LECTURE TEXT

Gas hydrates in nature and in the laboratory: necessary requirements for formation and properties of the resulting hydrate phase

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Abstract

Clathrate hydrates—also known as gas hydrates—are ice-like compounds consisting of gas and water molecules. They occur wherever elevated pressures and low temperatures prevail; and where enough water and hydrate-forming gas molecules are available. Therefore, natural gas hydrates occur at all active and passive continental margins, in permafrost regions, in some deep lakes, and under unfavorable circumstances, also, in pipelines. This article provides an overview of the (thermodynamic) requirements and various models for the nucleation and growth of gas hydrates and the different gas hydrate structures that may occur and which have been detected in nature. Furthermore, this study also shows the influence of the properties of the enclosed gas molecules such as size and shape on the structure and thermodynamic properties of the resulting hydrate phase. Finally, the complexity of a natural environment with regard to the various influences of sediments, microbial activity, and salinity of the pore fluid on hydrate formation is also discussed.

Keywords Gas hydrates · Nucleation and growth · Thermodynamic properties · Guest-to-cavity ratio · Occurrences

Introduction

Clathrate hydrates, also known as gas hydrates, are ice-like, crystalline solids composed of water and gas molecules. Water molecules form defined cage (cavity)[1] structures via hydrogen bonds, which are connected into a three-dimensional network. The cages are stabilized by the encasement of a mostly nonpolar guest molecule; however, it should be noted that gas hydrates are nonstoichiometric compounds. From a chemical point of view, gas hydrates therefore belong to the inclusion compounds (clathrates). They form under elevated pressures and low temperature conditions when sufficient amounts of gas and water are available.

The English chemist Humphry Davy is considered to be the first scientist who formed gas hydrates in his laboratory by dissolving chlorine gas into water at low temperatures, which was reported to the Royal Society of Chemistry [1, 2]. In the following years, gas hydrates were examined in some laboratories, but for a long time they were considered as laboratory curiosities. Schroeder described in his work on the history of gas hydrates in 1927 that there were a large number of researchers performing experiments in which an attempt was made to determine the structure and composition of gas hydrates. The fact that gas hydrates are nonstoichiometric compounds made these efforts even more difficult and methods that are used today in many laboratories to analyze gas hydrates such as Raman spectroscopy were not available to researchers at the time. Therefore, at the end of the nineteenth century, it was assumed that a direct analysis of gas hydrates was not possible [3].

With the production of oil and gas at the beginning of the twentieth century, gas hydrates were discovered in a completely new context. Hammerschmidt realized that the ice-like solids that formed in pipelines were gas hydrates [4]. The scientific studies of gas hydrates then concentrated on the conditions under which gas hydrates form and how their formation could be avoided to prevent blockage of pipelines. It took further decades before Makogon realized in 1966 that the conditions for the formation of gas hydrates are also present in nature [5]. In 1972, the recovery of a drill core containing hydrates in Prudhoe Bay in Alaska provided evidence that gas hydrates also occur in nature. Since then, several attempts have been made to detect and quantify natural gas hydrate deposits all over the world. It was possible to

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1 The terms "cavity " and "cage " are used synonymously.

prove their existence directly or indirectly at all active and passive continental margins, in permafrost regions, and also in deep lakes (e.g., [6, 7]).

Since natural gas hydrates contain predominantly methane and owing to their global occurrences, natural gas hydrates are seen as a potential energy source on the one hand. On the other hand, methane is also a strong greenhouse gas and therefore the response of gas hydrate deposits to global warming is also of great interest. In addition, the influence of gas hydrates on the geomechanical properties of the host sediments in which the hydrates occur has not yet been fully clarified.

In the following sections of this study, the prerequisites for hydrate formation will be discussed in detail before the various structures of the resulting hydrate phase and their properties are described. The occurrences of gas hydrates in nature and the influence of gas hydrates on their environment will also be discussed. Finally, the differences between the mostly simplified formation of gas hydrates in the laboratory and the more complex formation of gas hydrates in natural systems are discussed.

Thermodynamic requirements for the formation of gas hydrates

Gas hydrates are formed at elevated pressures and low temperatures, provided that sufficient gas and water are available. But what does that mean exactly?

According to Kashchiev and Firoozabadi [8], the formation of gas hydrates under given pressure and temperature conditions can be described with the following reaction equation:
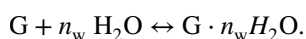
$$G + n_w \, H_2O \leftrightarrow G \cdot n_w H_2O.$$

It is assumed that one molecule of the dissolved gas G and n_w water molecules of the aqueous solution form one unit of the hydrate crystal ($G \cdot n_w H_2O$). Kashchiev and Firoozabadi [8] take the approach that the difference in the chemical potentials between the following three coexisting phases is the driving force for the formation or decomposition of hydrates: (a) a pure gas phase (the proportion of water molecules in the gas phase is neglected), (b) an aqueous solution, and (c) a hydrate phase. In their hypothesis, they differentiate between the chemical potential of the gas molecules in the gas phase (μ_{gg}) and the chemical potential of the gas molecules that are dissolved in the aqueous phase (μ_{gs}). They also define the chemical potential of a potential hydrate building unit (μ_{hs}), consisting of a gas molecule and n_w water molecules in the aqueous solution and the chemical potential of the hydrate phase (μ_h), consisting of a gas molecule and n_w water molecules within the hydrate structure.

Referring to the thermodynamic relation between chemical potentials in reaction equilibria, the chemical potential of the hydrate building unit in an aqueous solution can be defined as

$$\mu_{hs} = \mu_{gs} + n_w \mu_w.$$

Kashchiev and Firoozabadi [8] postulated that the driving force for the new phase formation is the difference between the chemical potentials of the old phase (aqueous solution) and the new phase (hydrate crystal). They called the driving force $\Delta\mu$ supersaturation, given as

$$\Delta\mu = \left(\mu_{gs} + n_w \mu_w\right) - \mu_h = \mu_{hs} - \mu_h.$$

Only if the aqueous solution is supersaturated with the hydrate-forming gas can the hydrate nucleate or grow ($\Delta\mu > 0$). A phase equilibrium in terms of a coexistence of dissolved and crystalline hydrate phases is reached if $\Delta\mu = 0$; in this case the aqueous solution is saturated. When $\Delta\mu < 0$ the solution is undersaturated; thus, hydrate crystals cannot nucleate in the solution, and existing hydrates decompose. Kashchiev and Firoozabadi [8] pointed out that their concept can also be applied to the formation of hydrates from the ice phase and the decomposition of hydrates to gas and ice, respectively.

Since Kashchiev and Firoozabadi [8] define the supersaturation of the liquid solution as a prerequisite for the formation of gas hydrates, they apparently assume that the gas molecule must first be dissolved in the aqueous phase before it can be incorporated into the hydrate phase. With this assumption, they support the labile cluster nucleation hypothesis [9], which is one model for the nucleation and growth process of gas hydrates and which will be described in more detail in the following section.

Models for nucleation and hydrate growth at the molecular level

First of all, it should be noted that a distinction is made between nucleation and growth of gas hydrates. In general, however, it is assumed that the nucleation comprises only a few gas-filled water cages and changes into hydrate growth when a critical size of the nucleus is reached ([10, 11] and the literature cited therein). If the thermodynamic requirements, as described in the previous section, are met, hydrate nucleation can be described as a stochastic and heterogeneous crystallization process for which the following mechanisms are suggested.

According to Christiansen and Sloan [9], who developed the *labile cluster nucleation hypothesis*, water molecules form labile clusters around dissolved gas molecules once the pressure and temperature conditions are within the hydrate

stability field. Depending on the size of the gas molecule, the number of water molecules that participate in these labile clusters varies. These labile clusters combine and form unit cells. This process is facilitated if the aqueous solution already contains clusters with a suitable number of water molecules that correspond to the cavity types in the resulting hydrate structure. Once the agglomeration of these labile clusters reaches a critical size, the hydrate crystal begins to grow.

Molecular dynamic simulations by Walsh et al. [12] show a more complex process. Here, fragments of hydrate structures form around the dissolved gas (methane) molecules, but some of these cavity fragments dissolve again whereas others form first cage structures. Jacobson et al. [13, 14] developed the "blob" hypothesis, which in a sense represents an extension of the labile cluster hypotheses. Here, dissolved gas molecules with their hydration shells and additional water molecules agglomerate and condense to form so-called blobs. These change into an amorphous hydrate phase in which the first cage structures are already formed. Here, as well as in the model published by Walsh et al. [12], unusual cage types such as $5^{12}6^3$ polyhedra form in this phase before the water and gas molecules change into an ordered, crystalline hydrate structure.

The *local structuring nucleation hypothesis* is based on molecular dynamic calculations by Radhakrishnan and Trout [15] and describes the very special case of a homogeneous nucleation mechanism at the liquid–liquid interface between water and liquid carbon dioxide. As a result of thermal fluctuations, some of the carbon dioxide molecules are arranged in the aqueous phase similar to that in the hydrate structure. This arrangement of the guest molecules influences the orientation of the water molecules. If such an arrangement of the carbon dioxide molecules and correspondingly the water molecules exceeds the critical size of a crystallization nucleus, hydrate formation occurs. Moon et al. [16] carried out similar simulations for the nucleation of methane hydrates at the interface between methane and water and concluded that the formation of a methane hydrate nucleus of critical size is the result of a locally denser arrangement of methane molecules in the aqueous phase and the associated changes in the arrangement of the water molecules.

Both Long [17] and Kvamme [18] developed the hypothesis of the *nucleation at the interface*. In this approach the hydrate formation occurs directly at the interface between the aqueous phase and the gas phase. While in the other hypotheses the hydrate-forming gas must first be dissolved in the aqueous phase, in the hypothesis of the nucleation at the interface the gas molecule is incorporated into the hydrate phase directly from the gas phase. In this hypothesis, the gas molecule is adsorbed on the water surface and diffuses on the surface to a suitable point where it can be initially partially and then completely incased into a hydrate cage by water molecules. As a result of the adsorption and the incorporation of further gas molecules at the interface between the aqueous phase and the gas phase, the nucleation and further growth are directed into the gas phase.

If enough crystallization nuclei of critical size have formed, hydrate growth begins. So that hydrate growth can take place without restriction, sufficient transport of the molecules to the reaction site (mass transport) and the incorporation of the guest molecule into the hydrate cage structure and the removal of the resulting heat of hydrate formation from the reaction site (heat transport) must be ensured.

Gas hydrate structures

As already mentioned, gas hydrates consist of gas and water molecules, whereby the latter form various cavity types (polyhedra) via hydrogen bonds. These polyhedra combine to three-dimensional networks. A special nomenclature was developed to describe the polyhedra: the various types of cages are defined with n^m. The variable m indicates the number of faces and the variable n the number of edges of this surface, e.g., a pentagonal dodecahedron (5^{12}) consist of 12 ($m = 12$) pentagonal ($n = 5$) faces.

Depending on which gas molecules are encased, the type and size of the cavities and thus the structure of the resulting gas hydrate vary. So far, a large number of different hydrates have been described. The encased gas molecules vary in size from small molecules such as hydrogen or nitrogen to larger molecules such as n-butane or cyclohexane. In general, non-polar, hydrophobic molecules such as methane are known as hydrate formers. In nature, the occurrence of three different hydrate structures has been reported, namely structure I (sI), structure II (sII), and structure H (sH). A unit cell of the cubic structure I is composed of 46 water molecules that form two pentagonal dodecahedra (5^{12}) and six tetrakaidecahedra ($5^{12}6^2$). The pentagonal dodecahedra are connected to each other via shared edges [19]. A unit cell of the cubic structure II consists of 16 pentagonal dodecahedra (5^{12}) and eight hexakaidecahedra ($5^{12}6^4$) [19]. In structure II, layers of face-sharing pentagonal dodecahedra alternate with layers of hexakaidecahedra. The unit cell of structure II contains 136 water molecules. For a unit cell of the hexagonal structure H, 34 water molecules form three pentagonal dodecahedra (5^{12}), two irregular dodecahedra ($4^35^66^3$), and one icosahedron ($5^{12}6^8$). The irregular dodecahedron is only slightly larger than the pentagonal dodecahedron. However, the icosahedron can encase relatively large molecules such as pentane or cyclohexane. In structure H, the pentagonal dodecahedra form two-dimensional layers over shared faces, which are interconnected by layers with irregular dodecahedra and icosahedra [20]. The aforementioned combinations
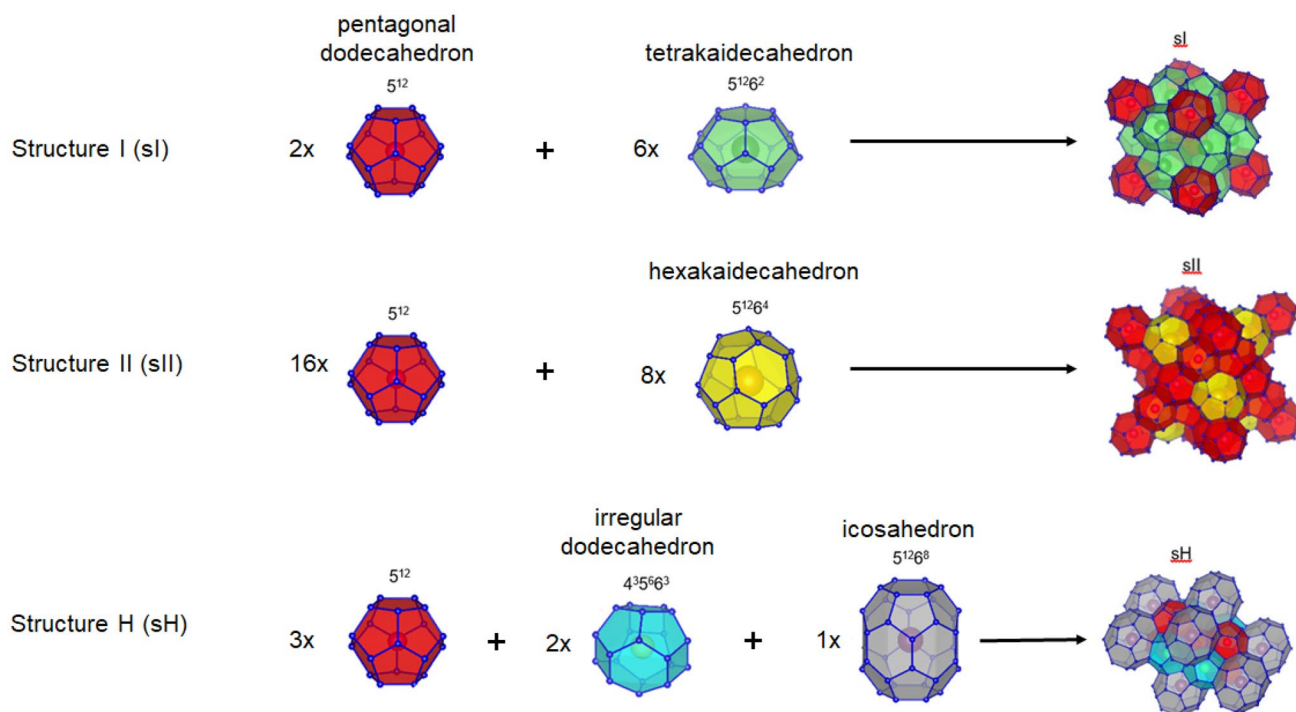
Fig. 1 Various hydrate structures are formed by combining different types of polyhedra (modified after Ismail [21] and Pan [22])

of the various polyhedra and the resulting hydrate structures are shown in Fig. 1.

The cubic structures I and II can be stabilized with the cages partially filled. For example, a propane hydrate with structure II can be formed with only the hexakaidecahedra filled and the pentagonal dodecahedra empty. For the hexagonal structure H, however, it is necessary that, in addition to the large gas molecules that are encased into the icosahedron, smaller gas molecules (a so-called help gas) have to occupy the dodecahedra of the structure.

Which hydrate structure is formed depends, among others, on the hydrate-forming gas molecule. While the attractive forces of the water molecules in the cage structures lead to a force directed into the center of the cage, the encased gas molecules exert a stabilizing effect on the hydrate cages through repulsive forces. For a stable hydrate, the gas molecule should on the one hand be large enough to adequately shield the attractive forces of the water molecules in the cages. On the other hand, it should be small enough to fill the cage without deforming it. The guest-to-cavity ratio provides a good estimate of how well a gas molecule can stabilize a cage. This ratio is determined by dividing the diameter of the guest molecule by the diameter of the cavity type [23]. It should be noted that the van der Waals radius of the water molecules (0.14 nm) should be subtracted from the average cage radius in advance.

According to Lederhos et al. [24] a guest-to-cavity ratio between 0.75 and 1.0 results in a minimization of energy and thus optimal stabilization of the cage structures. Nevertheless, hydrate structures may also occur where the guest-to-cavity ratio is less than 0.75 or greater than 1.0. In particular, during hydrate formation and hydrate growth processes, metastable hydrate structures can be formed in which the ratio of the encased gas molecules to the hydrate cage does not correspond to this ideal ratio. For example, it has been shown experimentally that during the formation of both methane hydrates and carbon dioxide hydrates, crystals with structure II as a coexisting metastable phase were formed besides the thermodynamically stable structure I hydrate crystals [25, 26]. According to Sloan and Fleyfel, the formation of the pentagonal dodecahedra (5^{12}) is favored. During the induction phase the hydrate structure oscillates between structure I and structure II before structure I achieves the critical size for a stable nucleus [27]. Such a preferred formation of pentagonal dodecahedra can also induce the formation of structure II hydrates, even if this structure is not thermodynamically preferred, since in a unit cell of structure II the number of pentagonal dodecahedra is twice as large as the number of hexakaidecahedra. This could be observed in experiments on the nucleation and growth of simple and mixed hydrates [28, 29]. In other laboratory studies, however, the formation of a structure I methane hydrate besides a structure II mixed hydrate could be observed, although the offered feed gas mixture contained higher hydrocarbons such as propane and thus a structure II mixed hydrate is the thermodynamically stable phase [30].

Fig. 2 Examples for the equilibrium curves (*p*, *T*) of methane hydrate and mixed gas hydrates that contain ethane (C_2H_6) and propane (C_3H_8) in addition to methane (CH_4). The hydrate phase is stable in the areas above the respective *p*–*T* equilibrium curve (Data taken from Schicks and Luzi-Helbing [29] and Schicks [33])
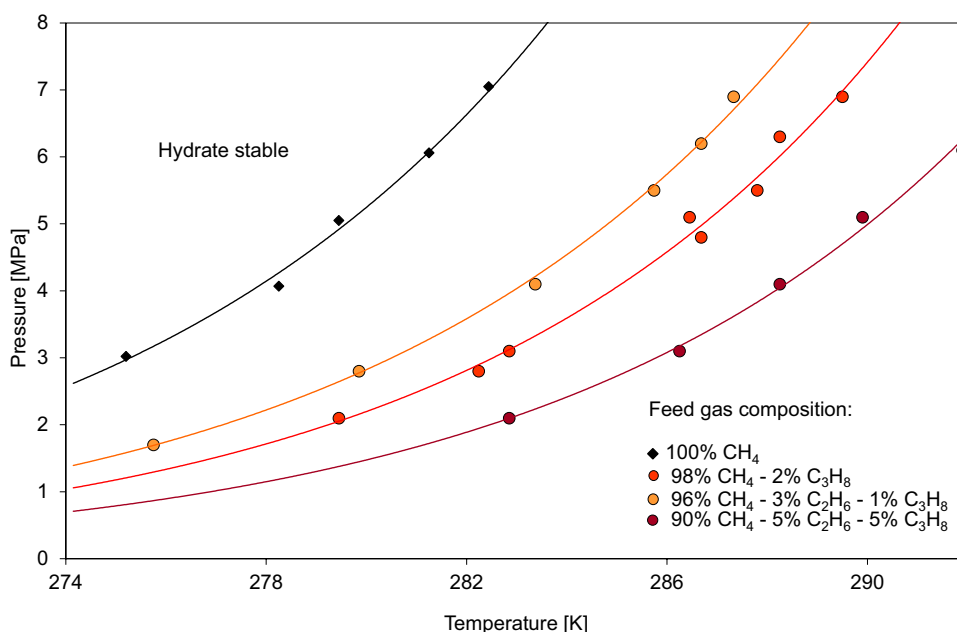
In these cases, the short-term formation of a metastable structure I methane hydrate phase can be attributed to its faster formation kinetics [29]. It should also be noted that the correlation between the molecular size of the encased gas molecule on the one hand and the resulting hydrate structure on the other hand is not always straightforward. This is especially true for mixed hydrates. For example, methane, ethane, and carbon dioxide alone form structure I hydrates. Gas mixtures containing methane and carbon dioxide also form structure I hydrates. In contrast, it depends on the composition of a methane–ethane gas mixture whether a structure I or a structure II hydrate is formed [31, 32].

The enclosed gas molecules not only have an influence on the structure formed. They also have a very strong influence on the thermodynamic properties of the resulting hydrate phase, as will be shown in the following section.

Influence of the guest molecule properties on the thermodynamic properties of the resulting hydrate phase

The properties of the gas molecules and their proportion in the hydrate structure have a decisive influence on the stability conditions of the resulting gas hydrate phase. For example, the equilibrium curve of mixed gas hydrates, which contain higher hydrocarbons or carbon dioxide in addition to methane, shifts to higher temperatures and lower pressures, respectively. This is demonstrated in Fig. 2, which shows the pressure and temperature conditions above the freezing point of water in which a few selected mixed hydrates are stable. Since only the composition of the feed gas phase is known exactly, this was given in mol%. However, even if the composition given in Fig. 2 relates to the coexisting feed gas phase, it can be assumed that with increasing partial pressure of a component in the gas phase, this component is also increasingly incorporated into the hydrate phase.

The stabilizing effect that occurs through the incorporation of larger guest molecules than methane, however, varies depending on the properties of the guest molecules. In general, a connection can be observed between the ratio of the guest molecule diameter to each host cavity diameter (guest-to-cavity ratio) of the different gas molecules and the shift in the equilibrium curve of the respective hydrate. If the guest-to-cavity ratio approaches the value 1.0, this usually leads to an increase in the stability field of the resulting gas hydrate phase in the sense of a shift in the equilibrium curve to higher temperatures and lower pressures, respectively. With increasing proportion of those cavities filled with larger molecules and thus approaching a higher guest-to-cavity ratio, the stability field of the hydrate phase also increases. The examples shown in Fig. 2 show this trend very well. The guest-to-cavity ratio for ethane in the hexakaidecahedra ($5^{12}6^4$) of structure II is 0.8, while it is 0.99 for propane [33]. Thus, with increasing proportion of propane in the gas phase and subsequently also in the hydrate phase, the stability field of the resulting hydrate phase increases significantly. If the guest-to-cavity ratio exceeds the value 1, then the molecule is too large for the cavity and distortions or defects in the cavity structure occur when it is encased. However, such molecules are also encased into hydrate structures. An example is *n*-butane, which, together with methane, forms a mixed hydrate of structure II. In its gauche conformation, *n*-butane occupies the hexakaidecahedra ($5^{12}6^4$) [34]. Since

the guest-to-cavity ratio of *n*-butane encased into the hexakaidecahedra of structure II is 1.12, the cage is distorted.

According to von Stackelberg and Jahns [35], with the enclathration of a "too large" molecule into a hydrate cage, its normal volume v_0 has to be expanded to a volume v and the energy E required for this is calculated according to (with χ = compressibility)

$$E = \frac{(v - v_0)^2}{2\chi v_0}.$$

The expansion work has the consequence that the equilibrium curve of these hydrates shifts towards lower temperatures at a given pressure and thus the stability field is reduced (compared to a hydrate, in which the incorporation of the guest molecules does not require any expansion work).

The aforementioned relationship between the guest-to-cavity ratios of the gas molecules enclosed in the hydrate and the stability of the hydrate phase is also evident in the enthalpies of formation and decomposition of the hydrates. This applies to simple hydrates, which were formed with only one hydrate former and water, as well as to mixed hydrates and can be shown on the basis of calorimetric measurements. Handa [36] used calorimetry to determine the enthalpy of decomposition of simple hydrates that contained either methane, ethane, propane, or *iso*-butane. His results show a clear increase in the enthalpy of decomposition with increasing guest-to-cavity ratio. The better stabilization of the hydrate cages through the incorporation of a spherical molecule (such as *iso*-butane) instead of a linear molecule of the same size (such as propane) leads to a slightly higher enthalpy of decomposition for the *iso*-butane hydrate (133 kJ/mol) compared to propane hydrate (129 kJ/mol). For mixed hydrates, which were synthesized from methane–carbon dioxide gas mixtures and from methane–ethane–propane gas mixtures, it could also be demonstrated that not only the qualitative composition of the hydrate phase but also its quantitative composition has an influence on the enthalpies of decomposition [37, 38]. As a general trend, it can be seen that with increasing absolute cage occupancy and with increasing cage occupancy with molecules with a guest-to-cavity ratio that approaches the value 1, the enthalpy of decomposition increases.

Gas hydrate formation and occurrences in nature

In the previous sections we learned that high pressures and low temperatures are necessary for the formation of gas hydrate formation. In addition, sufficient amounts of water and a hydrate-forming gas must be present, which means that the aqueous solution should be supersaturated with
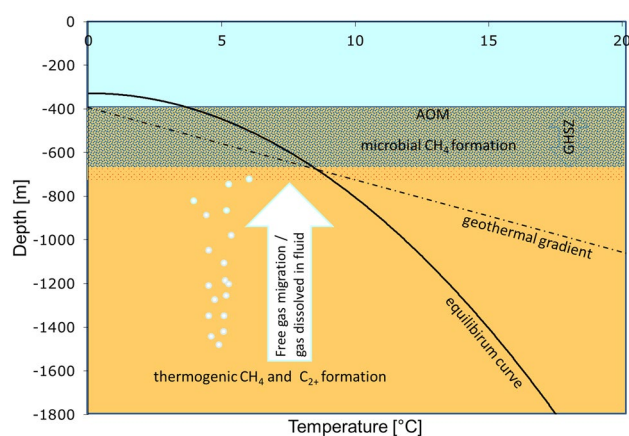
Fig. 3 Sources and processes for the formation and migration of gases as a prerequisite for hydrate formation in the gas hydrate stability zone (GHSZ) (based on Schicks [33]). The GHSZ is limited by the equilibrium curve of the gas hydrate (here methane hydrate, black curve) and the geothermal gradient (3 °C/100 m, dashed line). Hydrogen sulfide (H_2S) may be formed near the surface through anaerobic oxidation of methane (CH_4) (AOM). The production of methane by microbial processes can take place up to a depth of several hundred meters. Hydrate-bound methane can be released through the decomposition of hydrates if the hydrate reaches deeper layers through sedimentation processes and thus outside the stability field (red dotted area). Thermogenic processes in deeper layers can release methane and other hydrocarbons (C_{2+})

the hydrate-forming gas molecules. Of course, these general conditions also apply to hydrate formation in nature and we find them fulfilled on all active and passive continental slopes, in permafrost areas, and in some deep lakes. Compared to the formation of gas hydrates in the laboratory under controllable conditions, however, the formation of gas hydrates in a natural environment is much more complex. In addition to previously mentioned pressure, temperature, water, and hydrate-forming gas concentrations, other parameters play a role here. These include, e.g., the salinity of the pore water, the sediment and the associated properties such as porosity and permeability, the origin and thus the composition of the hydrate-forming gas, the presence or absence of a free gas phase, as well as the presence of microorganisms.

Figure 3 shows the equilibrium conditions of methane hydrate as a black curve. From a depth of at least 300 m, methane hydrates may form at a water temperature of 0 °C. At temperatures above this curve, methane hydrates are not stable because the temperature is too high at the given pressure. While the water temperature at the sea floor can be assumed to be relatively constant locally, it increases with increasing depth into the sediment, as the dashed line in Fig. 3 shows. This temperature increase is referred to as a geothermal gradient and can vary from region to region, with an average temperature increase of 3 °C/100 m. As a result of this increasing temperature in the sediment profile, the temperature at given pressure at a certain depth may be

too high for the formation of gas hydrates. This depth is defined by the intersection of the dashed straight line (geothermal gradient) and the black curve (equilibrium curve) in Fig. 3 and is referred to as the basis of the gas hydrate stability zone (BGHSZ). In the blue-yellow patterned area between the sea floor and the BGHSZ in Fig. 3, the pressure and temperature conditions are within the stability field of the methane hydrates. If enough gas and water molecules are present, gas hydrates may occur. This area is known as the gas hydrate stability zone (GHSZ).

The gas required for hydrate formation can be formed locally in very different processes as shown in Fig. 3. Thermogenic conversion processes in deeper sediment layers, which are often coupled with oil deposits, are, e.g., a possible source not only for methane but also for other hydrocarbons on the one hand. On the other hand, microbial degradation of organic material in the sediments of the ocean floors or the microbial reduction of carbon dioxide produces methane, which is the predominant component in natural gas hydrates [39]. At the continental margins there are relatively high amounts of organic material. However, only about 10% of this organic material reaches deeper sediment layers (> 10 cm) and is converted into methane by microbial processes. This proportion is much lower on the deep-sea floor, so that in general no gas hydrates are expected at the sea floor of the free ocean waters [40]. Another source of hydrate-forming gases such as methane are decomposing gas hydrates, which moved into a deeper and thus warmer sediment layer because of a continuous sedimentation process and thus outside the stability field. The gas released during the decomposition can migrate upwards and be encased into hydrates again [40]. Methane that has been formed or released deep down may migrate into shallower sediment layers and be oxidized there via anaerobic oxidation of methane (AOM) by a consortium of bacteria and archaea using sulfate. As a result, hydrogen sulfide can be formed locally in the sea floor [41, 42]. Hydrogen sulfide is also a good hydrate former and is therefore preferably encased into the hydrate structures even at low concentrations. In this context, it should be pointed out that the microbial activity not only leads to the availability of hydrate-forming gases. Microbial activity, however, also produces plenty of other organic materials, including biosurfactants which can act as nucleation seed during gas hydrate formation. Kalogerakis et al. [43] were able to show in experiments with synthetic surfactants such as sodium dodecyl sulfate that the rate of gas hydrate growth can be increased by several orders of magnitude by adding surfactants. In nature, bacteria have been found in hydrate-bearing sediments, which produces biosurfactants such as surfactin which could be found in natural sediment cores. Rogers et al. [44] studied the influence of surfactin on the formation and growth of gas hydrates and observed that the first hydrate crystals formed significantly

faster in the presence of surfactin compared to samples without biosurfactants and that the hydrate growth rate was increased significantly (by 288%).

How well the hydrate-forming gas can migrate through the sediments and get into the GHSZ or be distributed also depends on the type of sediment. In coarse sediments with high permeability and porosity such as sand or gravel, a methane-rich pore fluid or free methane gas can easily migrate into the GHZS and form gas hydrates in the pore space between the sediment grains or as nodules. In sediments with low permeability, such as clay, methane-rich fluids or free methane gas preferentially moves through existing pathways such as fractures, in which the gas hydrates form as soon as the GHSZ is reached and thus gas hydrate veins may occur. In the case that gas bubbles rise in the sediment, very porous, sponge-like hydrate structures can also form, which can contain a great portion of free gas and therefore have a relatively low density [45, 46].

It should be noted that sediment grains may also serve as crystallization nuclei in the heterogeneous crystallization process of hydrate formation. The presence of sediment grains can thus enable hydrate formation immediately after the equilibrium curve has been exceeded without supercooling, which could also be observed in experiments for sand and bentonite [47, 48].

While sediments or the products of microbial activity can promote the formation of gas hydrates, the presence of salts can hinder or reduce the formation of hydrates. Mekala et al. [49] observed a significant delay in hydrate formation at a salinity of 3 wt%. The hydrate formation was not only delayed; the amount of hydrate formed was also significantly lower compared to hydrate formation experiments using pure water. With an increasing concentration of NaCl, the equilibrium curve of methane hydrate also shifts to lower temperatures and higher pressures, and thus the stability field decreases. This relationship is observed until the saturation concentration of NaCl is reached. Even at higher concentration of NaCl in the aqueous phase no further changes with respect to the stability condition for methane hydrate were observed [50].

The complexity of hydrate formation in a natural environment is also demonstrated by the fact that in recent years there have been increasing reports of coexisting hydrate phases with different compositions and/or structures. In 2007, a complex hydrate sample with coexisting structure II and structure H hydrate phases containing *n*-pentane and *n*-hexane in addition to methane and lighter hydrocarbons was identified from Barkley Canyon on the northern Cascadian margin [51]. A few years later in 2010, Klapp et al. [11] reported the occurrence of sI and sII gas hydrates as coexisting phases from the Chapopote Knoll in the southern Gulf of Mexico. Similar results were observed from the South China Sea by Wei et al. [52], who analyzed gas

hydrate samples and confirmed the coexistence of sI and sII gas hydrates. Also, Jin et al. [53] detected the coexistence of two sI hydrates with different textures and compositions in natural gas hydrate samples recovered from the Umitaka Spur in the Joetsu Basin, Japan. Even hydrate samples from Lake Baikal showed the coexisting hydrate phases with different structures and compositions [54, 55].

It seems surprising that hydrate phases with different compositions and structures form in nature and coexist over a longer period of time. The reasons for the coexistence of hydrate phases with different structures and composition or strong heterogeneities in compositions within a hydrate crystal formed in a natural environment can be diverse. Depending on the local conditions, a possible explanation may be fluctuations of the composition of the feed gas flux from deeper sources or a fractionation of the gas in shallower sediments as a result of methane consumption and/or the production of hydrogen sulfide as a result of biological processes such as the anaerobic oxidation of methane [11, 56]. Depending on the local sediment types and other circumstances the migration of the feed gas may be limited and the local conditions can be described as a "closed system". Another possible approach to explain these observations is to consider different hydrate formation kinetics: The formation of methane hydrate seems to be kinetically preferred compared to the formation of mixed hydrates. Another explanation could be the formation of an initial hydrate phase with a structure corresponding to the present feed gas composition and the formation of a second, additional and coexisting hydrate phase in a second step because the composition of the migrating feed gas changes rapidly. The feed gas composition may also change, because some gases are preferentially incased into the hydrate structure compared to methane [57]. Therefore, the hydrate formation process may induce a fractionation of the feed gas and may result in the formation of coexisting hydrate phases with changing compositions in accordance with the changing feed gas composition. A recently published study, however, has shown that the latter explanation does not lead to the formation of coexistent hydrate phases at least in the laboratory [58]. Even if one possible explanatory approach can be ruled out, the reasons for the coexistence of gas hydrate phases with different compositions and/or structures have not yet been clarified.

Summary and Outlook

If you consider that the research on gas hydrates is still a comparatively young science, considerable progress has been made in understanding hydrate formation over the past few decades. Also, with regard to the predictions of the thermodynamic properties of hydrates, the current understanding is sufficient for many applications in the field of chemical engineering [59]. However, there are still unanswered questions in these areas, such as the coexisting hydrate phases mentioned in the last section. The kinetics of hydrate formation and decomposition especially in natural systems are not yet adequately described. However, this knowledge is crucial when it comes to the understanding of the response of natural gas hydrates to global warming and the question of how fast natural gas hydrate deposits will decomposed and how fast and how much gas will be released into the atmosphere. Since gas hydrates can also influence the geomechanical properties of the host sediments, the question also arises as to what extent decomposition of the gas hydrates could lead to destabilization of the subsurface and may induce slope failures.

A completely different interesting aspect of the research on gas hydrates and a future perspective is the utilization of gas hydrates in industrial applications. This may include the storage and transport of gases, gas separation, sea water desalination, or waste water treatments as well as cooling issues as reported elsewhere [60].

Author contributions Judith M. Schicks wrote the manuscript.

Declarations

References

1. Davy H (1811) The Bakerian lecture: on some of the combinations of oxymuriatic gas and oxygene, and on the chemical relations of these principles, to inflammable bodies. Phil Trans R Soc Lond. https://doi.org/10.1098/rstl.1811.0001

2. Faraday M (1823) XIV. On fluid chlorine. Note on the condensation of muriatic acid gas into the liquid form by H. Davy. Phil Trans R Soc Lond. https://doi.org/10.1098/rstl.1823.0016

3. Schroeder W (1927) In: Herz W (ed) Sammlung Chemischer und chemisch-technischer. Vorträge, Breslau

4. Hammerschmidt EG (1934) Formation of gas hydrates in natural gas transmission lines. Ind Eng Chem. https://doi.org/10.1021/ie50296a010

5. Makogon YF (1966) Features of natural gas fields exploitation in permafrost zone. Gazovaya Promyshlennost 5:14–15

6. Hester KC, Brewer PG (2009) Clathrate hydrates in nature. Annu Rev Mar Sci. https://doi.org/10.1146/annurev.marine.010908.163824

7. Kvenvolden KA, Lorenson TD (2001) In: Paull CK, Dillon WP (eds) Natural gas hydrates – occurrences, distribution and detection. American Geophysical Union, Washington.

8. Kashchiev D, Firoozabadi A (2002) Driving force for crystallization of gas hydrates. J Cryst Growth 241:220–230

9. Christiansen RL, Sloan ED (1994) In: Sloan ED, Happel J, Hnatow MA (eds) International Conference on Natural Gas Hydrates. Annals of the New York Academy of Science, New Paltz, New York

10. Ke W, Svartaas TM, Chen D (2019) A review of gas hydrate nucleation theories and growth models. J Nat Gas Sci Eng. https://doi.org/10.1016/j.jngse.2018.10.021

11. Klapp SA, Murshed MM, Pape T, Klein H, Bohrmann G, Brewer PG, Kuhs WF (2010) Mixed gas hydrate structures at the Chapopote Knoll, southern Gulf of Mexico. Earth Planet Sci Lett. https://doi.org/10.1016/j.epsl.2010.09.001

12. Walsh MR, Koh CA, Sloan ED, Sum AK, Wu DT (2009) Microsecond simulations of spontaneous methane hydrate nucleation and growth. Science. https://doi.org/10.1126/science.1174010

13. Jacobson LC, Hujo W, Molinero V (2010) Nucleation pathways of clathrate hydrates: effect of guest size and solubility. J Phys Chem B. https://doi.org/10.1021/jp107269q

14. Jacobson LC, Matsumoto M, Molinero V (2011) Order parameters for the multistep crystallization of clathrate hydrates. J Chem Phys doi 10(1063/1):3613667

15. Radhakrishnan R, Trout BL (2002) A new approach for studying nucleation phenomena using molecular simulations: application to CO_2 hydrate clathrates. J Chem Phys doi 10(1063/1):1485962

16. Moon C, Taylor PC, Roger PM (2003) Molecular dynamics study of gas hydrate formation. J Am Chem Soc. https://doi.org/10.1021/ja028537v

17. Long J (1994) Gas hydrate formation mechanism and its kinetic inhibition. PhD Thesis, Colorado School of Mines, Golden, USA

18. Kvamme B (1996) A new theory for the kinetics of hydrate formation. In: Proceedings of the 2nd International Conference on gas hydrates, Toulouse

19. von Stackelberg M, Müller HR (1954) Feste Gashydrate II. Struktur und Raumchemie. Z Elektrochem. https://doi.org/10.1002/bbpc.19540580105

20. Ripmeester JA, Tse JS, Ratcliffe CI, Powell BM (1987) A new clathrate hydrate structure. Nature. https://doi.org/10.1038/325135a0

21. Ismail NM (2021) Interfacial and kinetic studies of clathrate hydrates. PhD thesis, Colorado School of Mines, Golden, USA

22. Pan M (2022) Systematic studies on the thermodynamic properties of mixed gas hydrates and their formation/dissociation/transformation kinetics. PhD thesis, University of Potsdam, Potsdam, Germany

23. Sloan ED, Koh CA (2008) Clathrate hydrates of natural gases, 3rd edn. CRC, Taylor & Francis, Boca Raton

24. Lederhos JP, Christiansen RL, Sloan ED (1993) A first order method of hydrate equilibrium estimation and its use with new structures. Fluid Phase Equilib. https://doi.org/10.1016/0378-3812(93)87049-7

25. Schicks JM, Ripmeester JA (2004) The coexistence of two different methane hydrate phases under moderate pressure and temperature conditions: kinetic versus thermodynamic products. Angew Chem Int Ed. https://doi.org/10.1002/anie.200453898

26. Staykova DK, Kuhs WF, Slamatin AN, Hansen T (2003) Formation of porous gas hydrates from ice powders: diffraction experiments and multistage model. J Phys Chem B. https://doi.org/10.1021/jp027787v

27. Sloan ED, Fleyfel F (1991) A molecular mechanism for gas hydrate nucleation from ice. AIChE J. https://doi.org/10.1002/aic.690370902

28. Schicks JM, Luzi-Helbing M (2013) Cage occupancy and structural changes during hydrate formation from initial stages to resulting hydrate phase. SAA. https://doi.org/10.1016/j.saa.2013.06.065

29. Schicks JM, Luzi-Helbing M (2015) Kinetic and thermodynamic aspects of clathrate hydrate nucleation and growth. J Chem Eng Data. https://doi.org/10.1021/je5005593

30. Schicks JM, Naumann R, Erzinger J, Hester KC, Koh CA, Sloan ED (2006) Phase transitions in mixed gas hydrates: experimental observations versus calculated data. J Phys Chem B. https://doi.org/10.1021/jp0612580

31. Maekawa T (2001) Equilibrium conditions for gas hydrates of methane and ethane mixtures in pure water and sodium chloride solution. Geochem J 35:59–66

32. Subramanian S, Kini RA, Dec SF, Sloan ED (2000) Structural transition studies in methane + ethane hydrates using Raman and NMR. Ann NY Acad Sci. https://doi.org/10.1111/j.1749-6632.2000.tb06841.x

33. Schicks JM (2021) Gashydrate – Eine Einführung in Grundlagenforschung und Anwendung. Springer Spektrum, Berlin

34. Luzi M, Schicks JM, Naumann R, Erzinger J, Udachin K, Moudrakovski I, Ripmeester JA, Ludwig R (2008) Investigations on the influence of guest molecule characteristics and the presence of multicomponent gas mixtures on gas hydrate properties. In: Proceedings of the 6th International Conference on Gas Hydrates (Vancouver 2008)

35. von Stackelberg M, Jahns W (1954) Feste Gashydrate VI. Die Gitteraufweitungsarbeit. Z Elektrochem. https://doi.org/10.1002/bbpc.19540580305

36. Handa YP (1986) Compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270 K for clathrate hydrates of methane, methane, and propane, and enthalpy of dissociation of isobutane hydrate, as determined by a heat-flow calorimeter. J Chem Thermodyn. https://doi.org/10.1016/0021-9614(86)90149-7

37. Kwon T-H, Rees TJ, Rees EVL (2011) Thermal dissociation behavior and dissociation enthalpies of methane carbon dioxide mixed hydrates. J Phys Chem B. https://doi.org/10.1021/jp111490w

38. Rydzy MB, Schicks JM, Naumann R, Erzinger J (2007) Dissociation enthalpies of synthesized multicomponent gas hydrates with respect to the guest composition and cage occupancy. J Phys Chem B. https://doi.org/10.1021/jp0712755

39. Milkov AV (2005) Molecular and stable isotope compositions of natural gas hydrates: a revised global dataset and basic interpretations in the context of geological settings. Org Geochem. https://doi.org/10.1016/j.orggeochem.2005.01.010

40. Wallmann K, Schicks J (2018). In: Wilkes H (ed) Hydrocarbons, oils and lipids: diversity, origin, chemistry and fate, (Handbook of Hydrocarbon and Lipid Microbiology). Springer, Berlin

41. Boetius A, Ravenschlag K, Schubert CJ, Rickert D, Widdel F, Gieseke A, Amann R, Jørgensen BB, Witte U, Pfannkuche O (2000) A marine microbial consortium apparently mediating

anaerobic oxidation of methane. Nature. https://doi.org/10.1038/35036572

42. Kastner M, Kvenvolden KA, Lorenson TD (1998) Chemistry, isotopic composition, and origin of a methane-hydrogen sulfide hydrate at the Cascadia subduction zone. Earth Planet Sci Lett 156:173–183

43. Kalogerakis N, Jamaluddin AKM, Dholabhai PD, Bishnoi PR (1993) Effect of surfactants on hydrate formation kinetics. In: SPE International Symposium on Oilfield Chemistry (New Orleans 1993)

44. Rogers RE, Kothapalli C, Lee MS, Woolsey JR (2003) Catalysis of gas hydrates by biosurfactants in seawater-saturated sand/clay. Can J Chem Eng. https://doi.org/10.1002/cjce.5450810508

45. Suess E, Torres ME, Bohrmann G, Collier RW, Rickert D, Goldfinger C, Linke P, Heuser A, Sahling H, Heeschen K, Jung C, Nakamura K, Greinert J, Pfannkuche O, Trehu A, Klinkhammer G, Whiticar MJ, Eisenhauer A, Teichert B, Elvert M (2001). In: Paull CK, Dillon WP (eds) Natural gas hydrates—occurrences, distribution and detection. American Geophysical Union, Washington

46. Torres ME, Wallmann K, Tr'ehu AM, Bohrmann G, Borowski WS, Tomaru H (2004) Gas hydrate growth, methane transport, and chloride enrichment at the southern summit of Hydrate Ridge, Cascadia margin off Oregon. Earth Planet Sci Lett. https://doi.org/10.1016/j.epsl.2004.07.029

47. Riestenberg D, West O, Lee S, McCallum S, Phelps TJ (2003) Sediment surface effects on methane hydrate formation and dissociation. Mar Geol. https://doi.org/10.1016/S0025-3227(03)00100-2

48. Spangenberg E, Priegnitz M, Heeschen K, Schicks J (2015) Are laboratory-formed hydrate-bearing systems analogous to those in nature? J Chem Eng Data. https://doi.org/10.1021/je5005609

49. Mekala P, Babu P, Sangwai JS, Linga P (2014) Formation and dissociation kinetics of methane hydrates in seawater and silica sand. Energy Fuels. https://doi.org/10.1021/ef402445k

50. Hu Y, Makogon TY, Karanjkar P, Lee K-H, Lee BR, Sum AK (2017) Gas hydrates phase equilibria and formation from high concentration NaCl brines up to 200 MPa. J Chem Eng Data. https://doi.org/10.1021/acs.jced.7b00292

51. Lu H, Seo Y, Lee J, Moudrakovski I, Ripmeester JA, Chapman NR, Coffin RB, Gardner G, Pohlman J (2007) Complex gas hydrate from the Cascadia margin. Nature. https://doi.org/10.1038/nature05463

52. Wei J, Fang Y, Lu H, Lu H, Lu J, Liang J, Yang S (2018) Distribution and characteristics of natural gas hydrates in the Shenhu Sea. Mar Pet Geol. https://doi.org/10.1016/j.marpetgeo.2018.07.028

53. Jin Y, Kida M, Yoneda J, Konno Y, Tenma MN, Nagao J (2020) Natural gas hydrates recovered from the Umitaka Spur in the Joetsu Basin, Japan: coexistence of two structure-I hydrates with distinctly different textures and gas compositions within a massive structure. ACS Earth Space Chem. https://doi.org/10.1021/acsearthspacechem.9b00249

54. Hachikubo A, Khlystov O, Manakov A, Kida M, Krylov A, Sakagami H, Minami H, Takahashi N, Shoji H, Kalmychkov G, Poort J (2009) Model of formation of double structure gas hydrates in Lake Baikal based on isotopic data. Geophys Res Let. https://doi.org/10.1029/2009GL039805

55. Manakov AY, Khlystov OM, Hachikubo A, Minami K, Yamashita S, Khabuev A, Ogienko AG, Ildyakov AV, Kalmychkov GV, Rodionova TV (2019) Structural studies of Lake Baikal natural gas hydrates. J Struct Chem. https://doi.org/10.1134/S0022247661 9090087

56. Schicks JM, Ziemann MA, Lu H, Ripmeester JA (2010) Raman spectroscopic investigations on natural samples from the Integrated Ocean Drilling Program (IODP) Expedition 311: indications for heterogeneous compositions in hydrate crystals. SAA. https://doi.org/10.1016/j.saa.2010.08.033

57. Uchida T, Takeya S, Kamata Y, Ohmura R, Narita H (2007) Spectroscopic measurements on binary, ternary, and quaternary mixed-gas molecules in clathrate structures. Ind Eng Chem Res. https://doi.org/10.1021/ie070153w

58. Pan M, Schicks JM (2021) Influence of gas supply changes on the formation process of complex mixed gas hydrates. Molecules. https://doi.org/10.3390/molecules26103039

59. Sloan ED (2003) Fundamental principles and applications of natural gas hydrates. Nature. https://doi.org/10.1038/nature02135

60. Hassanpouryouzband A, Joonaki E, Farahani MV, Takeya S, Ruppel C, Yang J, English NJ, Schicks J, Edlmann K, Mehrabian H, Aman ZM, Tohidi B (2020) Gas hydrates in sustainable chemistry. Chem Soc Rev. https://doi.org/10.1039/c8cs00989a

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