

## Natural Gas Hydrates and their Potential for Future Energy Supply

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### Abstract

In recent years the topic of naturally occurring gas hydrates have attracted major interest worldwide due to the fact that they may play a dominant role as possible energy resources in the future. Prior to this natural gas hydrates were mainly viewed at as a source of operational problems in gas processing and transportation equipment. The historical background and development of gas hydrates and natural gas hydrates is reviewed as well as the necessary fundamental information about the structures of gas hydrates. One prerequisite of stable operation of gas processing plants as well as the allocation of gas deposit is the exact knowledge of the hydrate stability (equilibrium) data. Whereas a lot of data have already been measured and based on this reliable computation methods have been developed, there is still the necessity to measure equilibrium data to further improve the accuracy of the models. The organisation of own measurements carried out with natural gases as well as key binary systems with water-electrolyte systems and also inhibitors are presented together with some representative results. Some review of the currently vast growing investigations on detection of natural gas hydrate locations, exploratory and first production efforts as well as some issues on possible hazards identified today in connection with naturally occurring gas hydrate deposits are highlighted.

Key words: natural gas hydrate, electrolytes, hydrate inhibitor.

### 1. Background to and development of Gas Hydrates

It is about 200 years ago that gas hydrates were discovered. Most of the literature gives the tribute of this discovery to Davy in 1811 [1]. When investigating the system chlorine – water he noticed that a crystalline substance was stable also above the melting temperature of water, 0 °C. This was chlorine hydrate. In his book Makogon [2] indicates that the retrieval of gas hydrates actually should be assigned to Joseph Priestley (best known for the discovery of oxygen), who in the late 1770ies, about thirty years prior to the experiments of Davy, came across gas hydrates when investigating sulphur dioxide in its water solution as well as the gaseous phase and ice. However, the

temperatures then (-10 °C) were well below the freezing point of water.

It was soon realized that gas hydrates differ significantly from what are commonly known as “hydrates”. Gas hydrates do not develop covalent bonds between the water and the gas molecule. Water molecules due to their capability of forming hydrogen bonds form cages which encapsulate the “guest” gas molecule of suitable size. The interaction between the guest and the water molecules are restricted to physical dispersion or van der Waals forces. Therefore these combinations of solid water-guest molecules are also called inclusion or clathrate hydrates. Due to the fact that not all the cages formed have to be filled by a guest molecule to stabilize the crystalline structure, clathrate hydrates are non stoichiometric compounds.

During more than a century gas hydrates remained a mere niche curiosity. This did not change when by the end of the 19<sup>th</sup> century Villard [3,4] showed that also hydrocarbons like methane, ethane, ethylene or propane can form hydrates. First tabulated results date back to de Foucard [5], a collaborator of Villard. Only in the late 20ies and early 30ies of the last century when in the United States transport of natural gas in pipelines started operation on a larger scale and at higher pressures natural gas hydrates began to play its since then ongoing role as a source of severe operational problems including operational breakdowns due for instance to plugging the lines. The first to show that blockages of pipes did not trace back to ice but to gas hydrates was Hammerschmidt [6] in 1934. Hammerschmidt in 1939 [7] also presented the first algorithm to calculate the amount of methanol necessary to inhibit the formation of stable natural gas hydrates. Now having been recognized as a possible source of highly undesirably costs due to the operational problems caused in technical applications gas hydrates from a mere curiosity immediately turned into a real troublemaker in natural gas industry. It was recognized that there was urgent need to enter systematic research activities for getting to know the conditions –pressure, temperature, gas composition– under which natural gas hydrates will form. The American Gas Association initiated a large research project in which Deaton and Frost [8] pioneered these systematic investigations, Katz and co-workers [9] developed the first method for estimating the conditions under which natural gas hydrates will form. This method as well as the Hammerschmidt algorithm

for hydrate inhibition still widely continue to be used in practical work today, for instance in Germany in recommendations of DVGW Technical Report G 285 [10].

However, revealing the structures of gas hydrates took yet more than another decade. By applying X-ray diffraction methods von Stackelberg [11,12] in the middle of last century was able to present the information of the detailed structure of these compounds. Stackelberg and his coworkers then described two different structures. Based on this knowledge and applying statistical thermodynamics, van der Waals and Platteeuw [13] laid the basis for calculating gas hydrate phase equilibria. Parrish and Prausnitz in the early 70ies of last century [14] were the first to extend it with additional assumptions on the occupation of the cages to gas mixtures including natural gases and to present a first computer applicable algorithm. With several modifications which are being carried out until today this method is nowadays state of the art to predict gas hydrate formation conditions and has widely replaced the method of Katz. Sloan gives a more complete overview over milestones in the early years of gas hydrate history as well as the recent developments in his book "Clathrate Hydrates of Natural Gases" in its second edition 1998 [15]. This book since the appearance of its first edition in 1990 has become a standard work covering information on nearly all aspects of natural gas hydrate related topics. It also includes a computer program (Release 1996) for predicting formation conditions for natural gas hydrates as well as the possible hydrate prevention by taking into account the inhibition properties of methanol and salt (NaCl).

About forty years ago for the first time natural occurring gas hydrates in form of the first natural gas hydrate deposits were confirmed to exist in Siberia. This laid the ground for possible prospects of fossil fuel reserves in the form of natural gas hydrates. Makogon [2] gives the background on the up to date sole continuous gas production from natural gas hydrates in the Messoyaka field, Siberia. Research on natural gas hydrates has entered a new stage since then that still accelerates pace till today. In the meantime potential natural gas hydrate deposits in suitable pressure and temperature regions are being reported virtually all over the world with the majority of occurrence in offshore regions. Since the first discovery research also is focussing on kinetics of formation and dissociation of natural gas hydrates as only a thorough understanding of these phenomena including the interaction with the ambient like sediments or electrolytes will present the key to open the door to a stable and safe handling and production possibility of natural gas hydrates.

With the advent of the first international conference on natural gas hydrates [16] in New York in 1993 new developments in this field of interest are documented, discussed in a wide international forum and potential areas of application of gas hydrates suggested in a regular triennial conference schedule with the latest (4<sup>th</sup> Intl. Conference on Gas Hydrates) having been held in Yokohama in 2002 (2<sup>nd</sup> 1996 in Toulouse, 3<sup>rd</sup> 1999 in

Salt Lake City, the coming 5<sup>th</sup> in 2005 in Trondheim, Norway). The recent increase of contributions clearly shows the vivacious and vast expanding activities in the field of natural gas hydrates: in 1999 there were a total of 143 papers (including posters), in 2002 204 papers. In total eight topics were covered in 2002 ranging from exploration, resources and environment over fundamentals (thermodynamic aspects, kinetics, structural studies, physical properties, multiphase mechanics and heat/mass transfer) to hydrate formation and prevention in pipelines and to hydrate-based technologies [17]. The currently dominant role of the US and Japan in natural gas hydrate research is documented by the fact that out of a total of 204 papers alone 115 were presented from representatives of these two countries. In addition numerous national as well as international symposia, workshops and conferences give evidence of the ever increasing world wide interest in natural gas hydrates as a potential alternative source of fossil energy.

This is also documented by the fact that large research projects have been launched during the last few years [18,19]: In the USA, the "Methane Hydrate Research and Development Act" became Law in May 2000 covering a period of five years (2001-2005) and bringing together different governmental authorities such as the Secretary of Energy, the Secretaries of Commerce, of Defence and the Interior as well as the Director of the National Science Foundation (NSF). Also Japan, Russia, India, Norway, Germany and Canada have established active natural gas hydrate programs with a 5 year program for the Japanese which is considered to be the most advanced. In Germany the Deutsche Forschungsgemeinschaft (DFG) in 1999 defined Gas Hydrate Research as one out of thirteen large projects for the next 10 to 15 years, in 2000 the Ministry for Education and Research (BMBF) set up a "Gas Hydrates in the Geosystem R&D Center" encompassing three multi-research centre projects. In India the Indian Government charged an expert group in March 1999 which defined four phases totalling 47.1 Mio US \$ (exchange 6.8.2000) as follows: Phase I to examine existing geological, geophysical data (2.2 Mio \$), Phase II the acquisition and processing of seismic data (8.4 Mio \$), Phase III stratigraphic drilling, 3-5 wells (3.3 Mio \$) and Phase IV drilling and completion 3 to 5 wells (\$ 33.2 Mio \$). Two areas have been shortlisted: on the west in the Arabian Sea off Mumbai coast, to the east off Calcutta, south of Bengal Delta.

Also in 1999 the first US patent for hydrate recovery and conversion to liquid onboard a vessel was granted.

What is most promising and may show the coming into maturity for the natural gas hydrate development is that oil and gas producers begin to break with the attitude of looking at the scenery as being mainly of academic interest and start also to engage in the field of exploration and production [19]. Hopefully, this will continue also when research funds no longer will be granted to make natural gas hydrates on the long run a real viable and reliable energy source alternative.

## 2. Fundamentals and Experiments

### 2.1 Fundamentals

Water is known to exhibit structural behaviour due to its possibility of forming hydrogen bonds. Distinct from chemical bound hydrates gas hydrates are real inclusion components or clathrate compounds in which water forms the lattice cages and gas molecules as “guests” inside the lattice lend the stability to the hydrate. Without such guests the water lattice alone is not stable thermodynamically. To be able to act as a guest molecule, it must be suitable in form and size, it should not contain hydrogen atoms capable of forming hydrogen bonds, it should be homopolar, it should not exhibit very large van der Waals forces and it should of course be water resistant (acc. to [11]). To date more than 100 components capable to form gas hydrates are known. Different structures of natural gas hydrates are known being distinguished by the number and sizes of the lattice cages for a unit cell:

- The so called “Structure I” consisting of 2 small cages made up by 12 pentagonal surfaces called “ $5^{12}$ ” and 6 larger cages of again 12 pentagonal and two hexagonal surfaces called  $5^{12}6^2$  ( $12 \times 5^{12} + 2 \times 5^{12}6^2$ , the unit cell consisting of 46 water molecules) ;
- “Structure II” consisting of 16 small cages made up by 12 pentagonal surfaces called “ $5^{12}$ ” and 8 larger cages of again 12 pentagonal and four hexagonal surfaces called  $5^{12}6^4$  ( $16 \times 5^{12} + 8 \times 5^{12}6^4$ , the unit cell consists of 136 water molecules);
- “Structure H” including  $3 \times 5^{12} + 2 \times 4^3 5^6 6^3 + 1 \times 5^{12} 6^8$  cages.

The structures I and II were first described by von Stackelberg about half a century ago, structure H by Ripmeester et al [20]. What kind of structure a guest substance will form depends on the size of the molecule and on the composition of a mixture. Recently, Udachin and Ripmeester [21] by using a choline as a bio-model substance showing hydrophobic and hydrophilic behaviour reported about a new “mixed” structure of gas hydrates which consists of altering stacks of structure H and structure II hydrates. They presume that such sort of structures may be found in locations where gas hydrates form naturally. They also hypothesize the possibility of the natural occurrence of still other forms of mixed hydrates. It is also known that depending on the composition of a mixture changes in structure can take place. For instance, pure methane forms structure I. By adding less than one mol percent propane the structure changes to structure II, being formed by pure propane [31]. Also, under extreme pressure conditions (in the range of GPa) restructuring can occur leading to still different structural formations of gas hydrates. However in general, for most applications being dealt with in natural gas industry structures I and II are by far the dominant representatives. Figure 1 shows the relevant cage configuration information for these two structures.

In order to assess the possibility of formation of natural gas hydrates in production, processing and transportation one needs to have reliable computation methods, their validity also extending to higher

pressures as found in seasonal storage and in transportation. In addition, reliable predictive tools are

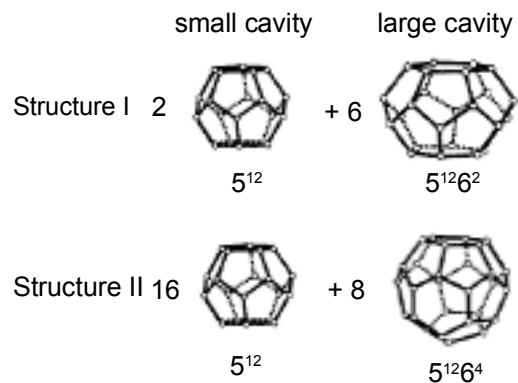


Fig. 1: Hydrate cavities for structure I and structure II [22]

required in order to assess the location and occurrence which in the case of natural gas hydrate deposits means depths in which they may be expected, for instance, in the oceans [23]. To locate the exact stability conditions of natural gas hydrates knowledge of precise data of equilibrium conditions of mixtures of the guest molecules, water and in the case of offshore locations, also electrolytes is required.

Until today only a limited number of data with mixtures of electrolytes and also alcohols as inhibiting agents (for processing) is available. On top of this the available literature data often show quite considerable scatter which hinders the further development of reliable predictive tools. Even though based on an improved knowledge of the different structures the accuracy of the methods for phase equilibrium conditions available in open literature (e.g. [15]) has increased tremendously during the last decade or so, it is true that the predictive methods can only be as good as the underlying experimental data. Therefore also today in certain areas there remains the necessity of first achieving reliable experimental information on which the further development of the models can be based.

Formation or nucleation of gas hydrates does not occur instantaneously at the phase equilibrium conditions of pressure, temperature and composition but includes a metastable phase which in experiments can last for hours or even days before a macroscopic evidence of hydrate formation is manifested.

### 2.2 Experimental organization

In the early 90ies we found that inadequate data were available for gas hydrate formation conditions or equilibria in the temperature and pressure range of natural gases produced, received and distributed in Germany. Thus it was decided to accumulate systematic and reliable phase equilibrium data for representative natural gases in order to aim at further development of correlation methods. In addition during ongoing work it emerged that also basic data of pure compounds and binary key systems had to be remeasured due to some larger scatter in literature data [24]. In a further project the measurements were

extended to the binary key systems methane – ethane and methane – propane with electrolytes and electrolyte mixtures as well as some mixtures with electrolytes and alcohols. This enabled us to reliably extend the correlation procedure to lower temperatures and higher pressures for the gas electrolyte systems [25].

There are different possibilities to investigate hydrate formation, dissociation or equilibrium conditions on a laboratory scale. Recently developed dynamic apparatuses (often including a flow loop) the origin of which can be traced back to Hammerschmidt are especially suited to investigate the formation and dissociation behaviour of gas hydrates as well as the influence of inhibitors and also of electrolytes on these phenomena.

For the determination of phase equilibrium data static methods are preferred. These are divided into

- isothermal methods, where the gas – water (and possibly electrolyte or alcohol/inhibitor) mixture is being held at pressures above the equilibrium line. When gas molecules are encapsulated by hydrate formation the pressure decreases until the equilibrium line is reached. By slowly lowering the pressure the point of dissolution of the last hydrate crystal can be interpreted as the equilibrium point.
- isobaric methods where by suitable means (like variable buffer volume) the pressure is being kept constant and the temperature is lowered to below the equilibrium point until hydrates form. The temperature then is slowly increased at still constant pressure and - as above- the equilibrium point is reached when the last hydrate crystal has been dissolved.
- isochoric methods where the experiments are being performed in a constant volume autoclave.

There are a few advantages of the isochoric method over the first two. The equilibrium information is received only from temperature and pressure measurements. No visual observation as in the first two methods is required, thus eliminating one possible source of individual inaccuracies. In addition with the isochoric method the whole experiment can be fully automated and thus also can be carried out over night. Therefore for our experiments we have chosen the isochoric method by using a constant volume autoclave with a magnetic stirrer to ensure constant mixing.

Figure 2 shows the pressure temperature diagram obtained with the isochoric method where water and the hydrate forming gas is enclosed in a constant volume autoclave. The result is a loop-like pressure-temperature trace as shown in figure 2 for the example of a binary 96 mol-% methane- 4 mol% ethane gas mixture in the presence of an aqueous methanol solution (with 10.8 mass % methanol).

The microscopic scale of this loop was described by Christiansen and Sloan [26] and the sections shown in figure 2 are discussed below (taken from [25]):

**Start of the experiment** – The gas-liquid equilibrium is established outside the hydrate stability region at a temperature well above the hydrate equilibrium. Here, labile, short-lived, clusters are formed by dissolution of gas in water due to hydrophobic effects.

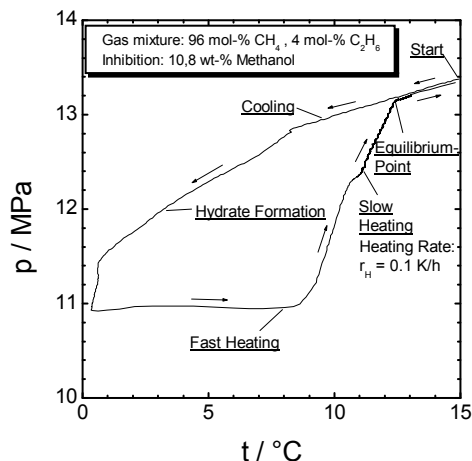


Fig. 2 Characteristic pressure-temperature loop obtained from the isochoric procedure. Example: Binary methane-ethane (4 mol-%) gas mixture and 10,8 mass-% methanol inhibition [25]

**Cooling period** - The mixture is rapidly ( $\approx 10$  K/h) cooled down into a metastable gas-liquid region whereby the cooling trace first follows real  $p, V, T$ -behavior. In the liquid phase clusters agglomerate to more long-lived, but yet unstable, structures. Cluster agglomeration is attributed to hydrophobic attraction of non-polar molecules and the natural tendency to minimize the absolute solution excess entropy [27]. Agglomerates are in a dynamic equilibrium with each other or with labile clusters; they can decompose or grow until their size exceeds a critical radius and stable nuclei are formed at a sufficiently low temperature. The period of primary nucleation is also referred to as the induction period, since no macroscopic effects of nucleation can be observed in this period. Intensive stirring inside the autoclave ensures a large continuously renewing surface between liquid and gas.

**Hydrate Formation** - Macroscopic hydrate growth can be detected by a spontaneous, rapid pressure reduction since gas molecules are more densely packed in the hydrate phase than in the gas phase. In that period an increase of liquid temperature may also be observed for a short time due to the exothermic phase transition. The extent of agitation strongly affects the sub cooling required to form enough critical nuclei which initiate macroscopic crystal growth. However, for comparable operating conditions, the molecular size and composition of hydrate formers will also have large effect on the required sub cooling. Additionally, to our experience, there is an influence of liquid composition. Most surprisingly, we qualitatively found that electrolytes in certain ranges of ionic strength might even promote hydrate formation in the sense of less sub cooling required. This might be explained by some local order imposed on the liquid phase by ionic hydration.

**Fast Heating** - After a certain amount of hydrate was formed, the system was reheated at a fast rate ( $\approx 10$  K/h) to approach the hydrate stability border. The

pressure remained nearly constant in this section in most cases.

**Slow Heating** - Upon reaching the three-phase (V-L<sub>w</sub>-H) equilibrium line, hydrate dissociation causes a sharp increase of pressure due to the re-release of enclathrated gas molecules into the gas phase. We then adjusted a static state at sufficient distance to the cooling trace. From that point the system temperature was automatically increased by computer control with rates between 0,03 and 0,2 K/h such that static states were obtained for each temperature step (while continuously stirring).

**Equilibrium point** - Dissociation of the last hydrate crystal causes the heating trace to change its slope discontinuously (break point) and resume the initial cooling trace. The break point on the heating trace, representing the final hydrate stability condition, was taken as equilibrium point and was assigned to the original gas composition since we chose the gas volume large enough to ensure that gas composition would not change notably through solubility effects. The break point pressure and temperature conditions were evaluated from the raw data by regressing data in linear regimes neighboured on both sides of the break point and intersecting the regressed lines. The total error assigned to an equilibrium point was conservatively estimated accounting for single measurement accuracy, statistical deviations of temperature and pressure and regression parameter confidence intervals, and was evaluated to  $\pm 0,1$  K and  $\pm 25$  kPa, respectively.

At the final hydrate stability point, heat and mass transfer resistances, which affect the dissociation rate of extended hydrate particles, should disappear for the hydrate phase volume tending to zero. However, at the particle surface there is an additional intrinsic resistance against hydrate dissociation, as was lately determined by Clarke and Bishnoi [28]. Thus, the break point coordinates might be also dependent on the heating rate. This in part might explain some of the scatter found in literature data. In order to exclude this source of error from our results, we systematically examined the effect of heating rate for all mixtures considered in our work. For each mixture experiments were repeated on the highest pressure level with gradually decreased heating rates. For a complete experimental row we then chose the largest heating rate suitable for providing reproducible results. In most cases appropriate heating rates were 0,1 K/h.

For few mixtures, however, we found that hydrate dissociation was obstructed in the presence of electrolytes and we had to reduce heating rates to 0,05 or 0,03 K/h.

## 2.3 Some results obtained for natural gas hydrates and the effect of inhibitors

### 2.3.1 Natural Gases

Figure 3 shows results obtained for pure methane and several natural gas – water systems. The natural gases of European origin represent experimental data obtained [22,24], the data for the two Indonesian Gas

compositions and the Malaysian natural gas are calculated results [29].

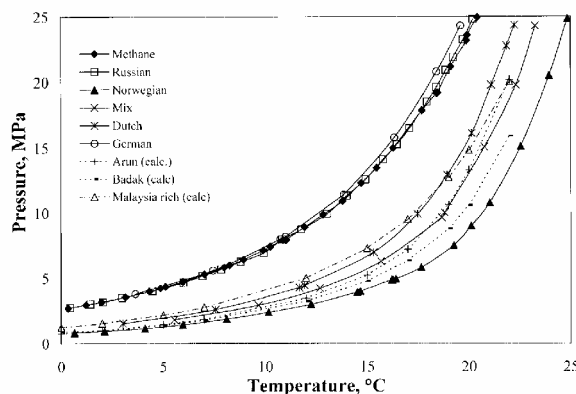


Fig. 3 Equilibrium Conditions for methane and natural gases [22,29]

The gases of European origin represented more than about 90% of the natural gas qualities distributed in Germany in 1996. A comparison shows that at 10 MPa the equilibrium temperature of pure methane is about 12.5 °C, about the same as a dry natural gas from the Russian origin. Compared to this a natural gas with a higher content of ethane and propane indicating its origin from associated gas (Norwegian origin) exhibits an equilibrium temperature of about 21 °C. The calculated equilibrium conditions for the two Indonesian gases and the Malaysian gas fall in between. About the same range of hydrate equilibrium conditions for other natural gases are reported in literature as summarised by Sloan [15].

The importance of being able to reliably predict the equilibrium conditions for the multicomponent mixture natural gas to ensure stable operation can be exemplified by the fact that the cost during breakdown of production caused by (unwanted) hydrate formation are considerable. Gerdes [in 16] for a 0.5 mill. m<sup>3</sup>/day production gives a figure of approx. 40.000 US \$ per day breakdown cost per drilling.

### 2.3.2 Inhibitors

If one is not able to operate outside temperature and pressure conditions of possible hydrate formation the only possibilities to avoid the occurrence of gas hydrates during operation are:

- Drying of the natural gas down to water levels to safely cope with the worst operating conditions either by adsorption or by absorption or
- Addition of inhibitors.

In the case of inhibitors one differentiates between two classes for preventing the problems caused by hydrates:

- “Thermodynamic” inhibitors the addition of which shifts the equilibrium curve at constant pressure to lower temperatures or increase the pressure when retaining the temperature (analogue to freezing point depression agents) and
- “Kinetic inhibitors” whose addition is aimed at avoiding the growth and agglomeration of hydrate crystals and slowing down their growth.

Kinetic inhibitors like some special polymers only need to be added in small amounts (100 to 1000 ppm), they are, however currently very expensive and active research aims at increasing efficiency and reducing cost. In practice nearly exclusively thermodynamic inhibitors are used up to date. The classical agent used in production of natural gas to avoid or inhibit natural gas hydrate formation is methanol. However, due to its toxic and unfavourable environmental impact when being released the future use of methanol is questioned and alternatives like higher alcohols are discussed as inhibitors. Due to its lowest molecular mass the use of methanol necessitates the lowest mass requirements as the classical inhibitors largely act in the same way as freezing point depression agents with the number of added molecules having the main impetus on the hydrate formation depression. Figure 4 gives a comparison of the depression of the hydrate equilibrium conditions of methane[22] when adding about the same mass (35 to 39 mass %) of methanol[30,31], diethylene glycol (DEG) and triethylene glycol (TEG) [31]. The respective larger effect of adding methanol compared to the same mass of DEG or TEG is clearly visible.

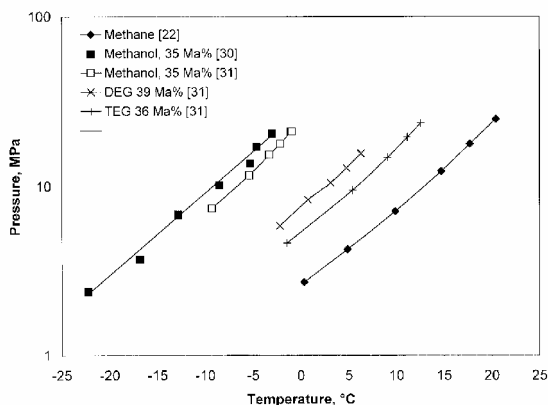


Fig. 4 The influence of different alcohols as inhibitors on the equilibrium conditions of methane hydrates

However, the application of inhibitors, too, involves high cost which can also affect the profitability of gas production. To illustrate two figures as given by Sloan [in 16] are highlighted:

- The operating cost for hydrate inhibition by methanol in an offshore field with a production rate of 6.6 mill. m<sup>3</sup>/d" are quoted to amount to annually 2.5 mill. US \$.
- The investment for a hydrate inhibition system working based on glycol (including its recovery) for a field with a production rate about half as above (3.5 mill. m<sup>3</sup> per day) are given as 10 mill. US \$.

Despite the fact that the hydrates are exclusively formed by guest molecule - (in the case of natural occurring hydrates nearly always methane) - water the equilibrium conditions in electrolyte solutions (dissolved salt-water solutions) depend strongly on the concentrations of the electrolytes and more so on the composition in the case of electrolyte mixtures. To illustrate, figure 5 shows the influence of different electrolyte water systems on the hydrate equilibrium conditions of hydrates for a methane – ethane mixture.

In order to give some idea about the formulation of the procedure with which the results indicated as "calculated" were arrived at figure 6 gives a schematic indicating the required background for the phase equilibrium solid-liquid-vapour calculations.

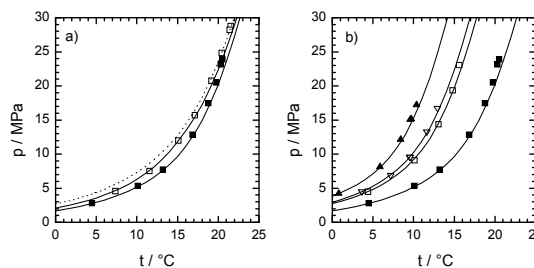


Fig. 5 Experimental and predicted hydrate dissociation pressures vs. temperature for binary methane-ethane gas mixtures in pure water a) and in the presence of electrolyte inhibitors b) [25]. Experimental data [31]: a) 4,02 mol-% ethane; 1,97 mol-% ethane; calculated; calculated pure methane. b) 4,02 mol-% ethane; pure water; 10 mass-% NaCl; 7.15 mass-% NaCl; X 5 mass-% NaCl / 6,89 mass-% CaCl<sub>2</sub>; calculated.

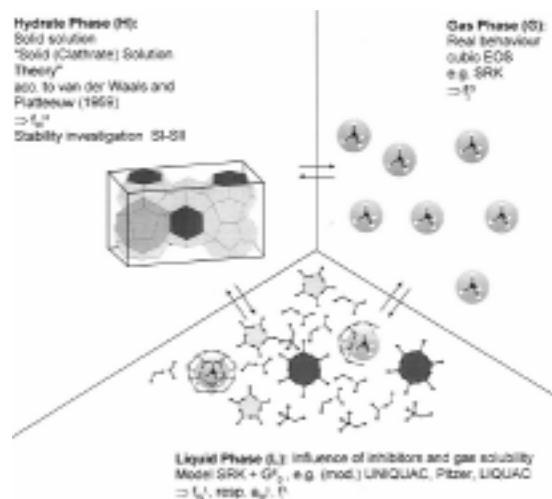


Fig. 6 The required building blocks for performing the three phase gas-liquid-hydrate equilibrium calculations [31]

### 3. Occurrence of natural Gas in hydrate deposits

The assumptions of naturally occurring gas hydrates were initiated by unusual observations made during exploratory drillings in the 1950ies (Malone in [16]). However, it was not until in the mid-1960's that Russian scientists (Makogon in [16]) succeeded in providing practical proof of this theory when hydrate saturated cores were extracted in exploratory drilling [2]. Since then a large number of deposits in onshore areas (permafrost areas) and particularly in the offshore areas of the continental shelves have been and still are being discovered. The proof of such deposits/occurrences can be obtained by the analysis of drilling cores from deep sea drillings. Seismic

procedures in which special reflections of acoustic signals which are interpreted as indicating the location of possible hydrate deposits are also used. Such reflections are known as “Bottom Simulating Reflections” or BSR because they indicate the base of the hydrate layer parallel to the ocean floor. Hydrates are to be found where the required high pressures and low temperatures occur together with suitable sediment and hydrate formers. In permafrost regions, hydrate deposits have been discovered in depths between about 130 and 2000 m. It is also known that in part conventional free gas deposits are to be found below these deposits. This is also the case in the Messoyaka field (West Siberia) which to date is the only field where successful production of natural gas from hydrates has been performed. Up to date, 14 bill. m<sup>3</sup> of natural gas have been produced from this deposit, approximately one third of which comes from the hydrate layer [2,15]. In greater depths no hydrate deposits are expected to be found, since due to the geothermal gradient the temperatures exceed the stability limits. The onshore deposits known today are primarily located in Russia and the northern part of Alaska, all exclusively in permafrost regions. In offshore regions, hydrate deposits have been found at depths anywhere from a few meters to about 1000 m below the ocean floor. There is evidence of such deposits existing on the coasts of North, Central and South America, the Bering Sea, Japan, Norway, Africa, India as well as in the Caspian and Black Seas.

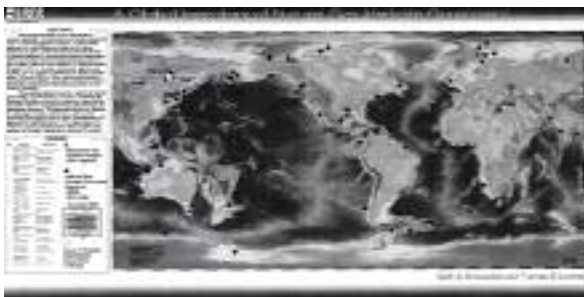


Fig. 7: Status of worldwide Hydrate Deposits according to Kvenvolden and Lorenson, 2000 [32]

In figure 7 the currently known and presumed continental and ocean deposits are shown on a map of the world [32]. This global inventory has been updated by Kvenvolden and coworkers over the decades and its development gives some insight in the boosting activities of natural gas hydrate deposit research. In 1980 it showed 14 areas of hydrate bearings, in 1988 this was increased to 36 and in 2000 now over 80 locations are included. An exact quantification of the amount of natural gas existing in hydrate form, however, is not yet possible. Sloan in 1999 [15] summarizes the results of the estimates for the occurrence of natural gas hydrate deposits of several researchers:

Onshore (permafrost)	$1.4 \times 10^{13}$ - $3.4 \times 10^{16}$ m <sup>3</sup>
Offshore	$3.1 \times 10^{15}$ - $7.6 \times 10^{18}$ m <sup>3</sup>

In order to give a feeling for the magnitude of these figures one can take Kvenvolden's 1988 estimate of  $1.8 \times 10^{16}$  m<sup>3</sup> for the offshore reserves. He stated that

this figure would be more than double the methane equivalent of all fossil fuel depots worldwide. Of course only a portion of the hydrate figures can be expected to be economically recoverable if the pending technical problems can be solved. However, even if only a small portion (10%) of the conservatively estimated amount could be produced under (still to be proven) technically feasible and profitable conditions, the statistic range of the current worldwide natural gas reserves and resources ( $3.98 \times 10^{14}$  m<sup>3</sup>) would already be doubled (from 160 years to 320 years) [33]. These statistics show clearly what large potential these deposits constitute. In order to be able to exploit natural gas from a hydrate deposit, first the gas must be occluded from the solid phase. There are various ways of achieving this:

- by decreasing the pressure;
- by increasing the temperature (by means of supplying steam or in-situ combustion)
- by adding inhibitors.

Holder et al [34], in a comparison in terms of profitability for a study of a gas hydrate field offshore California and producing from a conventional field in Alaska comes to the conclusion that pressure reduction is the most profitable procedure.

End of first quarter 1998 a first drilling was finished by a Japanese – Canadian consortium at Beaufort-Mackenzie Basin's Mallik Anticline (Mallik 2L-38) finding a hydrate zone predominantly containing fine methane (said to be of thermogenic origin) grains in sediment with underlying five foot free gas [18]. It has been reported that lately a consortium enlarged by US Geological Society, US DOE and GFZ Potsdam, Germany has performed successfully the first intentional sustained production of methane in March 2002 at 3825 foot/1166 m Mallik 5L-38, a well drilled by a multi research consortium [19, Dallimore et al. [37],[38]]. Pressure draw down experiments were carried out, however, with only small gas flow. A longer duration flow testing was effected over a 13 m interval which was thermally stimulated via circulation of about 400 l/min of 60 °C warm water resulting in dissociated gas hydrate as well as free gas. It is reported that their energy content has exceeded the energy required downhole to stimulate hydrate dissociation. Due to confidentiality agreements with energy companies that have in part funded the project detailed results on these findings, however, will only be issued in 2004. Detailed information of the Mallik drilling experiments as well as those at the Nankai trough near Japan's Honshu Omae Zaki peninsula can be found in [17].

Economical production on a large scale, however, is not to be expected during the next 10 or 20 years, which even might turn out to be a too optimistic prognosis. There still is too little knowledge of and technology for producing natural gas from hydrate deposits, especially for offshore locations. Economically acceptable solutions still have not been found for a number of technical problems. These problems do not only pertain to controlled dissociation of hydrates, but also to the possibility of maintaining a stable resist coating, the prevention of gas outflow

along the pipelines and hydrate production also during oil production etc. From about the middle of the century on, natural gas hydrate deposits could provide a part of the natural gas supply, however.

#### 4. Potential Hazards originating from natural gas hydrates

When investigating the possibility of producing natural gas from the offshore reservoirs one must also take into consideration possible hazards that can evolve from their recovery as well as from their mere existence and also natural dissociation. Natural occurring gas hydrates often are distributed very differently in the ocean sediments, as solid hydrate inclusions or finely dispersed in the sediments. In this case hydrates act as a cementing agent giving the necessary stability to the sediment itself. Small changes in local temperature profile can lead to dissociation and possibly to unstable conditions. There are hypotheses that huge slides of sub-sea sediments having occurred in the past are associated with the decomposition of hydrates also with possible impact on the world's climate (e.g. [35], GEOMAR [36], Paull et al [39]).

Also it has been discussed that (uncontrolled) hydrate dissociation may be a potential hazard to the foundations of production platforms and pipelines [40] and drilling activities have reported instabilities of hydrates [15]. A detailed analysis about drilling and production hazards caused by gas hydrates has been presented recently by Collett and Dallimore ([41]) showing that gas hydrates can and have create severe problems in oil and gas drilling such as well bore casing damage, uncontrolled gas leakage outside the bore casing due to dissociation, uncontrolled gas flow during drilling. They stress the utmost importance of understanding the geological formation and occurrence of natural gas hydrates and the need for detailed information of gas hydrate distribution, reservoir temperatures and pressures as well porosities and permeabilities to ensure safe handling.

So there is still a long way to go until natural gas hydrate deposits will be developed as the same safe production fields as conventional natural gas fields are today. The recently established and very much tied up international efforts in research consortiums and technological developments represent a promising development in this direction.

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#### References

1. H. Davy, Phil.Trans.Roy.Soc. London 101, 1, 1811
2. Y.F. Makogon, Hydrates of Hydrocarbons, Pennwell Publ. Comp. Tulsa, Oklahoma, 1997
3. P. Villard, Compt. Rend. Vol. 106, 1602-1603, 1888
4. P. Villard, Compt. Rend. Vol. 111, 302, 1890
5. R. De Forcrand, Compt. Rend. 135, 959, 1902
6. E.G. Hammerschmidt, Formation of Gas Hydrates in Natural Gas Transmission Lines, Ind.Eng.Chem. Vol.26,No. 8, 851-855, 1934
7. E.G. Hammerschmidt, The Oil and Gas Journal, May 11, 66-72, 1939
8. W.M. Deaton, E.M. Frost, The Hydrates of Natural Gas, Pure Gas and Synthetic Gas Mixtures, Gas Vol. 16, No. 6, 1940
9. D.L. Katz, D.B. Carson, W.I. Wilcox, Natural Gas Hydrates, Ind.Eng.Chem. Vol. 33,No. 5, 1941
10. Technische Mitteilung G 285, DVGW, Hinweise für die Hydratinhibierung mit Methanol, Sept. 1974
11. M. von Stackelberg, Feste Gashydrate, Naturwissenschaften 36, No. 11, 327-359, 1949
12. M. von Stackelberg, H.R. Müller, Feste Gashydrate II, Zeitschrift für Elektrochemie 58, Nr. 1, 104, 1954
13. J.H. van der Waals, J.C. Platteeuw, Clathrate Solutions, in: I. Prigogine, ed., Adv. In Chem. Phys., Vol. II, Interscience Publ. Inc. New York, 1-57, 1959
14. W.R. Parrish, J.M. Prausnitz, Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures, Ind. Eng. Chem.Proc.Des.Dev., Vol. 11 no. 1, 26-35, 1972
15. E.D. Sloan jr. Clathrate Hydrates of Natural Gases, Marcel Dekker Inc. New York, 1<sup>st</sup> ed. 1990 and 2<sup>nd</sup> ed. 1998
16. Proceedings of the 1<sup>st</sup> Intl. Conference on Natural Gas Hydrates, New Paltz, The New York Academy of Sciences, New York, 1994
17. Proceedings of the 4<sup>th</sup> Intl. Conference on Gas Hydrates, Yokohama, Japan, on CD, 2002
18. D. F. Morehouse, Natural Gas Hydrate Update 1998-2000, Energy Inform. Adm.
19. David F. Morehouse, Natural Gas Hydrate Update 2001-2002, Energy Information Administration Also to appear in Potential Supply of Natural Gas in the United States, Report of the Potential Gas Committee, Dec. 31, 2002, Potential Gas Agency, Colorado School of Mines, Golden, CO, April 2003
20. J.A. Ripmeester, J.A. Tse, C.I. Ratcliffe, B.M. Powell, A new clathrate hydrate structure, Nature 325, 135-136, 1987
21. K. A. Udachin, J.A. Ripmeester, A Complex Clathrate Hydrate Structure showing bimodal guest hydration, Nature 397, 420-421, 1999
22. J. Nixdorf, Experimentelle und theoretische Untersuchung der Hydratbildung von Erdgasen unter Betriebsbedingungen, Dissertation, Universität Karlsruhe (TH), 1996
23. O.Y. Zatsepina, B.A. Buffet, Thermodynamic Conditions for the Stability of Gas Hydrate in the Seafloor, J. Geophys. Res. 103, Vol. B10, 24127-24139, 1998
24. J. Nixdorf, L.R. Oellrich, Experimental determination of hydrate equilibrium conditions for pure gases, binary and ternary



- mixtures and natural gases, Fluid Phase Equilibria, 139, 325-333, 1997
25. A. Rock, L.R. Oellrich, Hydrate Equilibria in Aqueous Solutions Containing Inhibitors, to be published in Wiley VCH within DFG Schwerpunktprogramm „Komplexe Gemische“, end 2003
  26. R.L. Christiansen, E.D. Sloan, Mechanisms and kinetics of hydrate formation, 283-305, 1994, in [16]
  27. F. Franks, The Hydrophobic Interaction, in F. Franks, ed., Water: A Comprehensive Treatise, Vol. 4, Plenum Press, New York, 1975
  28. M. Clarke, P.R. Bishnoi, Determination of the Intrinsic Rate of Gas Hydrate Decomposition Using Particle Size Analysis, 556-563, 2000, in Proc. of the 3<sup>rd</sup> Intern. Conf. On Gas Hydrates, Salt Lake City, 1999
  29. L.R. Oellrich, J. Nixdorf, Equilibrium Conditions for Natural Gas Hydrates to high Pressures and Influence of some Inhibitors in Proceedings ISAAE '97, Johor Bahru, Malaysia, paper 5A.7, 381-387, 1997
  30. D.B. Robinson, H.-J. Ng, J. Can. Petrol. Techn. 26, 1986 quoted in [15]
  31. A. Rock, Experimentelle und theoretische Untersuchung zur Hydratbildung aus Gasgemischen in inhibitorhaltigen wässrigen Lösungen, Dissertation, Universität Karlsruhe (TH), 2002
  32. K. A. Kvenvolden, T. D. Lorenson, <http://walrus.wr.usgs.gov/globalhydrate/browse.pdf>
  33. J. Nixdorf, L.R. Oellrich, Natural Gas Hydrates – from Bane to Boon?, Natural Resources and Development, Vol. 47, 83-98, 1998
  34. G.D. Holder, V.A. Kamath, S.P. Godbole, The Potential of Natural Gas as and Energy Resource, Annu.Rev.Energ. 427, 1984
  35. The National Energy Technology Laboratory Methane Hydrate Newsletter, p. 2, Summer 2003, in <http://www.netl.doe.gov/scng/hydrate/newsletter/HMNewsSummer03.pdf>
  36. GEOMAR, in <http://www.gashydrate.de/>
  37. S.R. Dallimore, T. S. Collett, T. Uccida, M. Weber, H. Takahashi, Overview of the 2002 Mallik Gas Hydrate Production Research Well Program, 36-39, 2002 in [17]
  38. The National Energy Technology Laboratory Methane Hydrate Newsletter, Spring 2003 in <http://www.netl.doe.gov/scng/hydrate/newsletter/HMNewsSpring03.pdf>
  39. C.K. Paull, P.G. Brewer, W. Ussler III, E.T. Peltzer, G. Rehder, D. Clague, Evaluation of Marine Slumping as a Mechanism to Transfer Methane from Seafloor Gas Hydrate Deposits into the upper Ocean and Atmosphere, 31-35, 2002 in [17]
  40. K.J. Campbell, Offshore, 46, 1991
  41. T.S. Collett, S.R. Dallimore, Detailed Analysis of Gas Hydrate Induced Drilling and Production Hazards, Proceedings of the 4<sup>th</sup> Intl. Conference on Gas Hydrates, Yokohama, Japan, 47-52, 2002.