0 \). Hence, according to Eq. (15) or (19), in this approximation \( \Delta \mu \) is given by
\[ \Delta \mu = kT \ln(P/P_c) + \Delta u_e(P - P_c). \tag{21} \]

The dotted curves in Figs. 3 and 4 represent this \( \Delta \mu(P) \) dependence also for methane and ethane hydrate, respectively, the \( T \) and \( P_c \) values being those already used. Curves 5 correspond to \( \Delta u_e \) from Table 1, and curves 6 are drawn with \( \Delta u_e = 0 \) to illustrate the \( \Delta u_e \) contribution to \( \Delta \mu \). Comparison with the solid curves displaying Eq. (15) shows that the use of the approximate Eq. (21) is legitimate only for pressures close enough to the equilibrium pressure \( P_c \).

3.2. Isobaric regime

In this regime \( \Delta \mu \) is varied by changing \( T \) at constant \( P \). This is schematized in Fig. 2 by the arrow heading through point B to point S. From thermodynamics \[14\], in isobaric regime \( \mu_{gg}, \mu_w \) and \( \mu_h \) are given by
\[ \mu_{gg}(P, T) = \mu_{gg}^*(P) - \int_{T'}^T s_{gg}(P, T') \, dT', \tag{22} \]
\[ \mu_w(P, T) = \mu_w^*(P) - \int_{T'}^T s_w(P, T') \, dT', \tag{23} \]
\[ \mu_h(P, T) = \mu_h^*(P) - \int_{T'}^T s_h(P, T') \, dT'. \tag{24} \]
Here $s_{gg}$, $s_w$ 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, $\mu_{gg}^*$, $\mu_w^*$ and $\mu_h^*$ 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

$$
\Delta \mu = \mu_{gg}(P) + n_w(P, T)\mu_w(P) - \mu_h(P) - n_w(P, T) \int_{T'}^{T} s_w(P, T') \, dT' - \int_{T'}^{T} \left[ s_{gg}(P, T') - s_h(P, T') \right] \, dT'.
$$

(25)

At the chosen pressure $P$, there exists a temperature $T_c(P)$ at which the solution and the hydrate phase can coexist, because then $\Delta \mu = 0$. This temperature is therefore the equilibrium (more accurately, phase equilibrium) temperature of the system. It corresponds to point B in Fig. 2 and is the solution of the equation

$$
0 = \mu_{gg}^*(P) + n_w(P, T_c)\mu_w^*(P) - \mu_h^*(P) - n_w(P, T_c) \int_{T_c}^{T} s_w(P, T') \, dT' - \int_{T_c}^{T} \left[ s_{gg}(P, T') - s_h(P, T') \right] \, dT'.
$$

(26)

which follows from Eq. (25). Employing Eq. (26) to eliminate $\mu_{gg}^*$ and $\mu_h^*$ from Eq. (25), we get

$$
\Delta \mu = \left[ n_w(P, T) - n_w(P, T_c) \right] \mu_w^*(P) - n_w(P, T) \int_{T_c}^{T} s_w(P, T') \, dT' + n_w(P, T_c) \int_{T_c}^{T} s_w(P, T') \, dT' + \int_{T_c}^{T} \left[ s_{gg}(P, T') - s_h(P, T') \right] \, dT'.
$$

(27)

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

(i) Approximation $n_w \approx n_w(P, T_c)$: This approximation ignores the temperature dependence of the hydration number for $T$ close enough to $T_c$ and results in elimination of $\mu_w$ and $T^*$ from Eq. (27).

This equation thus becomes

$$
\Delta \mu = \int_{T_c}^{T} \Delta s(P, T') \, dT',
$$

(28)

where

$$
\Delta s \equiv s_{gg}(P, T) + n_w(P, T_c) s_w(P, T) - s_h(P, T)
$$

(29)
is the hydrate dissociation entropy per hydrate building unit, i.e., the entropy change in the transfer at the given $P$ and $T$ of one gas molecule from the hydrate crystal into the gas phase and of $n_w$ water molecules also from the hydrate crystal, but into the solution. Eq. (28) has the form of the known expression for $\Delta \mu$ in melt crystallization [13] and allows calculation of the supersaturation from experimental data or theoretical formulae for the temperature dependence of $s_{gg}$, $s_w$ and $s_h$. For instance, a useful approximation for $s_{gg}$ as a function of $T$ is the known formula for the entropy per molecule of ideal gas [12].

(ii) Approximation resulting from Taylor series truncation: According to thermodynamics [14], 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. (28) can be expanded in the following Taylor series about $T = T_c$ [13]

$$
\Delta \mu = - \Delta s_c(T - T_c) - (\Delta c_{p,c}/2T_c)(T - T_c)^2 - [(T_c \Delta c_{p,c}' - \Delta c_{p,c})/6T_c^2](T - T_c)^3 - \cdots,
$$

(30)

where $\Delta s_c$ and $\Delta c_{p,c}$ are the differences between the entropies and the heat capacities of the old and the new phase at $T = T_c$, and $\Delta c_{p,c}' = d\Delta c_p/dT$ also at $T = T_c$. To a first approximation, in the case considered here of hydrate crystallization we can therefore write

$$
\Delta \mu = \Delta s_c \Delta T.
$$

(31)

Here $\Delta T$ (K), defined as

$$
\Delta T = T_c - T
$$

(32)

is the undercooling, and the quantity $\Delta s_c$ (J/K), given by

$$
\Delta s_c \equiv s_{gg}(P, T_c) + n_w(P, T_c) s_w(P, T_c) - s_h(P, T_c)
$$

(33)
is the value of $\Delta s$ from Eq. (29) at the equilibrium temperature $T_c$. To a higher approximation,
according to Eq. (30), the $\Delta \mu(T)$ dependence is of the form

$$\Delta \mu = \Delta s_c \Delta T - (\Delta c_{p,e}/2T_c)\Delta T^2,$$

(34)

where, in view of Eq.(29), the heat capacity difference $\Delta c_{p,e}$ (J/K) is expressed as $\Delta c_{p,e} = c_{p,gg}(P, T_c) + n_w(P, T_c)c_{p,w}(P, T_c) - c_{p,h}(P, T_c)$.

The constant-pressure heat capacities $c_{p,gg}$, $c_{p,w}$ and $c_{p,h}$ are, respectively, per gas molecule in the gas phase, per water molecule in the solution and per hydrate building unit (one gas molecule and $n_w$ water molecules) in the hydrate crystal.

Eq. (31) parallels the familiar formula for $\Delta \mu$ in melt crystallization [16] and was given by Sloan (Ref. [2], p. 100), but without a specified entropy factor. Eq. (34) is also a known result [17]. According to Eq. (31), $\Delta \mu$ increases linearly with lowering $T$. This equation is an acceptable approximation to Eq. (28) provided $\Delta T$ obeys the condition [13]

$$\Delta T \ll 2T_c \Delta s_c/\Delta c_{p,e}$$

(35)

which follows from the requirement for a negligible contribution of the last term in Eq. (34). The heat capacity difference $\Delta c_{p,e}$ as well as the quantity $T_c \Delta s_c$ are experimentally accessible. Indeed, from thermodynamics [14], $T_c \Delta s_c = \Delta h_c$ where $\Delta h_c$ (J) is the enthalpy or latent heat (per hydrate building unit) of dissociation of the hydrate crystal into gaseous phase and liquid water at $T = T_c$. For example, $\Delta h_c = 9.0 \times 10^{-20}$ J, $\Delta c_{p,e} = 3.82 \times 10^{-22}$ J/K and $\Delta h_c = 1.19 \times 10^{-19}$ J, $\Delta c_{p,e} = 4.63 \times 10^{-22}$ J/K for, respectively, methane and ethane hydrate at 0.1 MPa and 273.2 K [18]. These pressure and temperature do not correspond exactly to hydrate/solution equilibrium, but we can use the above values of $\Delta h_c$ and $\Delta c_{p,e}$ in the inequality (35) to assess the range of applicability of Eq. (31). We thus find $\Delta T \ll 471$ K and $\Delta T \ll 514$ K for methane and ethane hydrate, respectively. This means that for undercoolings $\Delta T < 15$ K Eq. (31) is a reliable formula for determination of the supersaturation for crystallization of both these hydrates (for such undercoolings $\Delta \mu$ from Eq. (31) is greater than $\Delta \mu$ from Eq. (34) by not more than about 3%). This conclusion may be expected to hold true also for the crystallization of other gas hydrates.

The isobaric $\Delta \mu(T)$ dependences given by Eqs. (31) and (34) are illustrated in Fig. 5 for methane and ethane hydrate (as indicated) at $P = 19.4$ and 1.74 MPa, respectively: solid lines—Eq. (34) with $\Delta s_c = 22.2 k$, $\Delta c_{p,e} = 27.7 k$ and $T_c = 293.2$ K for methane hydrate and $\Delta s_c = 30.5 k$, $\Delta c_{p,e} = 33.6 k$ and $T_c = 283.2$ K for ethane hydrate; dashed lines—Eq. (31) with the same $\Delta s_c$ and $T_c$ values.

![Fig. 5. Temperature dependence of the supersaturation for crystallization of methane and ethane hydrate (as indicated) at $P = 19.4$ and 1.74 MPa, respectively: solid lines—Eq. (34) with $\Delta s_c = 22.2 k$, $\Delta c_{p,e} = 27.7 k$ and $T_c = 293.2$ K for methane hydrate and $\Delta s_c = 30.5 k$, $\Delta c_{p,e} = 33.6 k$ and $T_c = 283.2$ K for ethane hydrate; dashed lines—Eq. (31) with the same $\Delta s_c$ and $T_c$ values.](image)

4. Absence of chemical equilibrium between solution and gas phase

We now consider the case when the pressure and the temperature of the system are fixed, but there is no chemical equilibrium between the solution and
the gas phase. In this case, the actual concentration of gas in the solution varies with time $t$ [5,7], because the condition for chemical equilibrium, Eq. (7), is not fulfilled. According to Eq. (6), this means that the supersaturation itself is also a function of time. Denoting by $\Delta \mu_t$ and $C_t$ these time-dependent supersaturation and gas concentration, instead of Eq. (6) we shall have:

$$\Delta \mu_t = kT \ln \left[ \gamma(P, T, C_t) \nu_w C_t \right] + \Delta \mu^*_{\text{gas}}(P, T) + n_w(P, T) \mu_w(P, T) - \mu_0(P, T).$$

(36)

To make physically more revealing this general formula for the variable supersaturation during hydrate crystallization in the absence of solution/gas chemical equilibrium it is convenient to relate $C_t$ to the equilibrium gas concentration $C$ by means of the expression

$$C_t = Cx(t).$$

(37)

The dimensionless function $x(t)$ takes into account the concrete kinetics of reaching the solution/gas chemical equilibrium at the given pressure and temperature and satisfies the condition $x(t) \rightarrow 1$ for $t \rightarrow \infty$. A model $x(t)$ dependence characterizing initially gas-free water is, for example,

$$x(t) = 1 - e^{-t/\tau},$$

(38)

where $\tau$ is the time constant for establishment of the solution/gas chemical equilibrium [7].

Substituting $C_t$ from Eq. (37) into Eq. (36) and using the approximation $\gamma(P, T, C_t) \approx \gamma(P, T, C)$ yields the general formula

$$\Delta \mu_t = \Delta \mu + kT \ln[x(t)].$$

(39)

Here $\Delta \mu$ is specified by Eq. (6) and is the time-independent supersaturation corresponding to established chemical equilibrium between the solution and the gas phase at the given pressure and temperature of the system. Hence, in general, in Eq. (39) we can use $\Delta \mu$ from Eq. (8) in order to present $\Delta \mu_t$ as

$$\Delta \mu_t = \Delta \mu + n_w(P, T) \mu_w(P, T) - \mu_0(P, T) + kT \ln[x(t)].$$

(40)

In particular, as shown below, in Eq. (39) we can employ any of the formulae for $\Delta \mu$ from Sections 3.1 and 3.2 in order to determine $\Delta \mu_t$ in isothermal or isobaric regime.

### 4.1. Isothermal regime

In this regime, depending on the approximation used, $\Delta \mu$ in Eq. (39) is given by Eq. (14), (15), (19) or (21). For instance, in the scope of approximations (i) and (ii), with the aid of Eq. (19), Eq. (39) becomes

$$\Delta \mu_t = kT \ln(P/P_c) + \nu_{\text{eq}}(P - P_c) + kT \ln[x(t)].$$

(41)

To illustrate the time variation of the supersaturation for an initially gas-free liquid water brought into contact with a gas phase at time $t = 0$, we can substitute $x(t)$ from Eq. (38) into Eq. (41). This leads to the expression

$$\Delta \mu_t = kT \ln(P/P_c) + \nu_{\text{eq}}(P - P_c) + kT \ln(1 - e^{-t/\tau}).$$

(42)

Fig. 6 depicts this time dependence of $\Delta \mu_t$ for methane and ethane hydrates at $T = 273.2$ K and at $P = 15$ and 1 MPa, respectively. The curves are drawn with exemplary values of $\tau = 2, 10$ and 20 min (as indicated), and the $P_c$ and $\nu_{\text{eq}}$ values are those used for Figs. 3 and 4. As seen, $\Delta \mu_t$ reaches...
its equilibrium value $\Delta \mu$ (represented by a dashed line for each of the two hydrates) only after time $t \approx 4\tau$. Moreover, initially, there is a period of time during which the solution remains undersaturated. For example, for methane hydrate Fig. 6 shows that if $\tau = 20$ min, it takes time $t_s \approx 6$ min until the solution becomes supersaturated (until that time $\Delta \mu, t < 0$). We can determine the time $t_s$ at which the solution becomes supersaturated by using Eqs. (38) and (39) in the general relation $\Delta \mu(t_s) = 0$ which defines $t_s$:

$$t_s = -\tau \ln(1 - e^{-\Delta \mu/kT}).$$

(43)

As seen from this general expression, and from Fig. 6 as well, $t_s$ depends not only on $\tau$, but also on the equilibrium value $\Delta \mu$ of the supersaturation: at a given $\tau$, the lower this value, the longer is $t_s$ (compare, e.g., curves 20 in Fig. 6).

4.2. Isobaric regime

In this regime we can employ Eq. (27), (28), (31) or (34) to express $\Delta \mu$ in Eq. (39) in the scope of the corresponding approximation. For instance, using Eq. (31) we find that

$$\Delta \mu = \Delta \mu_c \Delta T + kT \ln[x(t)],$$

(44)

where $x(t)$ can also be modeled by the exponential dependence specified by Eq. (38). The time $t_s$ associated with this dependence is again given by Eq. (43), but with $\Delta \mu = \Delta \mu_c \Delta T$.

5. Conclusions

The analysis presented in this work provides a general formula, Eq. (6), for the driving force for crystallization of hydrates of one-component gases in aqueous solutions of such gases. The driving force is the supersaturation $\Delta \mu$, which depends on the actual concentration of gas in the solution and is thus sensitive to the particular conditions of gas dissolution into the aqueous phase.

When the solution is in chemical equilibrium with the gas phase, $\Delta \mu$ is given by the general Eq. (8) which takes different forms in isothermal or isobaric regime of supersaturating the solution. In isothermal regime, Eq. (8) is represented by the general Eq. (14) which leads to concrete $\Delta \mu(P)$ dependences, Eqs. (15), (19) and (21), in the scope of different approximations. In isobaric regime Eq. (8) takes the form of the general Eq. (27). This equation results in concrete approximate $\Delta \mu(T)$ dependences represented by Eqs. (28), (31) and (34). According to Eq. (31), the supersaturation increases linearly with decreasing temperature.

When the solution is not in chemical equilibrium with the gas phase, the supersaturation is time-dependent and given by the general Eq. (36) which is approximated by the equally general Eq. (39) or (40). In this case, it may take a considerable time until an initially gas-free solution becomes supersaturated. To a certain approximation, the time dependence of the supersaturation in isothermal or isobaric regime is expressed by Eq. (41) or (44), respectively.

The driving force for dissolution of hydrates of one-component gases in aqueous solutions is $-\Delta \mu$. Therefore, upon accounting for the negative sign, all results and conclusions of this work are directly applicable to this process.

Acknowledgements

This work was supported by the company members of the Reservoir Engineering Research Institute (RERI). Their support is greatly appreciated. One of the authors (D.K.) gratefully acknowledges the hospitality that he enjoyed as a Visiting Professor at RERI.

References