GAS HYDRATES MODELLING WITH CPA

HYDRATE THEORIES AND MODEL VALIDATION

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Executive Summary

Gas hydrates, also named as clathrates, are ice-like crystalline solid composed of water and light gases or hydrocarbons. It usually forms in high pressure environment where water molecules form a cage to stabilize the guest light gas or hydrocarbon molecule.

Naturally occurring gas hydrates may be an important future hydrocarbon energy resource with the development of appropriate means of capture, transportation and storage. However, for conventional oil and gas production systems the presence of hydrates is considered to be an operational and safety problem. Hydrate plugs can form in gas and oil pipelines (and facilities) at typical operating temperatures and pressures under normal operating conditions, under pipeline shutdown where temperatures fall significantly as a result of closing a well or flowing gas through a choke valve. As a result, flow assurance studies including hydrate formation analysis and management have become an essential part of engineering work for the design, commissioning and operation of offshore and onshore well production facilities.

This white paper provides detailed description on the thermodynamic model of gas hydrates in Multiflash^{TM}, and its capabilities and performance in providing accurate predictions on hydrate formation and inhibition. Together with the accurate thermodynamic fluid model (Cubic Plus Association, CPA) for modelling the gas, hydrocarbon liquid and aqueous phases, the gas hydrate models in Multiflash^{TM}:

- Can accurately predict at what condition the gas hydrate forms, and how much it form.
- Can reliably predict what type of gas hydrates forms: Hydrate I, II or H as well as the complex phase transitions among the fluid and hydrate phases.
- Can predict not only the partitioning of the thermodynamic hydrate inhibitors among the fluid phases but also the accurate prediction on hydrate inhibition. The hydrate inhibitors that can be modelled by Multiflash^{TM} include: Methanol, ethanol, MEG, DEG and TEG.
- Can provide accurate calculation on the required inhibitor injection rates/dosages to suppress the hydrate formation for drilling and/or production.
- Has been extened to include a well-developed electrolyte model to model the effect of salts on hydrate inhibition and the salts precipitation.
- Is a fully integrated model that is readily imbedded in pipeline software, topside and a plant-wide processing facilities simulation environment.

Such a reliable and versatile flow assurance engineering tool will enable reservoir, petroleum and process engineers to achieve the more detailed field planning activities such as:

- Initial assessment of potential operational problem arising from hydrate formation.
- Life of field study on inhibitor requirement and formulation of hydrate prevention strategies.

If you are interested in further details on hydrate prediction and management strategies using Multiflash^{TM}, please feel free contact KBC at software@kbcat.com.

July 2016

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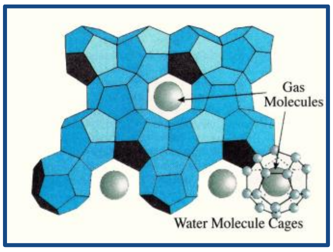
1. Introduction

Gas hydrates are compounds containing water. More specifically, in the oil and gas industry they are crystalline solid compounds composed of water and light gases or hydrocarbons.



The driving force to understanding how, where and when hydrates form or how to prevent their formation is the economic impact of hydrates to the oil and gas production and process industries. Loss of production due to a pipeline blockage can result in several million dollars of lost revenue, adding to the cost of hydrate plug removal. Also, there is a direct relationship between safety and cost, as remediation can lead to process damage, and even loss of lives.

Therefore the suppression and preventation of gas hydrates is of major importance, especially with the continuing trend towards deep-water exploration and production. The conventional engineering approach is to add inhibitors such as methanol or glycol to alter the thermodynamic equilibrium so that hydrates cannot form under production conditions. Although there has been much work recently on low-dosage kinetic inhibitors, there are many situations where it remains essential to use thermodynamic inhibitors in driling, production and tranportation.

However continuous injecting hydrate inhibitors in production line can be very expensive business. The ability in understanding and anticipating when and where the hydrates likely form, and having engineer tools that can provide reliable calculation of hydrate inhibition dosage, therefore, is essential. Thermodynamic models have been proved to be reliable tools to accurately predict the hydrate phase behaviour and to provide the industries the best knowledge on gas hydrates management.

The following sections are the summary of the basic fundamentals of the gas hydrates, the well-developed thermodynamic fluid model based on CPA (Cubic Plus Association), the gas hydrate formation and inhibition model, and the accuracy and performance of the gas hydrates models in Multiflash^{TM}.

2. Hydrate Basics

Three principal conditions are required to form gas hydrates. They include:

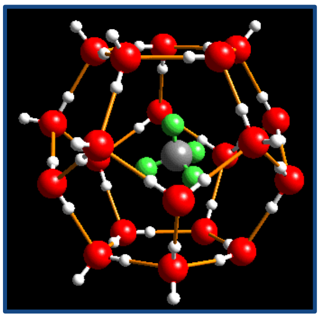
1) The presence of a hydrate former – This is the gas or light hydrocarbon molecule that sits within the water cage and stabilises the hydrate structure. Typical hydrate formers are methane, ethane, propane, carbon dioxide, nitrogen and hydrogen sulphide. However, some larger hydrocarbons can also form hydrates in the presence of these light gases.
2) Water – Water is needed to form the hydrate cage; typically hydrates contain 85% water. The amount of water may affect the hydrate formation conditions. It is certainly thermodynamically possible for hydrates to form even when no free water is present – whether the hydrates actually form in these conditions or, if they do, form in sufficient quantities to cause a problem is hotly debated.
3) A suitable combination of temperature and pressure – Hydrate formation is more likely at low temperatures and high pressures. The actual temperatures and pressures will depend on the gas, condensate or oil composition but hydrates can certainly form above 0°C, the freezing point of water. Typical seabed temperatures are 4°C, well within the hydrate formation conditions for many gases, especially at high pressures. On-shore conditions can often reach these temperatures in winter months in many gas-producing regions. At 4°C many natural gases will form hydrates at less than 10 bar, while at 100 bar many common gases will form hydrates at ambient temperatures.

While the conditions above are necessary for hydrate formation other factors may favour hydrate production.

1) Nucleation sites – This is a site which favours the formation of a new phase, in this case enhances the possibility of the first hydrate crystal forming from the fluid phase. In oil and gas production, such sites may vary from imperfections or disruptions in the smooth pipeline wall to the presence of other pipeline solids, such as sand or scale.
2) Free water present – Although not strictly necessary for hydrate formation, it is known that in many cases hydrates form at the gas-water interface. In gas-condensate-water systems, hydrates tend to form at the abundant gas-water interfaces, whereas in low gas-oil-ratio (GOR) gas-oil-water systems they tend to form at the oil-water interfaces.
3) Agitation – Mixing in process equipment encourages hydrate formation by creating more water/gas interfaces. Turbulence when the stream passes through a choke or valve has a similar effect with the added probability of a sudden drop in temperature.

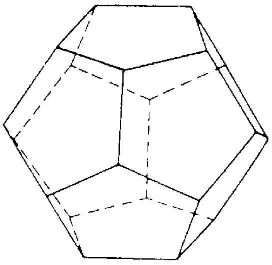
3. Hydrate Structures

Hydrates, or clathrates as they may be known, occur when water forms a cage-like structure round a "guest" molecule.

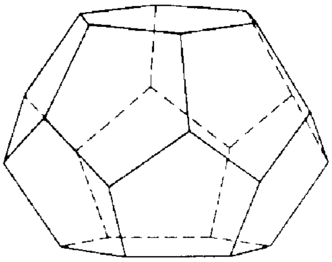


There are many compounds that can form hydrates and several hydrate structures, however, for practical purposes in the oil and gas industry only three forms of hydrate structure need to be considered, Structures I, II and H.

Structure I is the simplest hydrate structure made up of two types of cages, a dodecahedron (often referred to as the small cage) and a tetrakaidecahedron, 14-sided polyhedron, referred to as the large cage. The size of the cage determines the size of the "guest" molecule that can fit inside. Some of the common Structure I hydrate formers, methane, CO2 and H2S can fit into either the small or large cages. Ethane fits only into the larger cage.



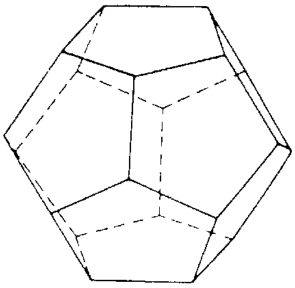
Small cage



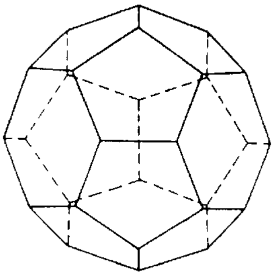
Large cage

A stable hydrate can form without a guest molecule occupying all the cages. The degree of saturation is a function of temperature and pressure. Structure I (sI) hydrates are the primary structure for the hydrate reserves found in the deep oceans.

Structure II hydrate also has a dodecahedron cage as Structure I but the second cage is a larger 16-sided polyhedron.



Small cage

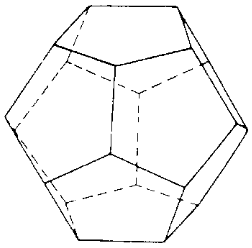


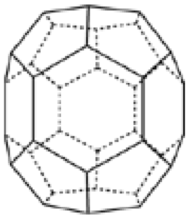
Large cage

Pure components that typically form Structure II hydrates are nitrogen, propane and isobutane. Nitrogen occupies both the large and small cages whereas propane and isobutane occupy only the large cages. The largest pure component that forms a hydrate is isobutane.

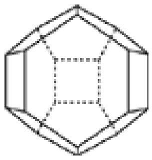
Hydrates can also be formed from occupation by more than one type of component. In most cases a hydrate former such as methane or nitrogen helps stabilise hydrate formation of a second, larger, component. An example would be n-butane, which does not form a hydrate as a pure component. However, its size is such that it can fit into the larger cages of Structure II and forms hydrates in the presence of another, lighter hydrate former. Other heavier hydrocarbons, found in oil and gas condensate systems, have an effective size which allows them to enter the large cavities of structure II gas hydrates. For instance, several cyclic hydrocarbons, such as benzene or cyclopentane, will form hydrates with small "help" gases, such as methane or nitrogen in the small cavities.

Structure H, is the last hydrate structure which is relevant to the oil and gas industry. Unlike Structures I and II, Structure H is never formed by a single pure component but requires two formers, a small molecule such as methane and a larger Type H forming molecule. Typical of the latter are branched butanes and cyclics. Structure H is made up from three types of cage: a regular dodecahedron, an irregular dodecahedron and an irregular 20 sided polyhedron.





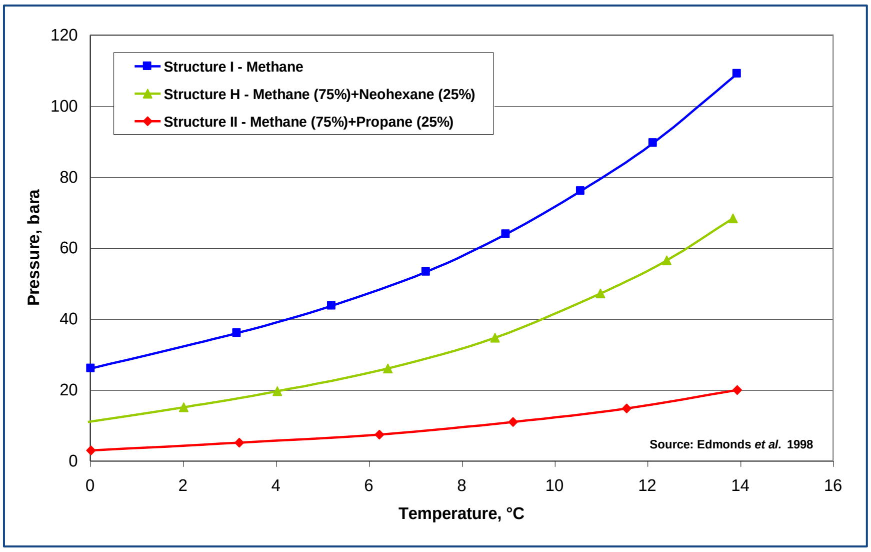
$5^{12}6^{8}$



$4^{3}5^{6}6^{3}$

The larger molecules of a gas mixture normally determine the structure formed so the presence of propane and isobutane means that the normal form found in gas production and processing is Structure II (sII). Indications from laboratory experiments are that Structure H (sH) hydrates can form at higher temperatures and lower pressures than sI and sII.

The figure below shows that the addition of 25% of sH former (neohexane) to methane produces a sH hydrate which is more stable than the pure methane sI hydrate. However, if the 25% neohexane is replaced with propane (a composition much more representative of a natural gas) then the sII hydrate is most stable. It is therefore likely that in the majority of oil and gas systems, sII will be the most stable and sH is unlikely to form unless all of the sII formers are consumed producing sII. One instance of in-situ Structure H has been reported in the Gulf of Mexico and components that may form Structure H are present in naphtha and gasoline.



Source: Edmonds *et al.* 1998

There is some evidence that the most stable hydrate structure can change from Structure II to Structure I, usually as the pressure increases. Changes in structure have been shown to be true for methane/ethane binaries in the laboratory and anecdotally reported for some heavy oils. The gas hydrate models in Multiflash™ is able to predict such phase transitions accurately, which will be shown in the later sections.

There is no clear evidence that the hydrate structure formed has direct implications for engineering applications. However, this could be a contributory factor to:

- The choice of kinetic inhibitor.
- Hydrate crystal growth.
- The formation of hydrate as a crystalline solid or a slurry.

4. Hydrate Forming Components

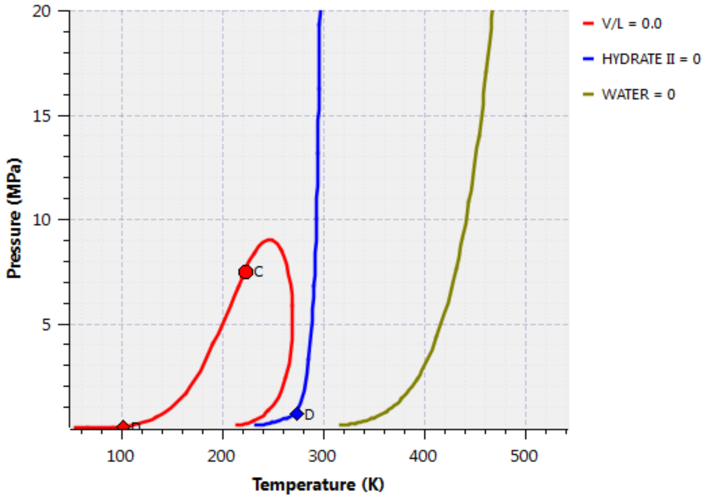
Gas hydrate formation requires the gas or light hydrocarbon components to occupy the hydrate cages to stablize the hydrate structures. As one may know, many of the components in condensates or oils that could form hydrates are not explicitly identified in compositional analyses and therefore will not be included in any modelling of hydrate formation.

However, the most common hydrate forming components that are relevant to oil and gas prudction and processing can be modelled by Multiflash^{TM}. The details are summarsied in the following table.

Natural Gas	Condensates/oils	Process
Nitrogen	Benzene*	Ethylene
Carbon dioxide	Cyclopentane*	Propylene
Hydrogen sulphide	Cyclohexane*	Other olefins
Methane	Methylcyclopentane*	
Ethane	Cycloheptane*	
Propane	Methylcyclohexane*	
Butane*	Ethylcyclopentane*	
Isobutane	Cyclooctane*	
Neopentane*	1,1 Dimethylcyclohexane*	
	cis 1,2 Dimethylcyclohexane*	
	2 Methyl butane*	
	2,2 Dimethyl butane*	
	2,3 Dimethyl butane*	
	2,2,3 Trimethyl butane*	
	3,3 Dimethyl pentane*	
	2,2 Dimethyl pentane*	
	2,3 Dimethyl-1-butene*	
	3,3 Dimethyl -1-butene*	
	3,3 Dimethyl-1-butyne*	
	cis cyclooctene*	
	bicyclo[2,2,2] oct-2-ene*	
	Adamantane*	

* denotes help gas needed

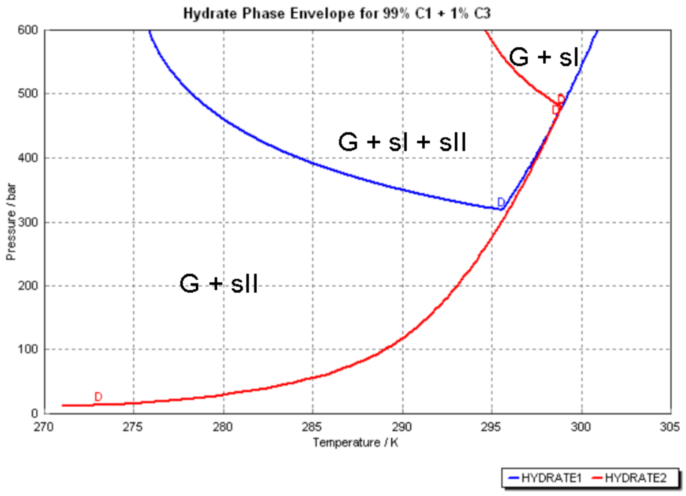
For engineering purposes, most gases and condensates have sufficient propane and isobutane for Structure II to be the most stable hydrate form and a typical phase diagram for a natural gas with free water predicted by Multiflash^{TM} is shown below.



5. Hydrate I and II Phase Transition

Hydrate phase transition may occur when the temperature, pressure as well as the composition is satisfied. For example, the transition between hydrate structure I and II may occur when the gas is very lean, with a typically high methane content (99+%), or has high levels of H_2S.

In the following case predicted by Multiflash^{TM}, the boundary for Structure II shows a very sharp change in direction as the pressure increases. Following the Structure I boundary from high to low pressure shows that this too changes sharply over a similar pressure range. In this example, there is a region where both Structure I and II are both present. The composite boundary for Hydrate I and Hydrate II defines the hydrate dissociation line.



Gas condensates and oils are usually composed of the natural gas formers plus varying amounts of heavier non-hydrate formers. The effect of this heavy end on the hydrate boundary will depend on:

- The composition of the gas,
- The nature of the heavy end,
- Whether the system is above or below its bubble point.

6. Water Content

As hydrates consist of approximately 85% water, water is a necessary element for hydrate formation. Water is often associated with natural gases in the reservoir and produced natural gas is often saturated with water. Occasionally formation water is produced along with the gas, and at later stages in the life of a reservoir water may also be injected. More water may be added during gas processing as a solvent for other components, e.g. alkanolamines used for gas sweetening. So water content as well as the water distribution among the fluid phases is a very important factor in gas hydrates management and water removal process.

It has been observed that gas hydrate forms regardless of the presence of free water phase, this phenomenon can be captured and predicted by the hydrate model in Multiflash^{TM}. Of course the truth may lie in a complex mixture of factors:

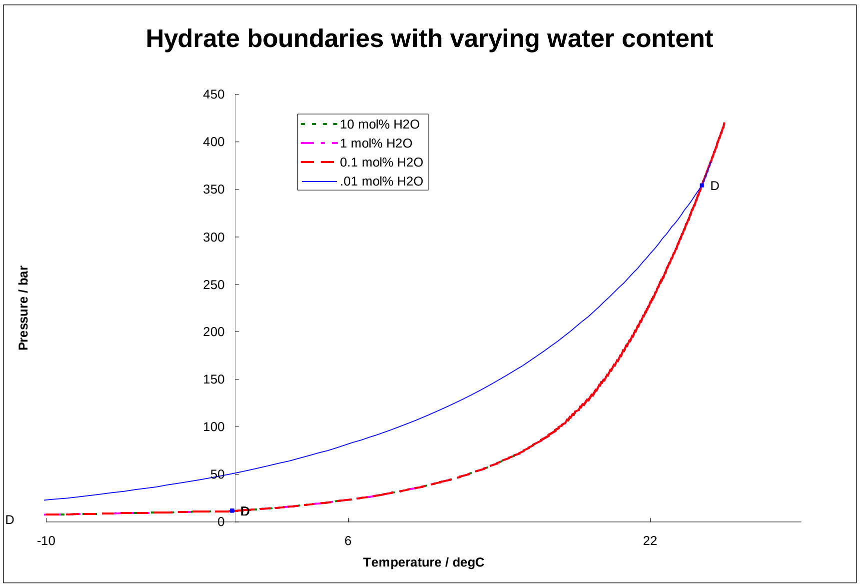
- In absence of free water, hydrates may form as frost on pipeline walls, but cause no operational problems.
- The amount of hydrates formed in the absence of free water may be small and flow with the hydrocarbon fluid.
- Hydrates may appear to have been formed from a "dry" gas, due to a change of conditions for a short period causing free water to form or there may have been a failure of a dehydration system or water carry-over.

There have been reported cases that hydrate apparently forms during processing of a dry gas. In one case, although the gas had been dehydrated, on passing through a pinhole screen prior to a heat exchanger a solid formed blocked the screen. Thermodynamic calculations by Multiflash^{TM} showed that even the reported water concentration after dehydration was sufficient for hydrates to form at the process conditions. Other examples of blockages occurring in gas processing that can be attributed to hydrate formation indicate that it is worth considering the possibility of hydrate formation even in the absence of free water.

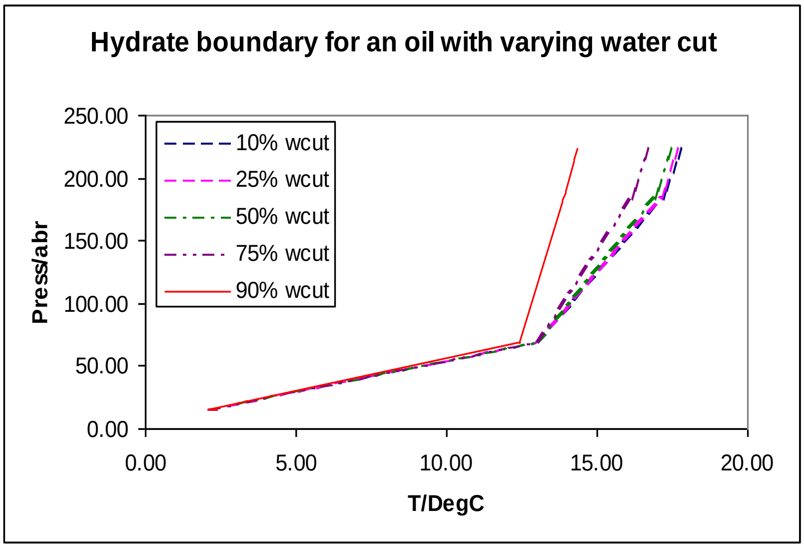
Hydrate measurements carried out in the laboratory are usually made in the presence of excess water. Similarly, most calculations of hydrate formation conditions will assume an excess of water. If the amount of water is not known, it is appropriate to calculate the saturation level of water at reservoir conditions or to assume that free water will be present.

Calculations of the hydrate dissociation boundary with typical natural gases indicate that the water content must drop to around 0.01 mol% to affect the hydrate phase boundary.

	Moles H2O per 100 Moles gas			
	10 mol%	1 mol%	0.1 mol%	0.01 mol%
P/bar	T/C	T/C	T/C	T/C
10	-3.01	-3.01	-3.01	-19.44
20	4.78	4.78	4.78	-11.48
50	12.35	12.35	12.35	-0.28
75	15.33	15.32	15.32	4.92
100	17.21	17.21	17.21	8.71
150	19.57	19.57	19.57	14.06
200	21.19	21.19	21.19	17.76



For acid gases, with high CO2 or H2S content, the higher solubility of CO2 or H2S in aqueous phase can lead to a decrease in the temperature of the hydrate boundary as the amount of water increases. A comparison of the hydrate boundary for a crude oil shows that with significant increases in the water cut, perhaps as the field matures, the boundary is largely unaffected in the two phase region but changes significantly as the pressure increases and the oil becomes single phase.



7. Gas Hydrate Model

The calculation of phase equilibria involving hydrates is, in principle, no different from any other phase equilibrium calculation. The equations that must be solved are for the equality of fugacities of each component in every phase:

$$f_{i1} = f_{i2} = f_{i3} = \ldots = f_{ip}$$

In practice, it is only possible to solve the complex systems of equations involved using numerical procedures implemented in software packages. Hydrate equilibria are even more difficult to handle than fluid phase equilibria, because of the number of phases that may exist and because the models required to describe the hydrate and ice phases are very different from those used for the gas and liquid phases.

Usually it is necessary to consider up to six phases: gas, hydrocarbon liquid, aqueous liquid, ice, Hydrate I and Hydrate II. To model the effect of salts on hydrate inhibition, additional solid salt phases are also required, leading up to total of 17 phases that may be considered. The types of models typically used to describe the properties of each of these phases are briefly reviewed in the following sections.

Hydrate Phases I, II and H

The gas hydrate model in Multiflash^{TM} is based on the work of Van der Waals and Platteeuw, which dates back to the 1950s. The formation of gas hydrate is thermodynamically thought of as having two steps:

- Firstly, pure liquid water solidifies to form an empty hydrate lattice. This is analogous to the formation of ice and is described by the same thermodynamic equations, although the parameter values of hydrate lattice are different.
- Secondly, gas molecules are adsorbed into the cavities in the hydrate lattice. The statistical mechanics of the hydrate adsorption process was derived by Van der Waals and Platteeuw, who modelled the interaction between the gas molecules and the hydrate lattice using an effective intermolecular potential. The difference in chemical potential between an empty and filled lattice is given by:

$$\frac{\Delta\mu^H}{RT} = \sum_k \upsilon_k \ln(1 - \sum_i n_{ik})$$

The sums are over the cavities k and components i

$$n_{ik} = \frac{C_{ik} f_i}{1 + \sum_j C_{jk} f_j}$$

The Langmuir constants for each component and cavity are functions of temperature

$$C_{ik} = C_{ik}(T; \mathbf{a}_{ik})$$

where the adjustable parameters $\mathbf{a}_{ik}$ are estimated by matching experimental hydrate dissociation data. This approach has been widely used and tested for many years and is capable of accurately representing the experimental data on hydrates provided that great care is taken in obtaining an appropriate set of fitted parameters.

The gas hydrate model in Multiflash^{TM} has been developed in collaboration with Shell, based on very large sets of experimental data. Later the model was extended and further improved as part of a deepwater JIP project.

Fluid Phases

Modelling the gas hydrate phase behaviour accurately demands modelling of not only gas and oil phase but must also encompass an aqueous phase that will usually contain alcohols, glycols, electrolytes and several possible solid phases.

The generic fluid modelling approach in Multiflash^{TM} is to enhance the basic cubic equation of state (EOS) by adding appropriate thermodynamic terms to the Helmholtz energy. Hence our general fluid phase model in Multiflash^{TM} has the following structure

$$A^{res} = A^{res}_{RKS} + A_{assoc} + A_{electrolyte}$$

where A^{res} is the total fluid phase residual Helmholtz energy, A_{assoc} is the contribution from chemical association and $A_{electrolyte}$ is the term that accounts for contributions in electrolyte solutions. A^{res}_{RKS} is the residual term from the cubic EoS. In Multiflash^{TM} the enhanced version of Redlich-Kwong-Soave (RKS) EOS is the recommended model for hydrate modelling, which has the “a” parameters determined by fitting the vapour pressure to improve the saturation pressure prediction and the peneloux volume correction is consdiered to improve the liquid density.

The aqueous phase is perhaps the most difficult to represent, particularly if inhibitors such as methanol and/or salts are present. The aqueous phase cannot be adequately modelled with a conventional cubic EOS and a variety of other methods have been used. Multiflash^{TM} offers the Advanced version of RKSA model either with an NRTL type mixing rule (RKSA-Infochem) or with an explicit association term (CPA). But the latter, CPA is the recommended model in Multiflash^{TM} that offers better prediction of the methanol partitioning and more reliable extroplation performance in the region outside of the conditions covered by the experimental data.

A reliable fluid model is essential to guarantee very accurate results in the solution of the fluid phase equilibria and the partitioning of polar components such as water and alcohols or glycols, playing a crucial part in hydrates formation, mitigation strategies and inhibition.

The CPA approach in Multiflash^{TM} makes it possible to model highly non-ideal aqueous phases containing hydrate inhibitors such as alcohols and glycols, whereas the electrolyte term allows us to handle mixed-solvent electrolyte solutions and to model the effect of salts on hydrate inhibition. The details of the CPA model will be presented in later sections.

Other Pure Solid Phases

Solving the thermodynamic phase equilibrium calculations simunetenously involing other solid phases together with gas, hydrocarbon liquid , aqueous and gas hydrate phases (sI,sII,sH) is important to ensure the true phase equilibrium solution and thermodynamic consistency.

Modelling pure solid formation such as ice or solid CO_2 purely depends on the thermal properties of an individual component; the melting point temperature, enthalpy of fusion and volume change on fusion. The model is used to calculate the thermodynamic properties of solid phases formed by freezing one or more of the components in the fluid mixture. It may be applied to any component with given thermal properties.

The freeze-out model in general is defined by:

$$\ln\phi_i = \alpha \ln\phi_i^{liq} - \left(\frac{\Delta H - T_{ref}\Delta C_p}{R}\right)\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) + \frac{S_{corr}}{R} + \frac{\Delta C_p}{R}\ln\left(\frac{T}{T_{ref}}\right) - \frac{(p - p_{atm})\Delta V}{RT}$$

For the freeze-out of pure solids, the parameters are defined as follows; φ_i the fugacity coefficient of pure solid component *i*, φ_i^{liq} is the fugacity coefficient of the same component as a pure liquid at the same pressure *P* and temperature *T* (calculated from the liquid phase model associated with the freeze-out model), $\alpha = 1$, $\Delta\mathrm{H}$, ΔC_p and $\Delta\mathrm{V}$ are the changes in molar enthalpy, molar heat capacity and molar volume respectively on fusion at the melting point, T_{ref} is a reference temperature which corresponds to the normal melting point when $S_{corr} = 0$, which is assumed in this case. P_{atm} is atmospheric pressure. $\Delta\mathrm{H}$, ΔC_p and $\Delta\mathrm{V}$ are constants, which are normally obtained from the chosen physical property data source.

Solid freeze-out can be used to model the solidification of compounds such as water, carbon dioxide or methane, for example in natural gases. It can also be used to model eutectics.

Another set of components that may form a solid phase, are the salts present in the water. The presence of these components may occur for several reasons:

- already present in the formation water
- added with the mud used to stabilize the well
- when sea water is used in the process

Another consequence of having salts in solution is that the water activity is reduced, hence, the salts have a hydrate inhibition inhibition effect. The model used to account for the presence of salts in Multiflash^{TM} is based on the Debye-Hückel theory which determines the effect of the electrolytes on the water activity.

8. Gas Hydrate Inhibition

Understanding the key requirements and the likely location at which gas hydrates form are crucial for the successful gas hydrates preventation and remediation in drilling, production and transportation.

Based on the three key criteria of hydrate formation, the possible means of preventation may be:

- **Removal of hydrate formers**
- **Dehydration** – removal of water from the system either by separation or dehydration.
- **Heat** – maintaining high temperatures through insulation and pipe-bundling or introducing heat using hot fluids or electrical heating.
- **Pressure** - Operating at reduced pressure, although this will decrease transportation efficiency.
- **Chemical Inhibition** – injection of a chemical components to alter the fugacity of water and move the hydrate formation conditions to lower temperatures and higher pressures (thermodynamic inhibition) or use of kinetic or anti-agglomerants to slow down hydrate crystals growth or maintain crystals as a dispersed phase.

Removal of Hydrate Formers

Preventing the formation of hydrates by removing the supply of hydrate forming molecules is not practical as most of the hydrate formers are the primary species in natural gas and petroleum systems. However this approach may be useful for subsea operation where gas and liquids are separated in subsea, and are transported to the processing facilities in separate pipelines. The gas pipeline still requires hydrate inhibition (through chemical inhibitors) but the liquids line (containing oil and water) is able to operate satisfactorily without forming hydrates due to the absence of hydrate formers. It is not known whether such a system has yet been installed and operated in this way.

Dehydration

If water could be removed completely then hydrates could not form. On the other hand, if it can be reduced significantly, then the formation of hydrates will be less likely and the amounts formed will be much smaller not to cause any dangerous damages. Dehydration is a therefore common method for hydrates prevention and has the additional engineering benefits of reducing the risk of corrosion and increasing transportation efficiency by reducing liquid accumulation in gas lines.

Dehydration may be achieved by glycol dehydration, molecular sieves or refrigeration. Glycols are usually used for gas dehydration as:

1) Water is highly soluble in glycols.
2) Hydrocarbons, in contrast, are not soluble in glycols, minimising loss of product.
3) Glycols have low vapour pressures, reducing solvent losses due to vaporisation.
4) Glycols are thermally stable, allowing regeneration of the solvent by heating to drive off water.
5) Glycols don’t react with CO_2 or H_2S and are generally non-corrosive.

The glycols most often considered for use are monoethylene glycol (MEG), diethyleneglycol (DEG) and triethyleneglycol (TEG). Of these, TEG is the most popular.

Often the water content of the gas leaving the contactor will be specified or it should be low enough to a avoid hydrate formation at later points in the process as when gases are cooled through gas expansion. Problems may occur if the gas is not dried sufficiently or there is water carry-over.

Molecular Sieves

Molecular sieves are based on an absorption process whereby the water, present in the gas phase, adheres to the solid phase that forms the sieve. They are usually used when a very dry gas in required, such as cryogenic gas processing and may follow a glycol de-hydrator used for bulk water removal. The bed must be regenerated once saturated with water.

Over time, if the desiccant is not adequate, sufficient water can pass through these sieves to allow hydrates to form in the colder sections of the downstream process.

Refrigeration

Refrigeration is often used when wet gas is being processed for hydrocarbon liquid recovery, and has the consequent effect of removing water. An advantage of this process is that it can be used to meet both hydrocarbon dew point and water content specification.

The metal walls of the chillers and heat exchangers can be cold enough for hydrates to form on the surfaces and cause hydrate fouling. To avoid this, glycol is sprayed into the exchangers and chillers. Owing to its better low temperature properties, MEG is the usual choice for this application.

However hydrate problems may occur due to unequal distribution of glycol in the heat exchanger tubes, excessive glycol viscosity, restricting flow in narrow tubes, and inadequate glycol injection for hydrate prevention. An added complication is that MEG and water have an eutectic at approximately 80 wt% MEG, i.e. mixtures of MEG and water freeze at lower temperatures than the pure components.

Heat

Maintaining high temperatures keeps the system in the hydrate free zone. The initial high reservoir temperatures may be retained by some degree by insulation. Pipeline burial is one means of providing insulation and protection, the degree of insulation depending on the thermal gradient along the pipeline route, the pipeline depth and the ambient temperature. Pipeline burial may be economic on land but very expensive in deep water.

Temperature control by passive insulation only offers hydrate control during normal operation when the system is being continually heated by hot production fluids. Sub-sea and buried pipelines will inevitably lose heat to their surroundings, especially following a shutdown the production fluids will cool down and can enter the hydrate envelope. Additional heating can be supplied by either line heaters or heat tracing, although neither may be practical or economic in all circumstances. A heater has to supply sufficient heat to maintain the fluid temperature outside the hydrate forming region until the next point where heat is supplied. Alternatively heat tracing may be used to inject heat continuously along a line, using electrical or fluid mediums. Common means of supplying heat are bundling hot water lines, induction heating with current flowing through cables outside the pipe but within insulation and direct electrical heating in which the pipe acts as a conductor with a current return line in parallel.

Supplying heat is usually limited to strategic points in a process, such as valves. Heating tools were later introductions for pipelines and, to be economic, may be available only when the line is most vulnerable, e.g. during shut-in.

Pressure

Much of the process may be controlled by pressure including transportation, compression and expansion. Depressurisation is not used as much in hydrate prevention as hydrate remediation.

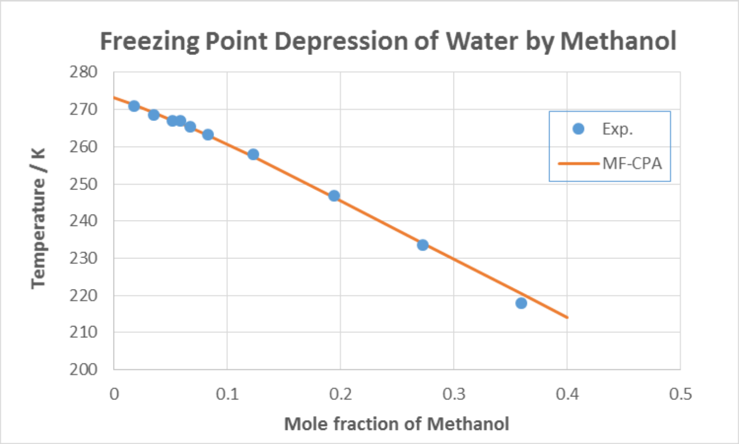
Chemical Inhibition

The final, and probably the most frequent and effective, means of hydrate prevention is by injecting an hydrate inhibitor, such as methanol or MEG, which acts as an antifreeze and decreases the hydrate formation temperature to below the operating temperature. These inhibitors are known as thermodynamic inhibitors. Ionic salts also act as inhibitors. These ionic salts are almost always present in the formation or production water that must be considered in hydrate inhibition.

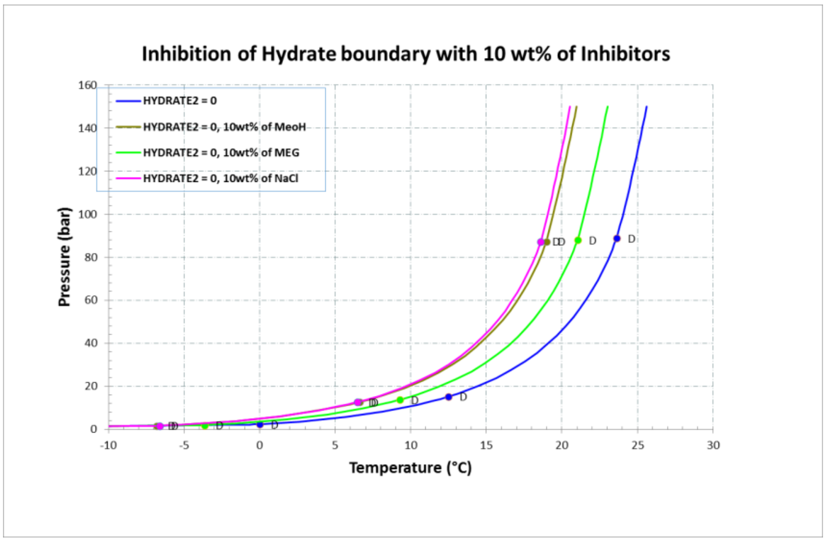
Thermodynamic Inhibitors

The mechanism for thermodynamic hydrate inhibition is the inhibitor dissolving in the free water phase thereby reducing the fugacity of water. As water is the principal component of hydrates, reducing the fugacity of water also reduces the tendency of hydrates to form.

It is also important to realise that thermodynamic inhibitors modify the properties of the fluid phases, not the solid gas hydrate phase, and as a result they have a number of other effects. The presence of inhibitors raises the solubility of gases and hydrocarbons in the water phase thereby inhibiting the formation of hydrates further. The inhibitor also depresses the ice point. It reduces the vapour pressure of water, i.e. it has a dehydrating effect on the vapour and hydrocarbon liquid phases.



Weight for weight methanol provides a greater inhibiting effect than the glycols. However, as can be seen from the plot below salt is also very effective at inhibiting hydrates. While the corrosion effects of salt mean that it would not necessarily be added as an inhibitor, it clearly should not be neglected when determining the injection dosage/rate of the thermodynamic inhibitors.



Although methanol is the most frequently used inhibitor for pipelines and process equipment it can have some adverse effects:

1) In subsequent processing of the hydrocarbon stream, the methanol may concentrate in the liquefied petroleum gas (LPG). LPG consists largely of propane and butanes, and both propane and n-butane form azeotropes with methanol, making it impossible to separate the systems using binary distillation.

2) Methanol may also cause problems in relation to corrosion. As some corrosion inhibitors are alcohol based, methanol dissolves the inhibitor leading to unexpected corrosion problems. Moreover, if stored on site in tanks open to the atmosphere, it dissolves air, adding to the long-term corrosion effects.

3) Another reported finding is that under-inhibition with methanol is worse than no inhibition because under-inhibited systems form hydrates faster than systems without inhibitors.

4) Hydrates stick to pipe walls more aggressively when insufficient methanol is injected.

Methanol is relatively volatile, so significant amounts of injected methanol are lost to the hydrocarbon gas, oil or condensate phases. This can add considerably to costs, particularly when the total fraction of the hydrocarbon phase is large compared to the water phase, for example in the early phases of reservoir production. Methanol can be recovered from the free water phase to reduce concentration such that the water can be dumped overboard. Methanol recovery from the vapour phase, while possible, is seldom done due to considerations of cost and safety.

The use of methanol has become so expensive in terms of capital cost, storage and operational costs that alternatives to methanol injection have been implemented, particularly in the North Sea.

MEG is the most frequently used of the glycols as it has a lower viscosity and is more effective per unit weight. MEG is also less volatile than methanol, so it is more easily recovered and recycled on platforms and less is lost to the hydrocarbon phases. One potential complication in MEG recovery is that MEG is recovered with water, and salt also concentrates in the MEG regenerator bottoms. The salt solubility limit in MEG is often exceeded leading to salt precipitation and consequent fouling of exchangers and other equipment.

Weight for weight methanol is still a more efficient hydrate inhibitor than MEG and its use is much more prevalent in the US and some sectors of the North Sea, especially for flow lines and platform topsides. MEG is used primarily for hydrates in wells and risers and has higher usage in the UK sector of the North Sea.

Methanol and MEG attributes		
	Methanol	**MEG**
Advantages	• Vaporises easily • No problems with salt • Used for flow lines and topside plugs	• Easy to recover • Low gas and condensate solubility • Used for plugs in wells and risers
Disadvantages	• Costly to recover • High losses to hydrocarbon phases • May have problems if under-inhibition	• Flow problems from high viscosity • Salt precipitation and fouling • Remains in water phase

Kinetic Inhibitors and Anti-Agglomerants

Kinetic hydrate inhibitors are injected in much smaller quantities compared to thermodynamic inhibitors and therefore offer significant potential cost savings, depending on the pricing policies of major chemical suppliers. They are also typically non-toxic and environmentally friendly. Moreover, considerable field experience is now available following a number of successful trials. However, they have some important limitations, including restrictions on the degree of sub-cooling (typically only guaranteed for less than 10°C) and problems associated with residence times (implications for shutdowns). In addition, the effectiveness of kinetic inhibitors appears to be system specific, meaning that testing programmes are required prior to implementation. Unfortunately adequate testing can require appreciable quantities of production fluids which may not be available, particularly for new field developments. Furthermore, they can interact with other chemical inhibitors (e.g. corrosion inhibitors). Finally, there are no established models for predicting the effectiveness of the kinetic inhibitors, which presents difficulties for field developers considering the application of these chemicals.

The benefits and limitations of anti-agglomerants are largely similar to those for kinetic inhibitors, although they do not have the same sub-cooling limitations. However, there is uncertainty about the effectiveness of anti-agglomerants under shutdown or low flow rate conditions and it is postulated that agglomeration may still proceed. In addition, they are limited to lower water cuts due the requirement for a continuous hydrocarbon liquid phase and field experience with anti-agglomerants appears to be lacking which is reflected by the relatively small number of publications available in the open literature.

9. Hydrate Calculations with Thermodynamic Inhibitors

The most common inhibitors used to suppress hydrate formation are alcohols (principally methanol) and glycols (usually ethylene glycol). As dissolved salts in produced water also acts as a hydrate inhibitor it is important to be able to predict the cumulative effects of the salts and other chemical inhibitors. All these chemicals suppress hydrate formation by decreasing the activity of water in the aqueous phase and hence making the liquid more stable than the solid hydrate phase.

Modern hydrate calculation methods involving thermodynamic inhibitors are, in principle, the same as those for ‘simple’ hydrate calculations. What is necessary is a set of thermodynamic models for all the phases that may be present plus the robust numerical methods required to solve the complex phase equilibrium equations.

The main practical difficulty is to develop a model that will accurately describe the effect of an inhibitor or mixed solvents on the aqueous phase and the loss of inhibitors between aqueous, gas and hydrocarbon liquid phases. The thermodynamic models in Multiflash^{TM} have been applied by the oil and gas, petroleum chemical and gas processing industries for nearly 30 years. The accurate fluid models together with the gas hydrate, waxes and asphaltene model provide the energy industires a parctical engineering tool to tackle all the flow assurance problems. Two of the well-developed fluid models are summarised in the following sections.

Alcohols and Glycols

The aqueous phase cannot be adequately modelled with a conventional cubic equation of state. KBC-Infochem has successfully used two approaches to model all the fluid phases simuteneously. Firstly, following modified mixing rules, combined with a RKS EOS:

$$b = \sum_i b_i n_i$$

$$a = b \sum_i n_i \frac{\sum_j n_j b_j \xi_{ji} G_{ji}}{\sum_j n_j b_j G_{ji}}$$

where:

$$\xi_{ji} = \frac{2\sqrt{a_i a_j}(1 - k_{ji})}{b_i + b_j}$$

and:

$$G_{ji} = \exp\left(\frac{\alpha_{ji}(\xi_{ji} - \xi_{ii})}{RT}\right)$$

These expressions are excess Gibbs energy mixing rules and the NRTL model based on the work of Huron and Vidal. There are three adjustable parameters for each binary pair - k_{ij}, k_{ji} and α_{ji} but the model reduces to the classical van der Waals mixing rules when no polar components are present. This allows complex phase behaviour including electrolytes and polar species to be represented whilst maintaining the good performance of the conventional cubic EOS for hydrocarbon phases.

The second approach combines a chemical association term with the RKS EOS. This is a robust general-purpose implementation of the CPA (Cubic Plus Association) model of Kontogeorgis et al.

The general mathematic formulation of the model is:

$$p = \frac{\sum_i n_i F_i (1 - X_i)}{V - 0.45 b_i} + \frac{NRT}{V - b} + \frac{a}{V(V + b)}$$

The model uses the standard (Van der Waals 1-fluid) mixing rules which are:

$$N = \sum_i n_i$$

$$a = \sum_{ij} \sqrt{a_i a_j}(1 - k_{ij}) n_i n_j$$

$$b = \sum_i b_i n_i$$

$$b_i = 0.08664 \frac{RT_{ci}}{p_{ci}}$$

The association term is complex; for a complete discussion refers to the scientific literature. In summary, the terms X_i are found by simultaneously solving the Wertheim equations, which in the CPA model have the form:

$$\frac{1}{X_i} = 1 + \frac{\sum_j K_{ij} F_j X_j}{V - 0.45b}$$

where F_j are the number of (donor) bonding sites on component *i* and k_{ij} is the association constant for components *i* and *j*.

This model explicitly takes into account the hydrogen-bonding in aqueous solutions and provides a reliable physically-based model for all the fluid phases involved in hydrate systems. The Muiltflash CPA (MF-CPA) approach is the recommended model in Multiflash^{TM} for better prediction of the methanol partitioning and more reliable extroplation performance in the region exceeded the experimental data range.

Note that the implementation of the MF-CPA model in Multiflash^{TM} is different from those in public domain in terms of the model paramertisation and the assoication model parameters.

Salts – Electrolyte Model

Modelling salt inhibition on gas hydrates is important as the formation water and drilling muds may contain concentrated solutions of sodium chloride, calcium chloride or other salts. Typical examples of composition of formation and seawater are as shown below.

Composition of North Sea Brine and Forties Formation Water		
	North Sea Brine, wt%	**Forties Formation Water, wt%**
NaCl	2.354	6.993
$CaCl_2$	0.116	0.735
$MgCl_2$	0.524	0.186
KCl	0.086	0.186
Na_2SO_4	0.428	
$SrCl_2$		0.099
$BaCl_2$		0.036

Although it is possible to estimate the effect of individual salts on hydrates quite well with an excess Gibbs energy mixing rule as described above, this approach is incapable of covering the whole range of pressures, temperatures and concentrations that are required, and is not quite accurate for modelling effect of mixed solvents. In practice, it is necessary to model the mixed solvent electrolyte solutions because in addition to water and salts the aqueous phase may contain alcohols or other solvents. KBC-Infochem have developed an electrolyte model based on Debye-Hückel theory plus virial corrections that performs very well for hydrate inhibition applications.

The general contribution term of Debye-Hückel theory to the total residual Helmholtz energy can be written in the following form:

$$A^{DH} = -\frac{4A_0 V}{Z^+ Z^-} \sum_{i,j} n_i n_j z_i z_j \frac{\tau_{ij}}{\left(b_{ij}^0\right)^3}$$

where A_0 is a constant, Z^+ and Z^- are the total positive and negative charge respectively. The index i represents the cations, and j the anions, and z_i is the charge of the ions. b_{ij}^0 is specific Debye-Hückel parameter for each pair of ions and τ_{ij} is defined as:

$$\tau_{ij} = ln\left(1 + y_{ij}\right) - y_{ij} + 0.5\ y_{ij}^2$$

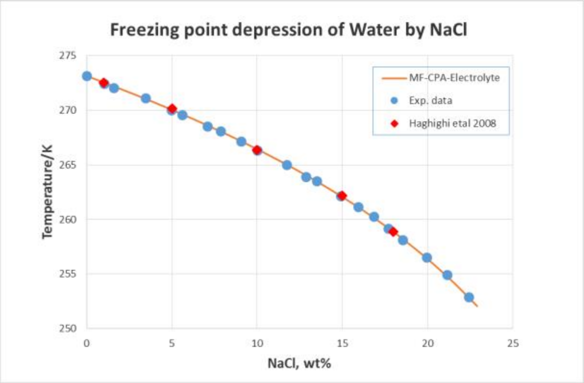
And

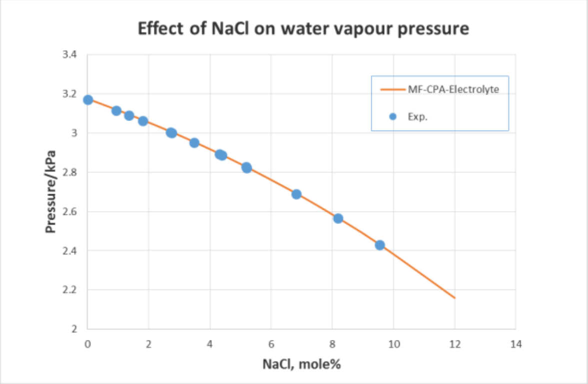
$$y_{ij} = \frac{b_{ij}^0}{\sqrt{V\epsilon T}}\Phi^{1/2}$$

where V is the total volume, T is the temperature, ϵ the relative permittivity of the solvent and Φ the ionic strength defined as

$$\Phi = \frac{1}{2}\left(\sum_{i\epsilon cation} n_i z_i^2 + \sum_{j\epsilon anion} n_j z_j^2\right)$$

With this method together with virial corrections it is possible to accurately predict the solubility of gases in salted water, the freezing point depression and vapour pressure lowering as well as the hydrate inhibition.





10. Field Applications

Hydrate Inhibition Strategy

The selection of hydrate mitigation and remediation strategies is based on technical and economic considerations and the decision is not always clear-cut. For example, in a deepwater development where the recoverable reserves and required capital expenditure mean that the development is struggling to meet economic hurdles, a low-cost hydrate strategy may be adopted which incurs a small risk of disruption due to hydrates formation. However, in a similar development with a significantly higher reserves base, the operator may elect for a higher cost strategy (e.g. electrical heating) in order to minimise risks.

In addition, the selection of a hydrate strategy is often swayed by other considerations, such as the requirement to avoid wax deposition which naturally leads developers towards insulated pipelines. The table below provides a summary of the applications, benefits and limitations of the three classes of chemical inhibitors.

Thermodynamic Hydrate Inhibitors	Kinetic Hydrate Inhibitors	Anti-agglomerant Inhibitors
Applications		
Multiphase Gas & Condensate	Multiphase Gas & Condensate	Multiphase Condensate

Crude Oil	Crude Oil?	Crude Oil
Benefits		
Robust & effective Well understood Predictable Proven track-record	Lower OPEX/CAPEX Low volumes (< 1wt%) Environmentally friendly Non-toxic Tested in gas systems	Lower OPEX/CAPEX Low volumes (< 1wt%) Environmentally friendly Non-toxic Wide range of sub cooling
Limitations		
Higher OPEX/CAPEX High volumes (10-60 wt%) Toxic / hazardous Environmentally harmful Volatile – losses to vapour 'Salting out'	Limited sub cooling (<10°C) Time dependency Shutdowns System specific – testing Compatibility Precipitation at higher temps Limited exp. in oil systems No predictive models	Time dependency? Shutdowns? Restricted to lower water cuts System specific – testing Compatibility Limited experience No predictive models

Thermodynamic models

The main benefits of the traditional thermodynamic hydrate inhibitors are their effectiveness, reliability (provided sufficient quantities are injected) and proven track-records. However, these benefits are outweighed by significant limitations, including the high volumes, high associated costs (both CAPEX and OPEX), toxicity and flammability. In addition, they are harmful to the environment and significant disposal into the environment is prohibited.

As discussed earlier you normally find that the hydrate dissociation temperatures can be predicted by Multiflash^{TM} to within 1°C, which is precise enough for most engineering calculations. What is the meaning of thermodynamic equilibrium? It is the situation that will arise if a mixture is left long enough under fixed conditions so that all changes that can occur have occurred. For fluid mixtures, equilibrium usually occurs quickly in seconds or minutes. However, when solid phases are involved the times can be much longer of the order of hours or days. This is often the case with gas hydrates.

The thermodynamic equilibrium for hydrates is very important for the following reasons:

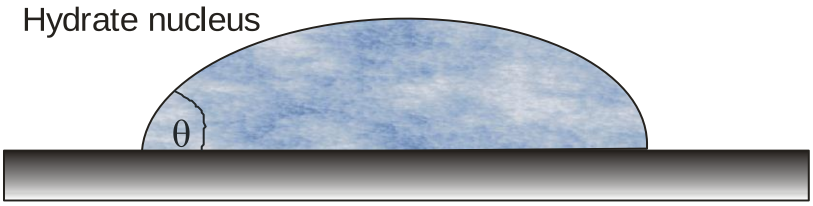
- It establishes a conservative position. If the equilibrium temperature at which hydrates will exist is known, it is guaranteed that hydrates will not form by ensuring that conditions lie outside the hydrate region. Provided this situation is maintained, there will never be a possibility of hydrate formation as it is thermodynamically impossible.
- An accurate thermodynamic model can be used to establish the "driving force" to hydrate formation. It is known that facilities can be run in the hydrate region in some circumstances without hydrates forming in practice. The further a mixture moves into the hydrate region, the stronger the tendency to form hydrates. This tendency can be loosely described as the thermodynamic driving force.
- If the thermodynamic model is used to calculate the fugacities of the components in the mixture, these can be used to set up an Arrhenius-type rate equation which can then be empirically fitted to match actual hydrate rate of formation data. Any quantitative calculation of hydrate kinetics will use thermodynamic properties. This is the reason why accurate thermodynamics is an important starting point for calculating hydrate kinetics; if the thermodynamic driving force is wrong, the kinetics will also be wrong.

Hydrate Nucleation model in Multifash™

KBC-Infochem was involved in the development of BP hydrate nucleation model (EUCHARIS JIP) based on multi-component nucleation theory.

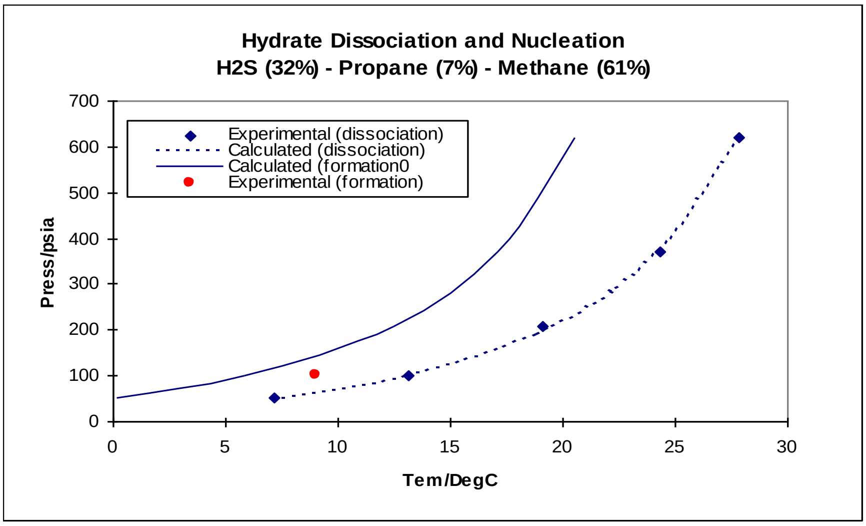
For engineering applications, the model required several simplifying assumptions and initially modelled homogeneous nucleation, largely based on data available for water/ice. To adapt this to heterogeneous nucleation further assumptions were included to take account of nucleation at a surface rather than from within the bulk of a fluid phase, including the geometry of a hydrate nucleus on a plane surface. Parameterisation of the model involved:

- expressions for the diffusion of hydrate formers,
- the hydrate-water interfacial tension and
- an approximate means of allowing for the influence of an external surface in lowering the free energy barrier to hydrate nucleation, such as might be provided by a pipeline wall. The latter was expressed in terms of a contact angle, effectively a wetting angle for the hydrate on the external surface.

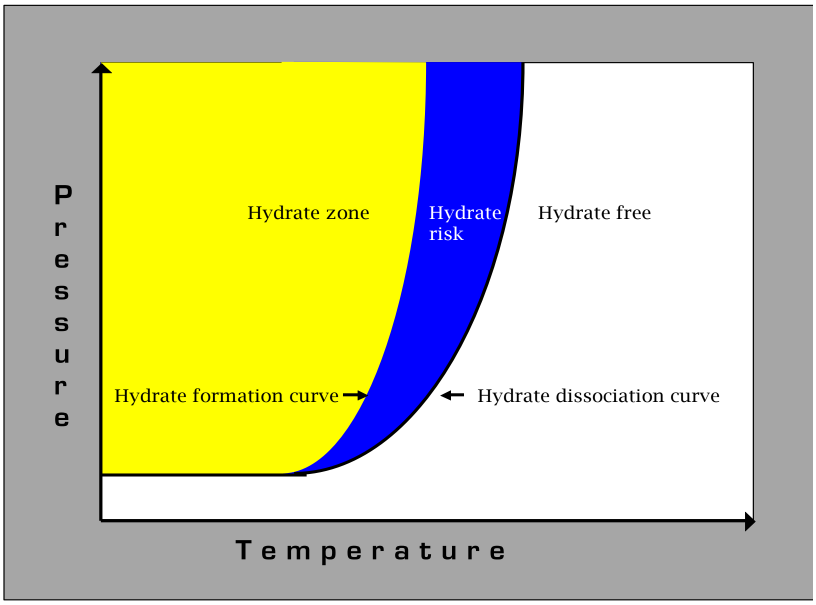


Contact angles were fitted to hydrate formation data for a variety of systems and a default value chosen that gave reasonable predictions for multi-component gas systems. If the contact angle were presumed to be zero there would be no barrier to nucleation and the hydrate formation curve will tend to towards the dissociation curve. Raising the value of the contact angle to 180 produces the highest possible value of sub-cooling, corresponding to a homogeneously nucleating system. Sub-cooling far outside the range is normally associated with the range of operating conditions experienced.

The BP nucleation model has been developed by KBC-Infochem as part of Multiflash™. It would normally be expected that the predicted hydrate formation temperatures would be lower than those observed in the field.



The BP hydrate nucleation model is commercially available in Multiflash^{TM}. With both the gas hydrate dissociation and the hydrate nucleation formation model in Multiflash^{TM}, the hydrate risk region can be fully identified as shown below.



Kinetic hydrate modelling

The thermodynamic and nucleation models only predict hydrate boundaries, albeit the extremely useful dissociation boundary from the former. They can be viewed as approximating to what happens at infinite time (thermodynamic) and at zero time (nucleation). For engineering applications they do not predict the hydrate induction time, i.e. how long a fluid can be held in a sub-cooled condition before hydrate formation starts and the rate at which, once nucleated, hydrate forms. Both aspects require a hydrate kinetics model.

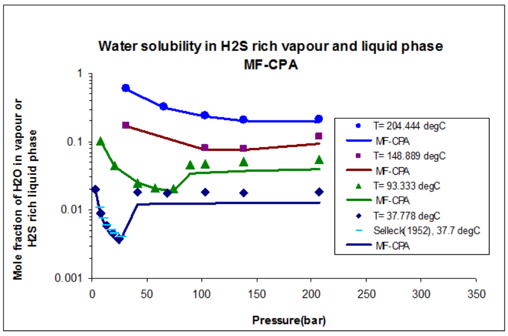
An excellent review of the state of kinetics modelling to 1998 is provided in Sloan's book. A kinetics model has to describe two stages in hydrate formatio; nucleation (induction time) and hydrate growth.

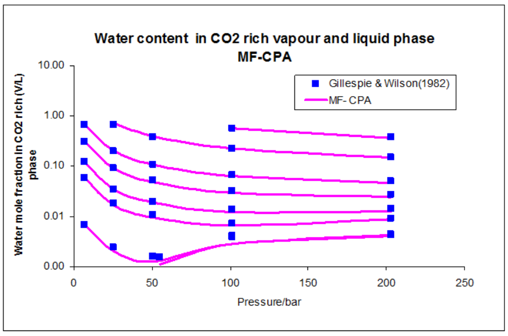
11. Validation of Gas Hydrates and CPA Model in Multiflash^{TM}

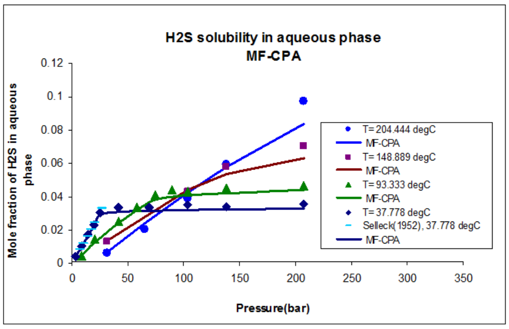
Multiflash^{TM}, a comprehensive physical properties, PVT and phase equilibrium software package, offers the accurate and robust CPA approach for many flow assurance applications. The purpose of this section is to provide the assessment study on how well the fluid phases and the hydrate conditions can be predicted using the gas hydrate and CPA model in Multiflash^{TM}.

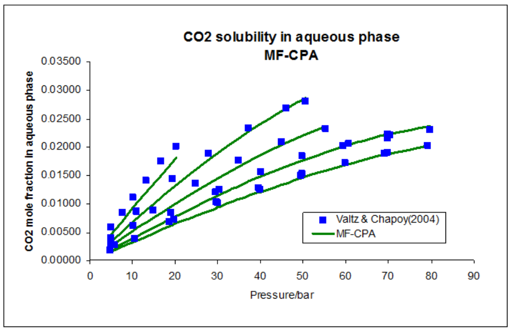
Complex Phase Behaviour of CO_2-H_2O and H_2S-H_2O

The complex phase behaviour of CO2-water and H2S-water is well predicted by CPA in Multiflash^{TM}. The accurate gas hydrate prediction strongly depends on the reliability of the fluid model applied.



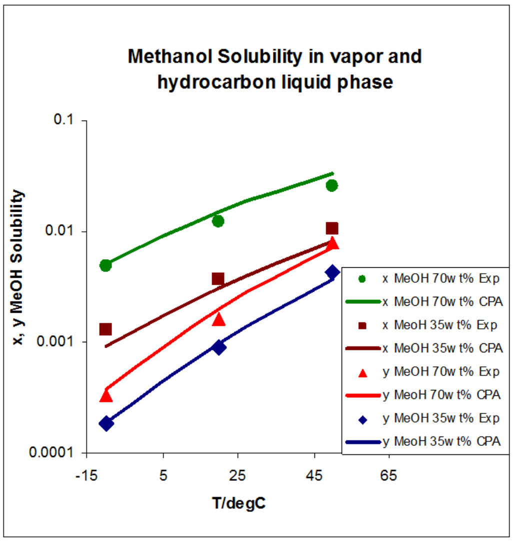


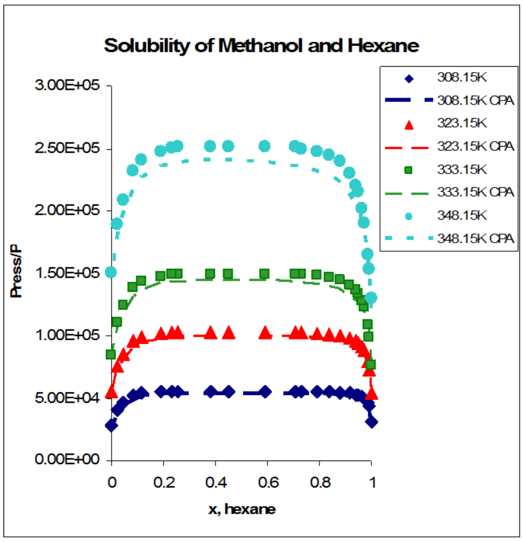




Methanol Partitioning and LLE

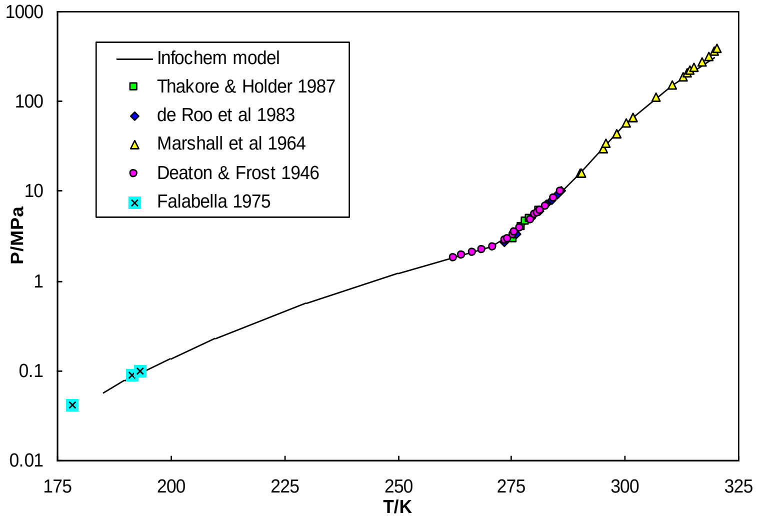
The methanol partitioning among the fluid phases and liquid-liquid equilibrium (LLE) are well predicted by the CPA model in Multiflash^{TM}.



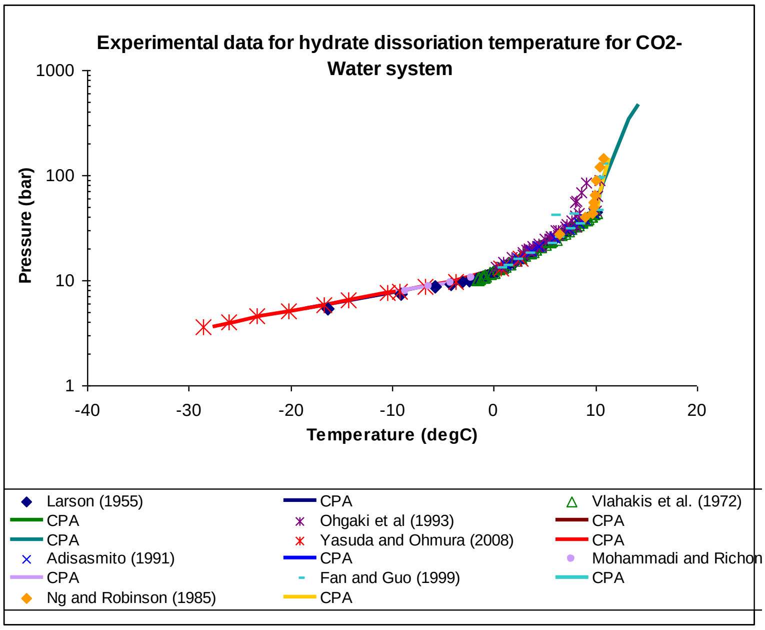


Structure Gas Hydrate I: Methane, CO_2 and H_2S

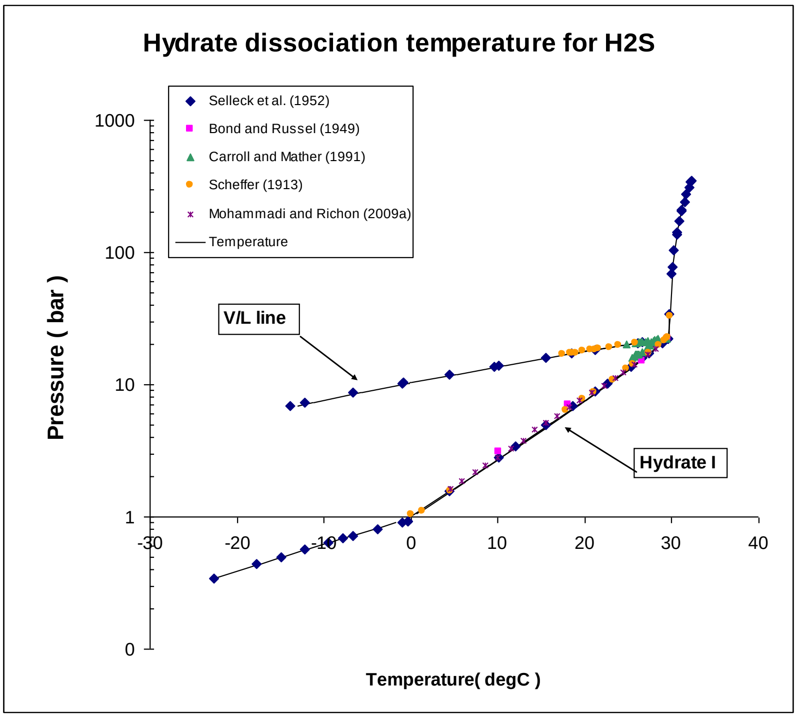
Methane forms a structure I hydrate and has been extensively studied. Measurements cover a very wide range of pressure and temperature conditions. The kink in the curve corresponds to the change from ice-hydrate-gas to water-hydrate-gas equilibrium, which is well predicted by Multiflash^{TM}.



CO_2 forms a structure I hydrate and has been extensively studied. Measurements cover a very wide range of pressure and temperature. The first kink in the curve at high temperature corresponds to the change from liquid(CO_2 rich)-water-hydrate to gas(CO_2 rich)-water-hydrate equilibrium. The second kink at lower temperature is the transition from gas (CO_2 rich)-water-hydrate equilibrium to gas(CO_2 rich)-ice-hydrate equilibrium. As shown below, all the complex phase transitions are well predicted by the models in Multiflash^{TM}, shown in solid lines.



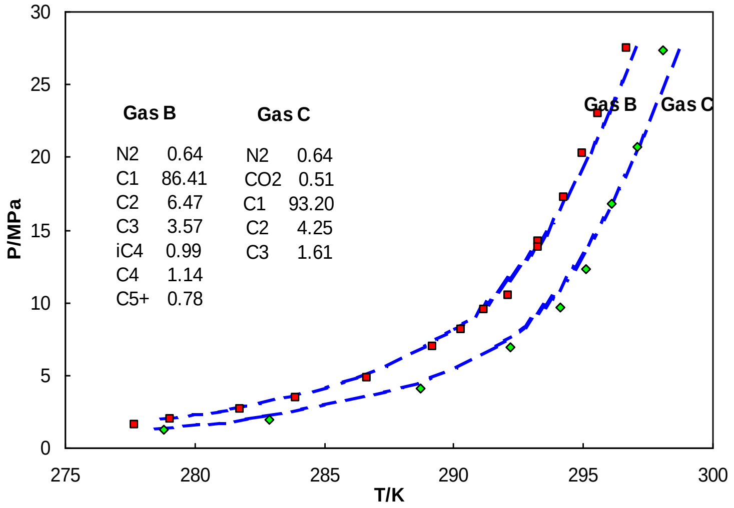
H_2S also forms a structure I hydrate and has been extensively studied. Measurements cover a very wide range of pressure and temperature. The first kink in the curve at high temperature corresponds to the change from liquid(H_2S rich)-water-hydrate to gas(H_2S rich)-water-hydrate equilibrium. The second kink at lower temperature is the transition from gas(H_2S rich)-water-hydrate equilibrium to gas(H_2S rich)-ice-hydrate equilibrium. The solid lines are the prediction by Multiflash^{TM}. As shown below, all the complex phase transitions are well predicted by the models in Multiflash^{TM}.



Natural Gases - Structure Gas Hydrate II

The data in this figure were measured by Wilcox. et al. Small amounts of heavier gases such as propane result in a structure II hydrate which forms at higher temperatures/lower pressures than structure I.

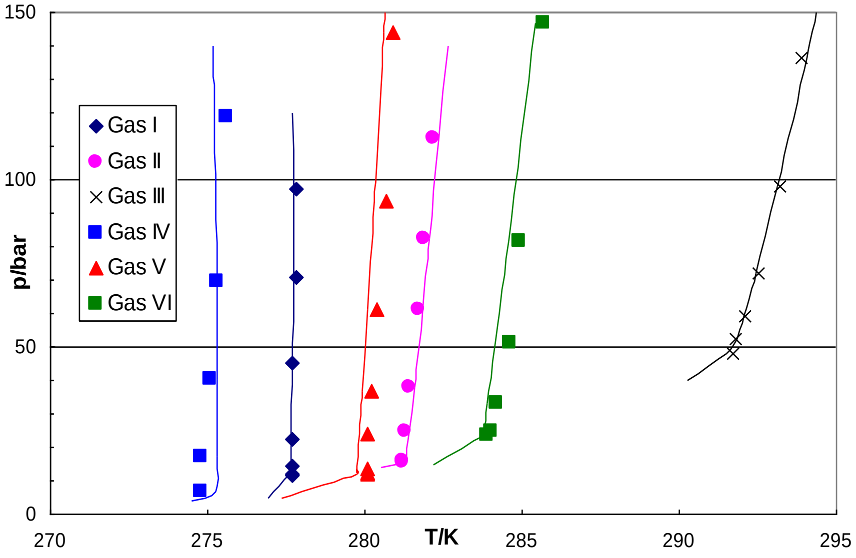
For simple mixtures of natural gas components up to moderate pressures Multiflash^{TM} is able to make accurate predictions of hydrate formation conditions in the absence of inhibitors. Typically, at a given pressure it should be possible to predict the hydrate formation temperature to within 1ºC.



Natural Gas Liquids - Structure Gas Hydrate II

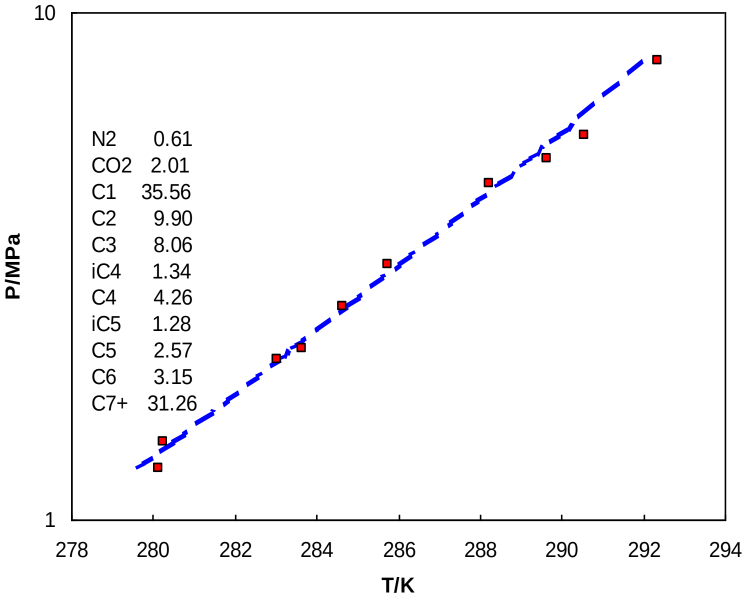
The data are from Ng and Robinson (1976). The liquids contain mainly ethane, propane and isobutane with traces of methane.

The four-phase equilibria involving water, hydrate, hydrocarbon liquid and gas provide a more difficult computational challenge because it is necessary to estimate accurate vapour-liquid equilibria in addition to the hydrate equilibria. As shown below, the complex phase behaviour and transitions are well predicted by the models in Multiflash™.



Crude Oil - Structure Gas Hydrate II

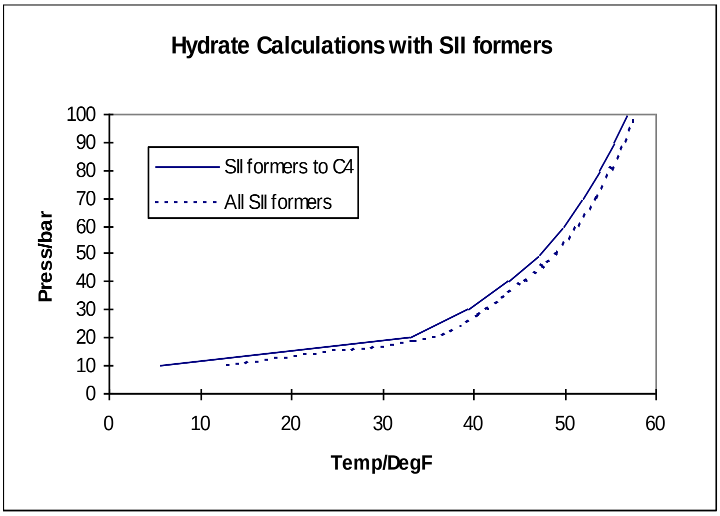
The measurements are from Avlonites. As in the previous example there are four phases present. A prerequisite for hydrate calculations for crude oils is to characterise the heavy end (C7+ fraction) in terms of petroleum fraction pseudo components.



Effect of Heavy Hydrate Formers - Structure Gas Hydrate II and H

It was a widespread assumption that molecules larger than butane were not hydrate formers. In fact there are very many larger molecules that will form hydrate structure II or hydrate structure H. Structure H is not likely to form in most natural gas/oil systems but structure II formers such as benzene are present in most oils. The following diagram shows the effect on hydrate predictions of correctly including benzene, cyclohexane etc. as hydrate formers.

The difference between the two lines is about 1ºC which is within the typical experimental uncertainty. However, for oils with higher concentrations of heavy hydrate formers the effect could be significant.

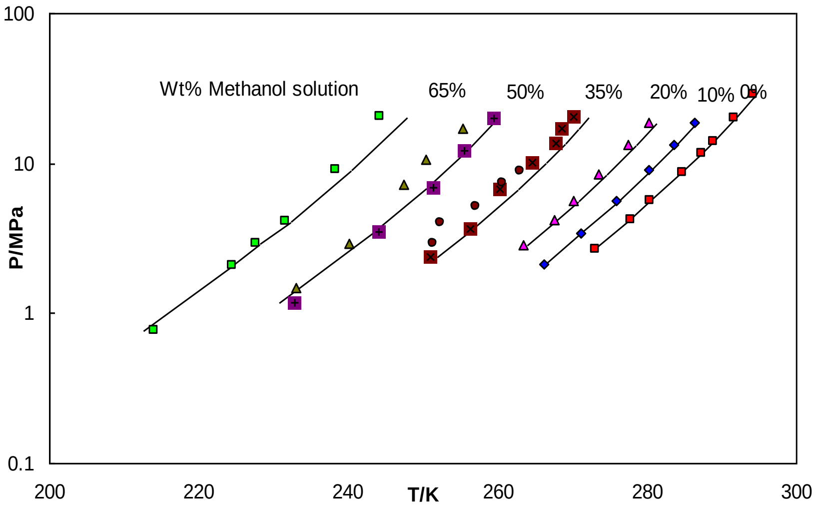


12. Multiflash^{TM} Hydrate Inhibition Model Validation

The purpose of this section is to provide an impression of how well hydrate conditions in the presence of inhibitors can be predicted using the gas hydrate model with MF-CPA. All the examples presented here have been calculated with Multiflash^{TM}.

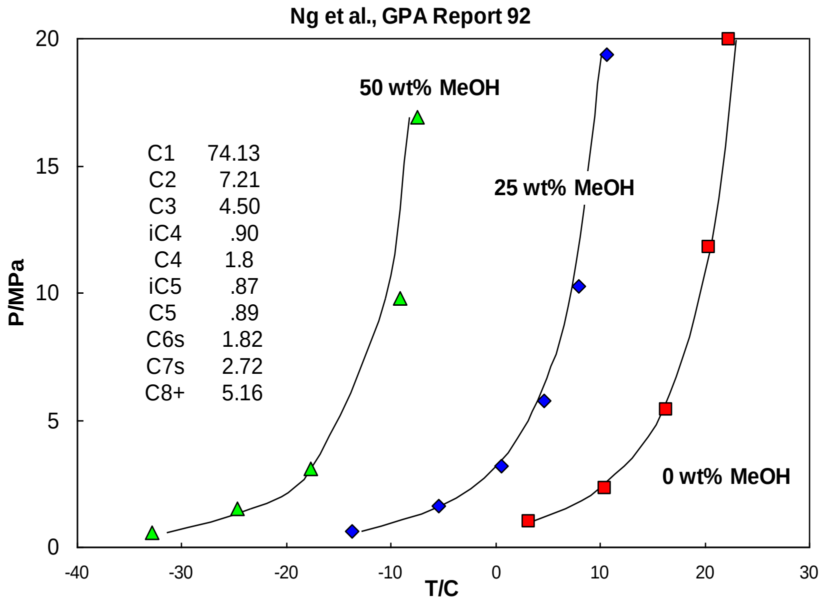
Effect of Methanol on Methane Hydrate

This system has been well-studied and although there is some scatter in the measurements the effect of methanol is predicted very well.



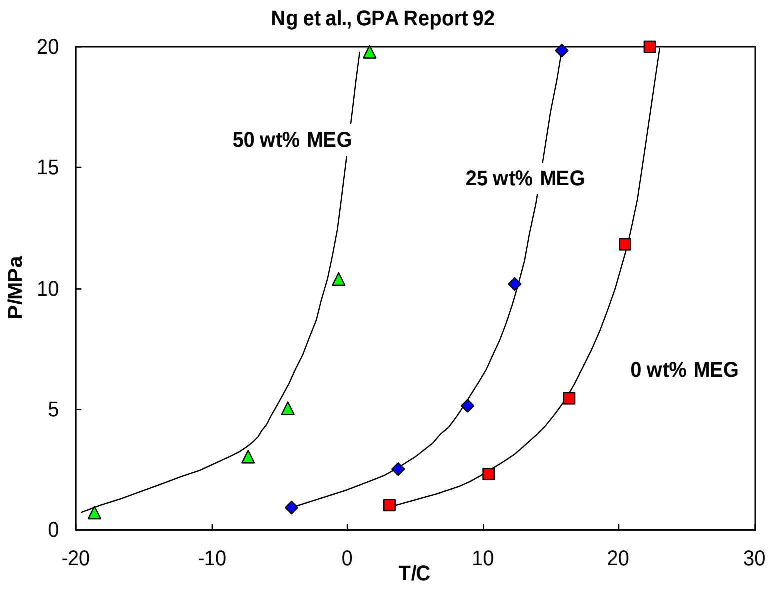
Effect of Methanol on Hydrate Formation for a Condensate

The predictions are again very good even though there are four phases (gas, aqueous liquid, hydrocarbon liquid and hydrate) present.



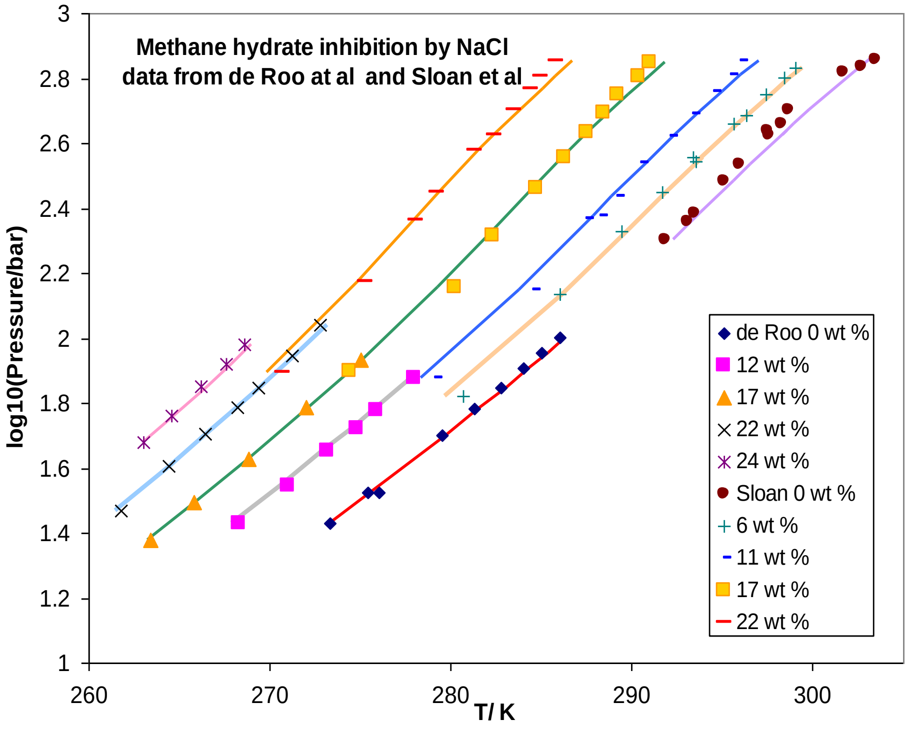
Effect of MEG on Hydrate Formation for a Condensate

This is the same condensate as in the previous example but this time MEG is used as the inhibitor. Because of its low volatility little MEG is lost to the gas phase but there is some solubility in the hydrocarbon liquid phase.



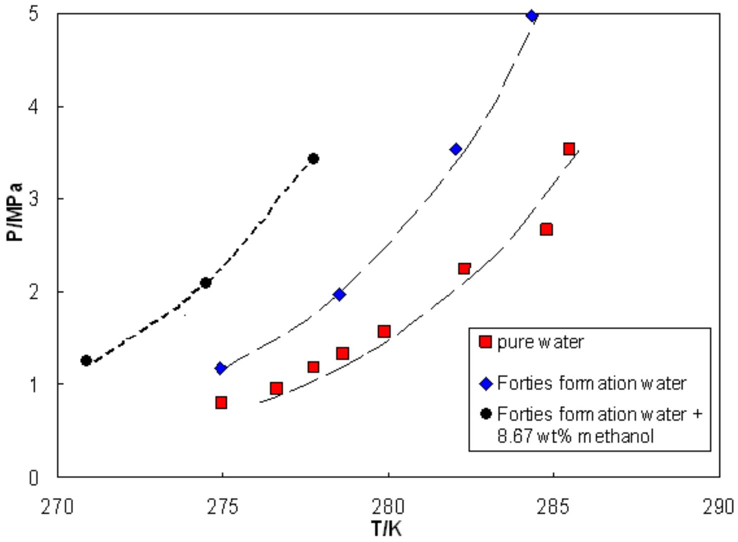
Effect of Salt on Hydrate Formation for Methane

The calculations in this figure were carried out with the electrolyte model. The data extend to near saturation conditions and up to nearly 1000 bar. They are well represented by the model in Multiflash^{TM}.



Black Oil with Salts and Methanol

In this example, we have taken data from Tohide et al. for an oil system. Both the effects of salt and methanol plus salt are handled well by the model in Multiflash^{TM}.



13. Conclusion

Gas hydrate formation analysis and management have become an essential part of engineering work for the design, commissioning and operation of offshore and onshore production and transportation.

This paper has presented the theory of gas hydrate formation and inhibition mechanisms, thermodynamic fluid models as well as the BP hydrate nucleation formation model in Multiflash^{TM}. The validation study with experimental data demonstrated the capabilities of the Multiflash^{TM} thermodynamic models in providing accurate predictions on hydrate formation and inhibition as well as the fluid phase behaviour.

Together with the accurate thermodynamic fluid model (Cubic Plus Association, CPA) for modelling the gas, hydrocarbon liquid and aqueous phases, the gas hydrate models in Multiflash^{TM}:

- Can accurately predict at what condition the gas hydrate forms, and how much it form.
- Can reliably predict what type of gas hydrates forms: Hydrate I, II or H as well as the complex phase transitions among the fluid and hydrate phases.
- Can predict not only the partitioning of the thermodynamic hydrate inhibitors among the fluid phases but also the accurate prediction on hydrate inhibition. The hydrate inhibitors that can be modelled by Multiflash^{TM} include: Methanol, ethanol, MEG, DEG and TEG.
- Can provide accurate calculation on the required inhibitor injection rates/dosages to suppress the hydrate formation for drilling and/or production.
- Has been extended to include a well-developed electrolyte model to model the effect of salts on hydrate inhibition and the salts precipitation.
- Is a fully integrated model that is readily imbedded in pipeline software, topside and a plant-wide processing facilities simulation environment.

Such a reliable and versatile flow assurance engineering tool enables reservoir, petroleum and process engineers to achieve the more detailed field planning activities such as:

- Initial assessment of potential operational problem arising from hydrate formation.
- Life of field study on inhibitor requirement and formulation of hydrate prevention strategies

If you are interested in further details on hydrate prediction and management strategies using Multiflash^{TM}, please feel free contact KBC at software@kbcat.com.