

# Kinetics of Hydrate Formation from Nucleation Theory

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## ABSTRACT

Hydrate reservoirs that are partly exposed towards the ocean floor will not be unconditionally stable even though the local temperature and pressure may be sufficient to maintain equilibrium among pure methane, water and hydrate. In this work we study the stability limits with respect to methane concentration in the seawater in contact with the hydrate. Since the average methane concentration in the oceans is very close to zero, the hydrate will not be thermodynamically stable when exposed to this seawater. The estimated driving forces for dissociation are limited, and the dissociation rate is expected to be correspondingly small. Accurate estimates for the dissociation kinetics in a system with these small driving forces require accurate values for the interfacial tensions as well as other rheological properties involved in the kinetics of dissociation, and the transport of heat and melted molecules away from the hydrate/seawater interface. Work is in progress on the estimation of these properties using molecular simulations. I have also presented a nucleation theory for the kinetics of hydrate formation and growth based on multi-component diffusive interface theory. Theoretical estimates indicate that methane hydrate initiation from the gas side of the gas/water interface may dominate when compared to initiation and growth from the liquid side of the interface.

## INTRODUCTION

One of the problems involved in the modelling of the kinetics of hydrate formation is that many pieces of the mechanisms involved in the total formation process for water and hydrate former to hydrate are still unknown. Basically we might say that the kinetic problem can be divided into 2 main stages, initial nucleation and stable growth. The nucleation stage is related to that of forming hydrate cores that are thermodynamically stable and as such will grow steadily. The actual content of these 2 stages, and in particular the nucleation stage, of the formation process in terms of mechanisms and corresponding detailed kinetic contributions remains experimentally unverified today. Hopefully, combinations of basic measurements like NMR and different spectroscopic techniques will be able to give us some fundamental insight in the future. Today we are, however, left with the option of setting up reasonable hypotheses and trying to verify these by experiments and/or molecular simulations.

In the open literature, there are basically 2 principally different approaches for modelling the nucleation part. These differ in the assumptions about where the initial nucleation takes place, in the liquid water interface or towards the hydrate's former part of the interface. Some other approaches—for instance, the approach of Christiansen and Sloan (1995)—model this stage without making any basic assumption about where the initial process actually takes place. They suggested using a thermodynamic cycle where the process of hydrate formation is modelled as a standard chemical reaction, and changes in free energies in the cycle going from liquid water and gas hydrate former are modelled according to classical thermodynamic relations. Skovborg (1993) has proposed other macroscopic models, where the ideas of Natarajan (1993)

and Yousif (1994) are based on different formulations of the driving forces. Kvamme (1996) proposed a scheme based on the assumption that the initial nucleation takes part towards the gas side of the interface. This proposal is in accordance with recent findings in NMR (Song and Kobayashi, 1996; Kobayashi, 1997). Kvamme's hypothesis (1996, 1995, 1997, 1998, 2000a) is that the initial nucleation takes place towards the gas side of the interface and depends mainly on gas transport, water surface and adsorption characteristics. Gas transport and collisions with the water surface involve random elements related to collision distribution. If we could take snapshots at different portions of the surface, we would probably find large differences in the populations of gas molecules at or close to the water surface. The water surface itself is definitely not flat on a microscopic scale, but contains waves as well as micro pores and even micro bubbles. Gas may even be trapped in this continuously changing water surface for shorter or longer periods. The presence of the gas phase will also have an impact on the dynamic surface structure of the water phase and will to a certain extent depend on the time passed after the union of gas phase and liquid phase.

Another feature of the water surface is that, even if the total average chemical potential for water is known, the chemical potential is actually a multi-particle property that certainly varies from one individual molecule to another at every instant of time. Every molecule has a characteristic energy at every instant as well as a corresponding entropy. For every instant of time this property will give a certain distribution of the chemical potential if we plot the values for all molecules in the volume. The average chemical potential for water may thus be a constant value throughout the system, but the variation in the chemical potential for water is expected to be higher at the interface. A water molecule that is ready to leave the water surface will have a high energy due to the low attraction in the direction towards the gas. The entropy, on the other hand, may be similar to other water molecules in the vicinity, since the water molecule is still stuck in a liquid-like situation, surrounded by water in 2 dimensions. These water molecules will be more easily released from the surface by gas collisions. Even after the collision, water molecules in such a state

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