#### THE UNIVERSITY OF CALGARY

## THERMODYNAMICS AND NUCLEATION KINETICS OF GAS HYDRATES

by

#### VENKATESWARAN NATARAJAN

**A DISSERTATION** 

## SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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#### ABSTRACT

Gas hydrates are industrially important compounds. The conditions and the rate of formation of gas hydrates need to be well understood to exploit gas hydrates as an energy reserve or to avoid their formation in gas pipelines. Hence the aim of the study was to study the thermodynamics and nucleation kinetics of hydrates.

In the thermodynamics portion of this study, the technique of molecular simulation was used and the guest (gas) - host (water) interactions were modelled without resorting to certain simplifying assumptions in the thermodynamic model for hydrates. The Langmuir constant is an important parameter in the thermodynamic model for hydrates and characterizes the guest - host interactions. As recent experiments have shown that argon and krypton hydrates are structure II hydrates, in this work, the argon and krypton hydrates were simulated as structure II hydrates and the Langmuir constants were obtained. These Langmuir constants obtained in the simulation were in agreement with experimentally determined constants.

The technique of molecular simulation itself, was then examined with regard to certain assumptions that were made to obtain Langmuir constants through simulation. The commonly made assumption that the fluctuations around the averaged potential obtained through simulation is uniform, in molecular simulation work of this kind (Monte Carlo) for hydrates, was found to affect Langmuir constants computed through simulation. Also the computation of free volume for obtaining Langmuir constants through simulation was found to affect the computed constants significantly.

On the kinetic side, the nucleation of gas hydrates was studied in detail, experimentally. The experiments were conducted as a part of this study to investigate the effect of water structure on hydrate induction time. The results suggest that water structuralization as carried out in this work does not affect the induction time. A model has been developed based on mass transfer and nucleation kinetics considerations to model the hydrate forming gas consumption and the induction time in the kinetic experiments. The model was found to agree with the experimental kinetic data obtained in this study as well as from previously reported data from the literature. It was shown that the proposed driving force for nucleation is similar to the driving force for hydrate growth and decomposition thereby enabling a unified approach to model all the three processes.

#### ACKNOWLEDGEMENTS

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.

To my brother and sister, Kumar and Rajalakshmi and to my wife Meenakshi

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#### NOMENCLATURE

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a	Mass transfer area per unit Volume, $m^2/m^3$
Agl	Area of gas-liquid contact, m <sup>2</sup>
A <sub>p</sub>	Surface Area of Particles, m <sup>2</sup>
b	Radius of a hydrate guest molecule, Å
С	Langmuir Constant or Concentration, 1/MPa or moles/Volume
С <sub>р</sub>	Heat Capacity at constant pressure, J/(mol K)
D	Diffusivity of gas in liquid, $m^2$ /sec
E	Energy term
f	Fugacity, Pa
f <sub>i</sub>	Fugacity of a Component i in a Mixture, Pa
G	Gibbs Free Energy, J
γ	Activity Coefficient
h	Enthalpy, J/mol
k	Boltzmann Constant in J/K
К	Constant in Induction Model, s
к* .	Combined Rate Parameter, $mol/m^2$ Pa s
К <sub>d</sub>	Hydrate decomposition constant, $mol/m^2$ Pa s
k <sub>l</sub>	Mass transfer coefficient, m/sec
L	Cluster particle size, m
L*	Critical cluster particle size, m
μ	Chemical Potential, J
m	Constant in Induction Model
n	Number of moles
N <sub>h</sub>	Number of hydrate forming gases
P	Pressure, Pa
r	Distance, m
<sup>r</sup> cr	Critical radius of the particle, m
R	Gas Constant in J/mol K

R <sub>n</sub>	Rate of Nucleation, nuclei/(Volume time)
S	Supersaturation ratio or $f_g^V/f_{eq}$
t	time, s
Т	Temperature, K
u, U	Potential Energy, J
V	Volume term or molar volume in m <sup>3</sup> /mol
X	Mole fraction
у	thickness, cm
Уl	edge of film on the bulk liquid side
Z	Configurational Integral (m <sup>3</sup> )
Z	Compressibility factor
Δ	Delta, Difference Operator

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## Subscripts

cell	Hydrate Cavity
d	decomposition
diff	differential
f	formation
g	gas species
eq	equilibrium
exp	experimental
i,j,n	index
ind	induction
ml	metastable limit
MDI	Multi dimensional Integration Method
MMC	Metropolis Monte Carlo Method
R	Reactor
ref	Reference Conditions
S	Supply reservoir

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tb	turbidity
uncond	Unconditionally Accepted Volume, Molecular Volume
w	Water
ij	Distance from i <sup>th</sup> molecule to j <sup>th</sup> molecule
ini	Initial

## Superscripts

β	Empty hydrate lattice
h	Hydrate
L	Liquid Phase
0	Pure water at reference conditions
v	Vapor Phase
*	Two Phase Gas - Liquid Equilibrium

## Greek

- α Proportionality constant in equation 5-22
- ß Constant in equation 5-23, s
- $\epsilon$  epsilon, LJ potential parameter, J
- $\Delta \mu$  chemical potential difference, J/mol
- $\sigma$  Surface energy, J/m<sup>2</sup> or LJ potential parameter Å
- $\theta$  degree of cavity occupancy
- $\nu_{j}$  Number of cavities of type j

#### **CHAPTER 1**

#### **INTRODUCTION**

#### **1.1 Background**

Natural gas hydrates are non-stoichiometric, crystalline, solid clathrate compounds. The crystalline clathrate is composed of hydrate forming gas molecules entrapped in a cage formed by surrounding hydrogen bonded water molecules. The hydrate forming gas molecules include the lighter alkanes of natural gas (methane to iso-butane) besides carbon dioxide, hydrogen sulphide, nitrogen and oxygen.

X-ray crystallographic studies of natural gas hydrates (von Stackelberg and Muller, 1954; Mak and McMullan, 1965; Jeffrey and McMullan, 1967) have revealed that there are commonly two known characteristic types of hydrate crystal structures, i.e Structure I (body centred cubic) and Structure II (diamond lattice). The two hydrate structures are shown in Figure 1.1. The smallest repeating unit of a crystal structure is called a "unit cell". The unit cell of structure I hydrate consists of 46 water molecules and includes two small and six large cavities. The maximum linear dimension of the small and large cavities are 5.2 °A and 5.9 °A, respectively. For structure II gas hydrates, the unit cell consists of sixteen small cavities and eight large cavities formed by 136 molecules of water. The large cavity of structure II has a mean diameter of 6.6 °A. The small cavity of structures I and II is a pentagonal dodecahedron. The large cavity of structure I is a tetrakaidecahedron and that of structure II is a hexakaidecahedron. The cavities are shown in Figure 1.2. The structural details of natural gas hydrates are well investigated and available in the literature (Claussen, 1951; von Stackelberg and Muller, 1954; Mak and McMullan, 1965; Jeffrey and McMullan, 1967).

## Figure 1.1 Structures of Gas Hydrates

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(from Sloan, 1990)



Structure I - Body Centered Cubic

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Structure II - Diamond Lattice

## Figure 1.2 Cavities of Gas Hydrates

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(from Sloan, 1990)

Structures I and II - Small Cavity (Pentagonal Dodecahedron)



Structure I - Large Cavity (Tetrakaidecahedron)







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#### 1.2 Gas Hydrates : Thermodynamics and Kinetics

As hydrates could form at temperatures above the normal melting point of ice, the formation of gas hydrates may generate complete or partial plugging that could damage pipelines (Hammerschmidt, 1934), valves and other processing facilities. Understanding the thermodynamics and kinetics of hydrate formation is therefore of key importance to the natural gas industry in order to avoid problems associated with hydrate formation. Knowledge of thermodynamic conditions of hydrate formation would enable the gas pipelines to be operated outside the hydrate forming conditions. The thermodynamics of hydrate formation has been investigated experimentally by several researchers (Bishnoi and Dholabhai, 1993; Dholabhai et al., 1991b; Englezos and Bishnoi, 1991; Ng and Robinson, 1976, 1983, 1984; Ng et al., 1985, 1987; Knox et al., 1961; Menten et al., 1981; Roo et al., 1983; Kubota et al., 1984; Paranjpe et al., 1987; Makogan, 1981; Reviews by Holder et al., 1988 and Sloan, 1990). The computational prediction of the hydrate forming conditions using thermodynamic models were also studied in detail (van der Waals and Platteeuw, 1959; McKoy and Sinanoglu, 1963; Parrish and Prausnitz, 1972; Ng and Robinson, 1976, 1977; Holder et al., 1980; Anderson and Prausnitz, 1986; Song and Kobayashi, 1982, 1987; John and Holder, 1985; Englezos and Bishnoi, 1988a; Bishnoi et al., 1989a).

The other area of hydrate research that is of vital importance is the kinetics of gas hydrate formation. Although not as extensive as thermodynamic studies, there has been some published data on hydrate kinetics (Barrer and Edge, 1967; Falabella, 1975; Englezos *et al.*, 1987a, 1987b, 1990; Vysniauskas and Bishnoi, 1983, 1985; Sloan and Fleyful, 1991; Bishnoi *et al.*, 1985, 1986, 1989b; Dholabhai *et al.*, 1993; Skovborg *et al.*, 1993). It has been suggested for a long time that the hydrate formation is a process of hydrate crystal nucleation and growth of the stable hydrate crystal nuclei (Englezos *et al.*, 1987a, 1987b, 1990; Englezos and Bishnoi,

1988b). Falabella (1975) studied the kinetics of hydrate formation from ice whereas several researchers (Englezos *et al.*, 1987a, 1987b; Vysniauskas and Bishnoi, 1983, 1985; Dholabhai *et al.*, 1993) have concentrated on determining kinetics of hydrate formation from aqueous solutions. The kinetics of hydrate decomposition has been studied by Kim *et al.* (1985). Based on crystallization concepts, the hydrate growth kinetics have been modelled by Englezos *et al.* (1987a, 1987b). Commonly the time taken for the formation of stable hydrate nuclei is known as the induction time or period. Induction periods have been obtained experimentally by Sloan and Fleyful (1991) for cyclopropane hydrates. Based on a total of 11 experiments, for methane, ethane and their mixture hydrates, Skovborg *et al.* (1993) have reported measured induction periods has been studied by Vysniauskas and Bishnoi (1983, 1985). A molecular mechanism to explain the induction phenomena in hydrate formation has been proposed by Sloan and Fleyful (1991) based on their experimental data and those obtained by Falabella (1975).

#### 1.3 Scope of this Study

In view of the importance of the thermodynamics and formation kinetics of gas hydrates as discussed in the previous section, this study is an effort to understand both the thermodynamic and kinetic aspects of hydrate formation. Accordingly, Chapter 2 deals with the application of a molecular simulation technique to the computation of the "Langmuir constant", which is a key parameter in the thermodynamic model used for predicting hydrate formation conditions. The molecular simulation technique as applied to Langmuir constant computations is examined in Chapter 3. Because of fluctuations in the guest - host potential in a hydrate cavity arising from hydrate cavity asymmetries, the molecular simulation technique used for Langmuir constant computations. These limitations of the molecular simulation technique are examined in this chapter. Chapter 4 is devoted to the hydrate nucleation process, wherein both the experimental and theoretical work related to hydrate nucleation are presented. The classical crystallization theory as applicable to hydrate formation processes is reviewed. Then the experimental work carried out to investigate the possible effect of water structure on methane hydrate formation is presented. The derivation of a nucleation kinetics model and discussion of model results with experimental hydrate nucleation data form the substance of chapter 5. The driving force in the proposed model for hydrate nucleation is shown to be similar to the driving forces used in the hydrate growth and decomposition kinetic models. Finally, in Chapter 6 the conclusions and recommendations are presented for future work on gas hydrates arising out of this study.

## CHAPTER 2 Molecular Simulation

#### **2.1 Introduction**

Molecular simulation provides a direct link from the microscopic details of a system to macroscopic system properties of interest. In molecular simulation one begins with a molecular model and calculates the desired macroscopic properties by statistically averaging over the molecular positions and motions using the exact relationships of statistical mechanics. The molecular model includes a detailed atomistic description of the material to be studied and an equation for the inter molecular forces acting between the molecules. The desired macroscopic properties could include the thermodynamic functions such as pressure, free energy besides other thermodynamic properties, transport properties such as viscosity, optical and surface properties. A comprehensive summary of the scope of molecular simulation applications is provided by Gubbins (Gubbins, 1989) and in a review paper by Quirke (Quirke, 1986) on the subject. A more detailed coverage of molecular simulation is provided by Allen and Tildesley (1987).

The analytical solutions of the statistical mechanics equations relating the molecular and macroscopic properties are difficult to obtain except for a few simple cases. The advent of high speed computers in the recent past has helped a lot in obtaining an exact numerical solution of these statistical mechanics equations. Two methods of molecular simulation are common, the Monte Carlo method (MC) and the molecular dynamics method (MD). In the MC method, the molecules are randomly moved and the random molecular moves are accepted or rejected according to a recipe that ensures that the various molecular arrangements are in conformity with statistical mechanics requirements. By generating a long series of such molecular arrangements and averaging over them one obtains the various equilibrium properties of the system of molecules. In the MD method, the molecules are allowed to move under the influence of their inter molecular forces. The positions and velocities of each molecule are followed in time by solving Newton's laws of motion using standard numerical methods. The macroscopic properties are then calculated by averaging the appropriate functions of molecular positions and velocities over time. Though the MC and MD methods have several features in common the MD method has the important advantage over the MC method in that it can be used to study time dependent and transport processes (Gubbins and Panagiotopoulos, 1989).

#### 2.2 Applications of Molecular Simulation to Gas Hydrates

In order to avoid plugging of gas pipelines owing to hydrate formation during the transportation of gas hydrates, and to exploit the vast natural hydrate deposits, there is a strong need to compute gas hydrate formation conditions reliably and well. A fundamental thermodynamic model based on statistical mechanics was proposed by van der Waals and Platteeuw (van der Waals and Platteeuw, 1959) for the chemical potential of water in the hydrate phase which is used to compute the conditions of hydrate formation. A key parameter in the van der Waals and Platteeuw model is the Langmuir constant. The Langmuir constant is an adsorption constant and is obtained by the Lennard Jones Devonshire cell theory (1937, 1938) by using an inter molecular potential function to describe the interactions between the guest and host molecules. The molecular simulation methods have focused on the assumptions made by van der Waals and Platteeuw in deriving the expression for Langmuir constant and on the inter molecular potential models for the guest - host interactions.

Both the MC and MD methods of molecular simulation have been applied to gas hydrate systems by several researchers (Tester *et al.*, 1972; Tse and Davidson, 1982; Tse *et al.*, 1983a,b; Rodger, 1989; Lund, 1990). The MC method was first applied to hydrate systems by Tester et al. (1972) to evaluate the Langmuir constant taking the exact crystallographic structure of gas hydrates into account. Tester et al. (1972) do not report the Langmuir constant values they calculated but instead report the values of hydrate formation pressures obtained with Langmuir constants computed using the MC method. It should be noted that van der Waals and Platteeuw had made an assumption in their derivation of the Langmuir constant expression that the hydrate cavity is approximately spherical with a spherically symmetrical field of force acting on the guest molecule. This assumption of the spherically symmetrical field in a hydrate cavity is commonly referred to as the 'smooth cell approximation' (Holder et al. 1988). Thus Tester et al. (1972) by taking the exact crystallographic structure of the hydrates in their work took the asymmetries of the hydrate cavities into account and hence did not need the smooth cell approximation. For structure I, they computed hydrate formation pressures in good agreement with experimental pressures for simple molecules like Ar, Kr and Xe using a Lennard Jones 6,12 potential and a non spherically symmetric Kihara potential for some linear molecules like  $CO_2$ ,  $N_2$  and  $O_2$  hydrates. Tse and Davidson (1982) also followed the MC method as applied by Tester et al. (1972) but they focused on examining the effect of an exponential 6-8-10 potential and LJ potential on Langmuir constant computations. Following the application of the MC method as suggested by Tester et al. (1972), Lund (1990) extended it to compute Langmuir constants incorporating guest - guest interactions directly as he considered the crystal structure of the entire unit cell for his MC simulation. The MD method was applied to hydrates by Plummer and Chen (1983). They applied the MD technique to study water microclusters and focused on the various properties of the micro-clusters like the pair distribution functions, radial distribution functions and the kinetic and potential energy of the microclusters. Since their study examines an isolated water cluster the results may not be applicable to bulk clathrate hydrates. However, their results showed that the cooperative effects of hydrogen bonding was responsible for the stability of the microcluster. The structure I methane hydrate and ice (structure

Ic) were studied using the MD method by Tse *et al.* (1983b). In a subsequent paper, Tse *et al.* (1984) reported MD simulation studies of structure I clathrate hydrates of methane, tetrafluoromethane, cyclopropane and ethylene oxide. The simulation results showed low frequency vibrations associated with the guest molecules in the hydrate cavities could be responsible for the lower thermal conductivities of the clathrate hydrates relative to ordinary ices. The thermal expansion of structure I hydrate, ethylene oxide hydrate, was studied by Tse and Klein (1987). It was predicted theoretically that the larger thermal expansivity of hydrates as compared to ice, is a result of guest - host interactions in hydrates. Finally, in a recent paper by Rodger (1989), the MD method was applied to study the cavity potential in structure I hydrates. The key result of Rodger's work shows that the presence of kinetic energy in the host lattice leads to distortion of the cavities and thereby could make them anisotrophic. Also the thermal fluctuations of the host molecules around their mean positions showed that the cavity wall may not be rigid as is assumed often in hydrate research.

In summary, molecular simulation methods have focused on the assumptions made by van der Waals and Platteeuw in their thermodynamic model of gas hydrates. Notably, the molecular simulation methods have examined the effect of cavity assymetries on the Langmuir constant computations and effect of guest-guest interactions which were all ignored in the original van der Waals and Platteeuw model. Also molecular simulation methods have attempted to obtain a more fundamental understanding of hydrates exploring the effect of hydrate lattice structure and the interactions between the guest and host molecules.

#### 2.3 Computation of Hydrate Formation Pressure - Molecular Simulation

The knowledge of hydrate formation conditions, formation pressure at a temperature, is important to avoid problems associated with hydrate formation in gas transportation as well as to exploit the vast hydrate reserves to obtain natural gas for the production of energy. Also as will be discussed later in detail, the knowledge of hydrate formation conditions is also important in hydrate nucleation studies where one is interested in the rate of hydrate formation for a given set of operating conditions.

As mentioned earlier, a very important hydrate model for computing hydrate formation conditions is the van der Waals and Platteeuw model (1959). The chemical potential of water in the hydrate phase,  $\mu_w^{h}$ , is an important quantity which is generally calculated by the van der Waals - Platteeuw model (1959) given below.

$$\mu_{w}^{h}(T,P) = \mu_{w}^{\beta} - RT \sum_{j=1}^{2} v_{j} \ln(1 + \sum_{i} C_{ij}f_{i})$$
 2-1

In the equation,  $\mu_w^{\ \beta}$  is the chemical potential of water in the empty hydrate lattice, R is the gas constant, T is the absolute temperature,  $v_i$  is the number of cavities of type j,  $C_{ij}$  is the Langmuir constant for a gas molecule i in cavity j and  $f_i$  is the fugacity of the hydrate forming gas i, in the hydrate phase. As seen from equation 2-1, the chemical potential of water in the hydrate phase is a sum of the two terms on the right hand side. The first term is the chemical potential of water in the empty hydrate lattice and is obtained through a correlation (Parrish and Prausnitz, 1972; Holder et al., 1980, 1988) for the chemical potential difference between the empty hydrate and pure water,  $\Delta \mu_{w}$ . The correlation requires the value of  $\Delta \mu_{w}$  to be known at a reference state (generally P = 0, T = 273 K). The value of  $\Delta \mu_w$  at the reference state has been estimated from experimental data and widely different estimates have been reported by various authors (Parrish and Prausnitz 1972, Holder et al. 1988) as also mentioned by Englezos et al. (1991) and Handa and Tse (1986). Such differences in the estimated reference state  $\Delta \mu_{w}$  affects the computation of formation pressures severely. The second term in equation 2-1 involves the Langmuir constant whose computation requires the use of an inter molecular potential to describe the interactions between the hydrate forming gas molecule in a cavity and the water

molecules that comprise the cavity structure around the enclosed gas molecule. To fit experimental equilibrium pressure data the potential parameters of the inter molecular potential function were also adjusted arbitrarily (Holder et al., 1988) by various researchers with the result that the computed Langmuir constants do not agree with each other. A more serious consequence of arbitrary adjustments of the inter molecular potential parameters is the fact that these parameters have lost their physical significance. Perhaps, the adjustments made on the inter molecular potential parameters were partly necessitated by the differences in the estimated data for the reference state chemical potential,  $\Delta \mu$ , and partly by the inadequacies of the inter molecular potential function in describing the interactions between the entrapped gas molecule and the surrounding water molecules in a hydrate cavity. Besides, as shown later, there are additional arbitrary parameters necessary in the correlation for  $\Delta \mu_w$  to account for differences in temperature and pressure from the reference state. Thus, we need a complete set of parameters for  $\Delta \mu_w$  and the inter molecular potential, arbitrary but consistent, in order to make a good prediction of hydrate formation pressure. The errors introduced by these empirical parameters in the model may cancel each other leading to the calculation of formation pressures in agreement with the experimental pressures. However, the prediction of formation pressures which are in good agreement with their experimental values, may not be consistent with hydrate structure. In this regard, the agreement between computed and experimental Langmuir constants could be expected to be a better indicator of the hydrate structure because the Langmuir constants are directly based on the crystal structure of the hydrate. Also the empiricism in the parameters associated with  $\Delta \mu_w$  does not affect the Langmuir constant computations.

In this work, it is shown that although we get good predictions of hydrate formation pressures, the chosen hydrate structure for computations could be inconsistent with the experimentally determined structure. Argon and krypton hydrates were chosen for study through molecular simulation. Since the structural aspects of hydrates are the basis of this study the method of molecular simulation which takes into account the exact crystal structure of gas hydrates in the calculation of Langmuir constants is used. The molecular simulation method also obviates the need for simplistic structural assumptions, making the calculation of the Langmuir constants more rigorous.

Argon and krypton were chosen because the recent work of Holder *et al.* (1988) and Davidson *et al.* (1987a, 1987b) indicates that they form structure II hydrates and not structure I hydrates as believed earlier. It is noted that the formation pressures, which are in agreement with the experimental values for argon and krypton hydrates have been computed, by Parrish and Prausnitz (1972), Holder *et al.* (1988) and by Tse *et al.* (1982) regarding them as structure I hydrates. The guest - host potential employed in the present study is the Lennard Jones 6,12 potential which is suited well for spherically symmetric argon and krypton.

The chemical potential of water in the co-existing phase with respect to the empty hydrate lattice, at the system temperature and pressure could be written as,

$$\frac{\Delta \mu \frac{\beta - L}{w}(T, P)}{RT} = \frac{\Delta \mu \frac{\beta - Lo}{w} (T, P, x_w = 1)}{RT} - \ln(\gamma_w x_w)$$
2-2

where  $\Delta \mu_w^{\beta-Lo}$  is only a function of temperature and pressure. The equation for  $\Delta \mu_w^{\beta-Lo}$  is as follows,

~

$$\frac{\Delta \mu_{w}^{\beta-Lo}}{RT} = \frac{\Delta \mu_{w}^{o}}{RT_{ref}} - \int_{T_{ref}}^{T} \frac{\Delta h_{w}}{RT^{2}} dT + \int_{P_{ref}}^{P} \frac{\Delta V_{w}}{RT} dP \qquad 2-3$$

where  $\Delta \mu_w^{o}$ ,  $\Delta h_w$  and  $\Delta V_w$  are the reference chemical potential, enthalpy and volume differences, respectively, between the empty hydrate lattice and pure ice or

liquid water phases.  $P_{ref}$  and  $T_{ref}$  are the pressure and temperature of the reference state (generally  $P_{ref} = 0$ ,  $T_{ref} = 273$  K). Combining equations 2-2 and 2-3, we get

$$\frac{\Delta \mu_{w}^{\beta-L}}{RT} = \frac{\Delta \mu_{w}^{o}}{RT_{ref}} - \int_{T_{ref}}^{T} \frac{\Delta h_{w}}{RT^{2}} dT + \int_{P_{ref}}^{P} \frac{\Delta V_{w}}{RT} dP - \ln(\gamma_{w} x_{w}) . \qquad 2-4$$

Since  $\Delta \mu_w^{\beta-L}$  is defined as the difference between the chemical potentials of the empty hydrate lattice and that of the co-existing phase at the system conditions, we can write,

$$\Delta \mu_{w}^{\beta-L} = \mu_{w}^{\beta} - \mu_{w}^{L}. \qquad 2-5$$

Since  $\mu_w^{L}$  is equal to  $\mu_w^{h}$  at equilibrium, we can combine equations 2-1, 2-4 and 2-5 to obtain the following equation used for the computation of formation pressure of a hydrate with single hydrate former,

$$\frac{\Delta \mu_w^o}{RT_{ref}} - \int_{T_{ref}}^T \frac{\Delta h_w}{RT^2} dT + \int_{P_{ref}}^P \frac{\Delta V_w}{RT} dP = \ln(\gamma_w x_w) + \sum_{j=1}^2 v_j \ln(1 + \sum_i C_{ij} f_i) . \qquad 2-6$$

The temperature dependence of  $\Delta h_w$  is given by the relation,

$$\Delta h_{w} = \Delta h_{w}^{o} + \int_{T_{ref}}^{T} [\Delta C p_{w}^{o} + \beta (T - T_{ref})] dT . \qquad 2-7$$

The volume difference,  $\Delta V_w$ , is assumed to be independent of pressure and taken to be the same as at reference conditions,  $\Delta V_w^{o}$ . The values of reference parameters( $\Delta h_w^{o}$ ,  $\Delta C p_w^{o}$ ,  $\Delta \mu_w^{o}$ ,  $\Delta V_w^{o}$ , and  $\beta$ ) at reference conditions are regressed

from experimental hydrate data and several different values are reported by various researchers as mentioned by Englezos *et al.* (1991).

As mentioned earlier, the chemical potential of water in the hydrate phase is calculated using the model of van der Waals and Platteeuw (1959) given by equation 2-1. The Langmuir constant for the i<sup>th</sup> molecule in j cavity,  $C_{ij}$ , is obtained using a potential function, U, from the following relation.

$$C_{ij} = \frac{1}{kT} \int_{V_{cell}} e^{-\frac{U}{kT}} dV$$
 2-8

In the above expression the integral is known as the configurational integral,  $V_{cell}$  is the volume of cavity available for the enclatharated guest molecule, and U is the potential energy of interaction between the guest and host molecules and k is the Boltzmann constant.

The configurational integral, given in equation 2-8 can be evaluated directly to obtain the Langmuir constant. The number of integrals to be evaluated is three for a symmetric guest and a maximum of six for an asymmetric guest. A direct evaluation of the multi dimensional integral is possible with present day high speed computers and is discussed later in the next chapter. Although a direct evaluation of the multi dimensional integral is possible, a simplifying approximation known as the "smooth cell approximation" is often used. According to this approximation, the cavities are assumed to be spherical and the water molecules are assumed to be evenly smeared over the surface of this sphere. With the smooth cell approximation the configurational integral is simplified and can be evaluated analytically as reported by van der Waals and Platteeuw (1959), Parrish and Prausnitz (1972) and Holder *et al.* (1988). Parrish and Prausnitz (1972) have also proposed an empirical correlation for calculating the Langmuir constants. The smooth cell approximation, however,

does not give the true Langmuir constant as all the cavities are to some extent asymmetric. So a true Langmuir constant could only be obtained by considering the potential energy of the gas molecule as a function of its angular as well as radial coordinates. A direct evaluation of the multi dimensional integral should hence be made preferably using a technique that shall make such an evaluation in an efficient manner. The technique of Monte Carlo molecular simulation is ideally suited (Wood, 1968; Mueller, 1971) for handling configurational integrals of many dimensions and has been used in the work presented in this chapter.

The molecular simulation method used in this work follows the Monte Carlo method first applied to hydrate systems by Tester *et al.* (1972) and later by Tse and Davidson (1982). The potential energy at any point in the cavity is calculated assuming that the discrete binary interactions between the guest and the host molecules are pairwise additive as follows,

$$U = \sum_{i} \sum_{j} u_{ij}(r_{ij})$$
 2-9

In equation 2-9, i is the summation index for the guest molecule (i=1), j is the summation index for the surrounding water molecules in the cavity, and  $u_{ij}(r_{ij})$  is the interaction potential energy between a guest molecule i and a host molecule j separated by a distance  $r_{ij}$  as obtained using LJ Potential. Simulation takes into account the actual crystallographic structure of the cavity and hence its asymmetries. By proper sampling of the various configurations available, to the guest molecule, an ensemble average of the potential energy is obtained (Metropolis *et al.*, 1953). For a cavity j and a guest molecule i, we can write the following expressions for evaluating the Langmuir constant through Monte Carlo integration
17

$$C_{ij} = \frac{Z_{cell}}{kT}$$
 2-10

Referring back to equation 2-8, we see that

$$Z_{cell} = \int_{V_{cell}} e^{-\frac{U}{kT}} dV$$
 2-11

The term under the integral in the above relation is approximated as the product of an averaged energy term,  $\exp^{-U/kT}$ , and an approximated volume term,  $V_{cell}$ . Letting the quantities enclosed by < > indicate their averaged values,  $Z_{cell}$  is written as,

$$Z_{cell} = \langle e^{-\frac{U}{kT}} \rangle V_{cell}$$
 2-12

The term  $\langle e^{-U/kT} \rangle$  in equation 2-12 is further approximated as  $\exp^{-\langle U \rangle/kT}$ . If the fluctuations about  $\langle U \rangle$  are uniform then equation 2-12 is a good approximation (Tester *et al.*, 1972). This approximation was made by Tester *et al.* (1972) to compute the configurational integral by the Metropolis Monte Carlo method and would be unnecessary if one attempts to evaluate the configurational integral directly using a Monte Carlo or Numerical Integration method. The use of this approximation is not expected to affect the results of the computations significantly as we are studying argon and krypton hydrates using a spherically symmetric LJ potential. The effect of this approximation is further investigated in the next chapter.

The average potential energy  $\langle U \rangle$  is calculated by the Monte Carlo averaging method and the volume term  $V_{cell}$  is computed as reported by Tester *et al.* (1972). The equation for calculating  $\langle U \rangle$  by the Monte Carlo method is given below.

$$\langle U \rangle = \frac{\sum_{n} U_{n}}{N}$$
 2-13

where N is the number of random moves made with the guest molecule and is typically a large number (5 million).  $U_n$  is the guest-host interaction energy calculated using equation 2-9 at move number n.

### **2.4 Computational Procedure**

The computation of a hydrate formation pressure at a given temperature requires solving equation 2-6 iteratively to compute the hydrate formation pressure, P. The fugacity of the hydrate forming gas in equation 2-6 can be calculated using an equation of state and in this work the Trebble - Bishnoi equation of state (Trebble and Bishnoi 1987, 1988) was used. The values of parameters at the reference conditions are taken from Holder *et al.* (1988) and used in equation 2-6. The Langmuir constants required in equation 2-6 were obtained from molecular simulation, as described below.

In molecular simulation as suggested by Tester *et al.* (1972), the guest molecule is moved randomly with uniform step size to new locations in the hydrate cavity. At each new location its total potential energy is calculated using equation 2-9 and the move is accepted or rejected on the basis of a criteria given by Metropolis *et al.* (1953) so that the energy probability distribution,  $\exp(-U/kT)$ , is sampled properly. From the mathematical theory of random processes (Metropolis *et al.* 1953) it has been shown that the acceptance or rejection of moves based on the Metropolis *et al.* (1953) criteria, would indeed select U's with a frequency proportional to  $\exp(-U/kT)$  as the number of moves becomes large. Hence the ensemble average

 $\langle U \rangle$  could be obtained using equation 2-13, where the U 's are selected according to the Metropolis et al. (1953) criteria. In Fig. 2.1, the movements of argon guest during the course of molecular simulation are shown for a small cavity. This figure could be generated if it is imagined that a pen is attached to the center of the argon guest molecule in a small cavity thus tracing a line as it moves. Approximately 10000 such moves were plotted to obtain Figure 2.1. In an interesting way, Figure 2.1 indeed shows that the free volume (zone in which argon can move freely under inter molecular forces) is approximately spherical and since these movements are controlled by inter molecular forces, it also suggests that the potential field around the argon guest could well be approximated by a spherical field as is done in a 'smooth cell approximation'. The free volume available for the guest molecule to move within the hydrate cavity,  $V_{cell}$ , is obtained as per the procedure suggested by Tester et al. (1972). Knowing  $V_{cell}$  and  $\langle U \rangle$  the Langmuir constant is computed for the guest in a cavity. For molecular simulation, the guest LJ potential parameters were taken from those obtained by matching second Virial coefficient data (Hirschfelder, Curtiss and Bird 1966) and the host parameters ( $\sigma_{water} = 2.5$  °A,  $\epsilon_{water}/k = 205.84$  K) were obtained as per the procedure suggested by van der Waals and Platteeuw (1959). The mixture potential parameters were obtained in terms of the individual guest and host parameters using the following mixing rules,

$$\sigma_{mix} = \frac{\sigma_{guest} + \sigma_{host}}{2}$$
 2-14

and,

$$\epsilon_{mix} = \sqrt{\epsilon_{guest} \epsilon_{host}}$$
. 2-15

Molecular simulation uses the guest - host potential in a discrete manner. Hence the crystallography of the hydrates is important. Detailed crystallographic information about the hydrate structures have been published (von Stackelberg and

Figure 2.1 Simulated Movements of Argon Guest Molecule in Small Hydrate Cavity



Muller 1954; Claussen 1951; Pauling and Marsh 1952; Jeffrey 1962; Mak and McMullan 1965) and there is a review paper by Jeffrey and McMullan (1967) on the subject. The coordinates of the oxygen atoms for each cavity is required for the simulation. For structure I hydrates, this information is available as reported by Tester *et al.* (1972). For structure II hydrates, in this work the oxygen atom coordinates have been calculated for both the cavities from the crystallographic data presented by Mak and McMullan (1965) using a commercially available software (XTAL version 2.6). The calculated coordinates are reported in Appendices I.

The molecular simulation was performed on an IBM RISC 6000, model 320 computer. All the computations were performed in double precision.

### 2.5 Simulation Results and Discussion

The computed formation pressures of argon and krypton hydrates at 273.16 K are reported in Table 2.1 where the Langmuir constants used in the computations were obtained using the Monte Carlo molecular simulation. The computed formation pressures obtained in this work are compared with those reported by Tse and Davidson (1982). As seen in Table 2.1 the computed formation pressures are in good agreement with the experimental formation pressures. It is to be noted that the computations in this work assume that argon and krypton are structure II hydrates whereas Tse and Davidson (1982) in their computations assume the hydrates to be of structure I type. The reason for this agreement between computed and experimental formation pressures regardless of the assumed hydrate structures could be the variations in the values of the several empirical parameters involved in the formation computations. Also since the small cavities of both the structures are structurally similar and equilibrium is to be maintained between the small and large cavities, the dissociation pressures could also expected to be similar. So it was decided to compare the computed Langmuir constants from molecular simulation with those experimentally determined (Barrer and Edge, 1967). The comparison

### Table 2.1 Computed Hydrate Equilibrium Pressures, MPa

Assumed Structure	Guest	P <sub>caic.</sub>		P <sub>expt.</sub> van der Waals
in Computations		This Work	Tse and Davidson (1982)	and Platteuw (1958)
Ι	Argon		9.227	9.676
II	Argon	9.200		9.676
I	Krypton		1.430	1.469
II	Krypton	1.323		1.469

T = 273.16 °K, LJ 6,12 Potential

of experimental and computed Langmuir constants instead of the formation pressures has several advantages. Firstly, the computation of the Langmuir constants is a stringent test of molecular simulation because it does not involve the choice of reference chemical potential parameters (Tse and Davidson, 1982). Secondly, Langmuir constants are directly based on the hydrate structural data and therefore could be sensitive to the hydrate structure. The only problem with the Langmuir constants is that very few experimental measurements are reported. For argon and krypton, however, Barrer and Edge (1967) have estimated experimentally the Langmuir constants, at 263 K. They determined volumetrically at constant temperature the amount of inert gas consumed for hydrate formation in a mixture of pre-formed chloroform hydrate and ice. Since chloroform forms structure II hydrates and stabilizes the large cavities of the hydrate, Barrer and Edge (1967) argued that the consumption of inert gas in their experiments represents the amount of inert gas molecules occupying the smaller cavities in the hydrate. By studying the sorption isotherms at various pressures and temperatures they estimated the Langmuir constants for the inert gas species in the small hydrate cavity. In Table 2.2, the computed Langmuir constants for the small cavity, assuming structure II for the hydrates are compared with the experimentally estimated constants. Other researchers have computed Langmuir constants for the hydrates assuming structure I, and these values are also reported in Table 2.2.

As seen in Table 2.2, the Langmuir constants computed by Parrish and Prausnitz (1972) significantly differ (by 300 %) from the experimental values since they used the smooth cell approximation in their computations and assumed the hydrates as structure I hydrates. Although the Langmuir constants computed by Tse and Davidson (1982) show relatively better agreement with the experimental values compared to those obtained with the smooth cell approximation, the computed values are still far from the experimental values. It is noted that the Langmuir constant computations by Tse and Davidson (1982) also regarded the hydrates as structure I hydrates. The Langmuir constants obtained in this work assuming structure II, are in good agreement with the experimental constants. The better agreement of the computed structure II Langmuir constants could be expected since it has been verified experimentally that argon and krypton do indeed form structure II hydrates.

### **2.6 Conclusions**

The structure II molecular simulation of argon and krypton hydrates yields Langmuir constants that are in better agreement with the experimentally measured Langmuir constants, compared to structure I molecular simulation of the hydrates. Thus, the results of molecular simulation are in agreement with the recent experimental findings that argon and krypton do indeed form structure II hydrates. However, the computed formation pressures of the hydrates, where the Langmuir constants were obtained through molecular simulation, were found to be independent of the hydrate structure chosen for the simulation. The Langmuir constants are sensitive to the hydrate structure and could therefore be used to predict the structure of a given hydrate. Such a prediction method is possible only when more experimental data on Langmuir constants become available.

Method	Assumed Structure	Argon	Krypton	Source
Smooth Cell	Ĭ	4.57	30.8	Parrish & Prausnitz (1972)
MC (exp 6,8,10)	Ι	2.16	18.4	Tse and Davidson (1982)
MC (LJ 6,12)	Ι	3.93	27.4	Tse and Davidson (1982)
MC (LJ 6,12)	II	1.51	12.6	This Work
Experiment (Structure II)	-	1.50	10.9	Barrer and Edge (1967)

Table 2.2 Computed Langmuir Constants, (1./MPa)T = 263 °K, Small Hydrate Cavity, LJ 6,12 Potential

MC - Monte Carlo Molecular Simulation

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### **CHAPTER 3**

### Molecular Simulation and Multi-Dimensional Integration

### **3.1 Introduction**

The application of molecular simulation methods as discussed in the previous chapter have enabled us to examine critically some of the simplifying assumptions made by van der Waals and Platteeuw (1959) in their thermodynamic model for hydrates. The Langmuir constant is an important quantity computed in the van der Waals and Platteeuw model, and is dependent on the partition function of the solute molecule in a particular cavity. With the help of some simplifying assumptions, van der Waals and Platteeuw (1959) applied the cell theory, developed by Lennard-Jones and Devonshire (Lennard-Jones and Devonshire, 1937, 1938) for the study of liquids, to evaluate the partition function and hence the Langmuir constant. In particular, one of the simplifying assumptions made by van der Waals and Platteeuw in their hydrate model relates to the nature of interactions between the guest and host molecules. They assumed that the hydrate cavities are nearly spherical and since relatively large number of host atoms comprise the host lattice the guest - host interactions have a field of spherical symmetry. This resulted in an approximation known as the 'Smooth Cell Approximation' which was widely used by several hydrate researchers (Parrish and Prausnitz, 1972; Holder et al., 1988). Although this approximation permitted analytical evaluation of the Langmuir constant, it did not consider the asymmetries in the hydrate cavities. Hence the Langmuir constants computed using this approximation were not very accurate (Holder et al., 1988). As the Langmuir constants are inversely related to the hydrate formation pressure in the van der Waals and Platteeuw model, errors in computed Langmuir constants could lead to variations in computed hydrate formation pressures.

An important method of molecular simulation, the Metropolis Monte Carlo method (MMC method), was first applied to hydrates by Tester *et al.* (1972) and later by Tse and Davidson (1982). The MMC method as suggested by Tester *et al.* (1972) was recently applied by Lund (1990) to hydrates albeit Lund extended it to take into account the guest - guest interactions in hydrates. Hereafter the MMC method as applied to hydrates by Tester *et al.* (1972) is referred to as simply the MMC method. As the exact crystallographic structure obtained from X-ray studies of hydrate crystal structures were utilised in an MMC method for calculating the Langmuir constant, the asymmetries of hydrate cavity were automatically incorporated in computations. Consequently for the MMC method based Langmuir constants computation there was no need for the simplifying assumption about a spherically symmetrical field, arising as a result of guest - host interactions.

In order to use the MMC method for evaluating the configurational integral, Tester *et al.* (1972) wrote the Langmuir constant as a product of an energy and a volume term. As the MMC method is suited for evaluating average properties rather than a configurational integral, Tester *et al.* (1972) made an approximation that the fluctuations of the cell potential about its averaged value, are uniform. With this approximation, the energy term could be calculated by the MMC method. The volume term is calculated approximately by dividing the cavity space into several small spherical sub-volumes of increasing radii and summing up the contribution of the individual sub-volumes. These volume contributions are weighted in calculations using the MMC method by the ratio of the number of times the guest molecule could move successfully into that sub-volume.

Owing to the fact that the hydrate cavities are asymmetric (Holder *et al.*, 1988) the fluctuations in cell potential about the averaged cell potential could not be expected to be uniform and therefore the approximation made to simplify the

energy term could contribute to erroneous computed Langmuir constant values by the MMC method. If the cavity asymmetries could affect the computed Langmuir constants by the MMC method, then, for structure I hydrates, the Langmuir constants computed for the larger hydrate cavity should be more in error since the large cavity is more asymmetric than the small hydrate cavity.

In this work, the potential field that would be faced by a guest gas molecule is examined. The nature of such a field would suggest the asymmetry effects of the hydrate cavity and hence possible potential fluctuation effects. The effect of the key approximation of the energy term on the Langmuir constants computed by MMC method, is then examined for its possible affect on the computed Langmuir constants.

### **3.2** Computational Procedure and Results

Since the effect of the fluctuations in the potential field faced by a hydrate guest molecule is the focus of this study, only the few equations that are solved to obtain the Langmuir constant by the MMC method are presented. It should be noted that in these computations, argon, krypton, oxygen and nitrogen are considered as structure I hydrates while there is theoretical and experimental evidence, (Holder and Manganiello 1982; Davidson *et al.*, 1984), to suggest that they are in fact, structure II hydrates. Since in this work only the numerical aspects of the methods for evaluating Langmuir constants are considered treating these hydrates as structure I hydrates does not alter the conclusions derived from this work. Also regarding these hydrates as structure I hydrates facilitates comparison of this work with computations reported in the literature (Tester *et al.*, 1972). Also, for these computations in a hydrate cavity, with the parameters of the potential model taken from Tester *et al.* (1972).

It is of interest to examine the effect of cavity asymmetries by studying the potential field encountered by a guest gas molecule in a hydrate cavity. The total potential energy of interaction between the guest and the host, assuming pairwise additivity, is computed as the summation of the potential interaction energy between the guest and each one of the surrounding host water molecules in a hydrate cavity (equation 2-9). The interaction between the guest gas molecule and a water molecule is modelled using the LJ potential.

Depending on the location of the guest molecule in the cavity, it faces an attractive or repulsive field as given by the sign of the total potential energy of interaction between the guest and the host molecules. This total potential interaction energy was obtained for each chosen location using equation 2-9. For example, a guest molecule near the wall of the cavity would face a strongly repulsive field and at the centre of the cavity the field is attractive. Of interest here, is the point from the centre of the cavity where the field changes from attractive to repulsive and viceversa. If there were no cavity asymmetries, the transition from one field to another would be smooth and at a location which is a function of only the absolute distance from the centre of the cavity. However, because of cavity asymmetries, there are locations in the cavity where the field could be attractive or repulsive depending on the direction of the radius vector joining the guest molecule's position from the centre of the cavity.

In Figures 3.1 and 3.2, there are two plots shown for several guest molecules in which the radial distance from the centre of the cavity is plotted against the LJ potential parameter,  $\sigma$ , for each guest molecule. The fields that are encountered by the various guest molecules are marked as attractive, repulsive or both attractive and repulsive. It should be noted, that on regions which are marked attractive or repulsive, the field is always attractive or repulsive irrespective of the



Fig. 3.1 Potential Field in a Structure I, Small Cavity

LJ Potential Parameter,  $\sigma$ 



Fig. 3.2 Potential Field in a Structure I, Large Cavity

direction of the guest molecule position from the cavity centre. In the region marked attractive **and** repulsive, a guest molecule could face an attractive or repulsive field depending on the direction of radius vector to its location from the cavity centre. The width of the attractive and repulsive field, which is the transition region from one type of field to the other, is a direct consequence of the asymmetries in the hydrate cavity. As the structure I large cavity is most asymmetric (Holder *et al.* 1988), it is readily seen from Figures 3.1 and 3.2 that the width of field transition is more for the large cavity than for the small cavity. Also Figures 3.1 and 3.2 suggest that the width of transition from one field to the other is not the same for all guest molecules. The width decreases with an increase in the molecular diameter  $\sigma$ , used in the LJ potential model. Hence Figures 3.1 and 3.2 do suggest that the potential minima for a small molecule (with small molecular diameter,  $\sigma$ ) is likely to lie closer to the center.

### Computed Langmuir constants - Effect of Cavity Asymmetries

In view of the nature of potential field faced by a guest hydrate molecule as elucidated above, it is important to see the effect of cavity asymmetries on Langmuir constant computations. The Langmuir constant, for a gas molecule in a hydrate cavity or cell, as derived in the van der Waals clathrate model (van der Waals and Platteeuw, 1959) is given as follows.

$$C = \frac{1}{kT} \int_{V_{cell}} e^{-\frac{U}{kT}} dV$$
 3-1

where  $V_{cell}$  is the volume of the hydrate cavity available for the enclathrated gas molecule, U is the potential energy of interaction between the

enclathrated gas molecule and the surrounding water molecules. The integral in equation 3-1 is a multi-dimensional configurational integral. For a symmetric guest molecule the number of integrals to be evaluated is 3 and for an asymmetric guest molecule with three degrees of freedom the number of integrals to be evaluated is six. Tester *et al.* (1972) first applied the MMC method to evaluate the multi dimensional configurational integral. Approximating equation 3-1 as a product of averaged energy and volume terms, the equation may be written as,

$$C = \frac{Z_{cell}}{kT}$$
 3-2

where,

$$Z_{cell} = \langle e^{-\frac{U}{kT}} \rangle V_{cell}$$
 3-3

 $Z_{cell}$  is the approximated integral term in equation 3-1,  $V_{cell}$  is the volume of space available for the enclathrated guest molecule in a cavity and the quantities enclosed by < > indicate their averaged values. To solve for the averaged energy term, Tester *et al.* (1972) made the following key approximation,

$$e^{\frac{\langle U \rangle}{kT}} \simeq \langle e^{-\frac{U}{kT}} \rangle \qquad 3-4$$

The  $\langle U \rangle$  was then evaluated using the Metropolis, Monte Carlo method. The approximation made via equation 3-4 holds well if the fluctuations about the averaged energy is uniform. Applying MMC method, as suggested by Tester *et al.* (1972), for some gas hydrates using the LJ potential we have computed the Langmuir constants for small and large hydrate cavities. These constants are

# TABLE 3.1 COMPUTED LANGMUIR CONSTANTS (1/ATM)LJ POTENTIAL, STRUCTURE I, SMALL CAVITY

Temperature = 273 °K

LJ Potential Parameters (from Tester et al., 1972)

Guest	MDI (IMSL)	MDI (Simpson)	MMC (Tester)	MMC (This Work)
Argon	0.23996	0.24002	0.23248	0.23761
Krypton	2.20070	2.19930	2.10052	2.37921
Xenon	39.05800	39.0210	36.93080	133.2260
Carbon dioxide	17.72600	17.6750	31.79290	373.9070
Nitrogen	0.21602	0.21592	0.76466	0.21270
Oxygen	0.18456	0.18459	0.45873	0.18143

# TABLE 3.2 COMPUTED LANGMUIR CONSTANTS (1/ATM)LJ POTENTIAL, STRUCTURE I, LARGE CAVITY

Temperature = 273 °K

LJ Potential Parameters (from Tester et al., 1972)

Guest	MDI (IMSL)	MDI (Simpson)	MMC (Tester)	MMC (This Work)
Argon	0.1962	0.1957	0.2507	0.2587
Krypton	1.3181	1.3171	1.7377	1.7801
Xenon	21.0210	21.0390	26.5240	31.5960
Carbon dioxide	87.2870	87.3380	8.8824	364.7900
Nitrogen	0.1954	0.1952	0.4675	0.2585
Oxygen	0.1586	0.1582	0.3795	0.2093

reported in Tables 3.1 and 3.2, for small and large cavities respectively. Although Tester *et al.* (1972) do not report the values of Langmuir constants in their results directly, one can obtain their computed Langmuir constants from their reported values of equilibrium fugacities and fractional occupancies at a particular temperature. For the small or large cavity at equilibrium, the fugacity of the guest, f, is related to its fractional occupancy,  $\theta$  and the Langmuir constant C, by the following relation,

$$C = \frac{\theta}{f(1-\theta)}$$
 3-5

Thus knowing the reported values of f and  $\theta$  in their (Tester *et al.*, 1972) work one can obtain the Langmuir constants from equation 3-5.

In Tables 3.1 and 3.2, the Langmuir constants computed using the MMC method suggested by Tester *et al.* (1972) have been listed along with those constants obtained in this work using the same MMC method. Also for comparison, the Langmuir constants that one would obtain by the direct evaluation of equation 3-1 using a multi dimensional integration (MDI) technique are shown. An iterated integral approach using Simpson's rule for MDI as well as a standard IMSL routine (QAND) was used for numerical integration of equation 3-1. The Langmuir constants were obtained through direct MDI calculations with a tolerance of less than 0.1 %. It is seen that the computed Langmuir constants for argon and krypton is higher for small cavity than for the large cavity of structure I. Hence argon and krypton have a greater stabilizing effect for the small cavity. Since the small cavities over the large cavities, the results for argon and krypton in Tables 3.1 and 3.2 suggest that argon and krypton could preferentially form structure II hydrates as mentioned earlier.

By inspection of results reported in Tables 3.1 and 3.2, it is seen that the two sets of Langmuir constants computed by the direct numerical integration (MDI) agree with each other very well (the difference is less than 0.5 %). In contrast, the constants computed through the MMC method either in this work or by Tester et al. (1972) do not agree so well with those calculated through direct numerical integration (MDI method). Specifically, for  $N_2$  in the small cavity the Langmuir constant computed by Tester et al. (1972) differs from that obtained through MDI by 253 %. Regarding the Langmuir constants computed in this work using the MMC method, there is a difference of 2000 % as compared to those obtained by MDI method for carbon dioxide in the small cavity. Similarly, for xenon in the small cavity there is a difference of 341 % between the Langmuir constant values obtained using the MMC method in this work and the MDI method. This large difference in the case of carbon dioxide and xenon between the Langmuir constants computed by MDI and MMC methods is probably because the LJ potential model may not work for the polarizable xenon and for the rod-like quadrupolar carbon dioxide. Thus the energy function is inadequate to model these two molecules and this inadequacy might manifest itself differently in the volumes  $V_{MDI}$  and  $V_{MMC}$  sampled. Also the differences between computed Langmuir constants by MMC method in this work and MDI method could be due to restricted movement of the guest in the cavity, and is discussed later in this chapter. The restricted movement of the guest is suggested by the differences for xenon and carbon dioxide between the Langmuir constants computed by MMC method in this work and MDI method is more for the small cavity (2000 % for CO<sub>2</sub> and 341 % for Xe) than for the large cavity (418 % for CO<sub>2</sub> and 150 % for Xe).

The results reported in Tables 3.1 and 3.2 also show that the computed results of Langmuir constants by the MMC method in this work does not agree with that of Tester *et al.* (1972) results using the same method. As details of  $\langle U \rangle$  and  $V_{cell}$  are not reported by Tester *et al.* (1972) we are unable to compare and verify their results with those computed in this work. However, it is shown further (Tables 3.3 and 3.4)

that the  $\langle U \rangle$  computations by the MMC and the MDI methods are the same in this work and that the MMC method as suggested by Tester *et al.* (1972) could lead to incorrect Langmuir constants being computed as was shown for the case of carbon dioxide in the small cavity.

The fluctuations around the averaged potential arising as a result of cavity asymmetries probably affects the computed energy and volume terms in equation 3-3, using approximation 3-4. If  $C_{MDI}$  denotes the Langmuir constant computed by the MDI method and  $C_{MMC}$  denotes the Langmuir constant computed by MMC method, then

$$C_{MDI} = \frac{1}{kT} E_{MDI} V_{MDI}$$
 3-6

and

$$C_{MMC} = \frac{1}{kT} E_{MMC} V_{MMC}$$
 3-7

where,

$$E_{MDI} = < \exp^{-\frac{U}{kT}} > 3-8$$

and

$$E_{MMC} = \exp^{-\frac{\langle U \rangle}{kT}}$$
 3-9

It is seen that if the approximation represented by equation 3-4 holds,  $E_{MMC}$  and  $E_{MDI}$  should be equal. In order to obtain  $E_{MMC}$  we used the MMC method suggested by Tester *et al.* (1972) to calculate  $\langle U \rangle$  from which  $E_{MMC}$  was obtained using equation 3-9. The MMC calculations were performed for over 5 million moves with the first million moves dropped in the averaging process. The step size of the guest molecule in the MMC computations was set to one tenth of cavity radius as suggested by Tester *et al.* (1972). The computation of  $\langle U \rangle$  could also be performed by the MDI method as defined by the following equation.

$$\langle U \rangle = \frac{\int\limits_{V_{cell}} U e^{-\frac{U}{kT}} dV}{\int\limits_{V_{cell}} e^{-\frac{U}{kT}} dV}$$
3-10

In Tables 3.3 and 3.4, the computed values of  $\langle U \rangle$  by both the MMC and the MDI methods are shown. It is seen that for all the guests in both the cavities the agreement in the computed values of  $\langle U \rangle$  by both the methods is very good. The good agreement in Tables 3.3 and 3.4 between computed  $\langle U \rangle$  values by both methods supports the usefulness of the MMC method in doing computations of average properties. It is possible to compute  $E_{MDI}$  independently, using the following equation

$$< e^{-\frac{U}{kT}} > = \frac{\int\limits_{V_{cell}} e^{-\frac{2U}{kT}} dV}{\int\limits_{V_{cell}} e^{-\frac{U}{kT}} dV}$$
3-11

In Tables 3.5 and 3.6, the ratios  $E_{MDI}/E_{MMC}$ ,  $C_{MDI}/C_{MMC}$  and  $V_{MDI}/V_{MMC}$  are shown. The reported values of  $V_{MDI}/V_{MMC}$  in Tables 3.5 and 3.6 were computed using equations 3-6 and 3-7. The difference in computed Langmuir constants by both methods,  $C_{MDI}$  and  $C_{MMC}$ , could arise owing to three possibilities. Firstly, approximation 3-4 may not hold as a result of non uniform fluctuations around the averaged potential energy computed by MMC method. Secondly  $V_{MDI}$  and  $V_{MMC}$  could be different when approximation 3-4 holds.

# TABLE 3.3<U> BY INTEGRATION AND SIMULATIONSTRUCTURE I, SMALL CAVITY, LJ POTENTIAL

.

Temperature = 273 °K

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LJ Potential Parameters (from Tester et al., 1972)

	<u> x 10<sup>19</sup>, J</u>		
Guest	MDI	MMC	
Argon	-0.2803043	-0.2803053	
Krypton	-0.3820076	-0.3818968	
Xenon	-0.5270555	-0.5270209	
Carbon dioxide	-0.5493989	-0.5489897	
Nitrogen	-0.2953383	-0.2952821	
Oxygen	-0.2732683	-0.2733068	

### TABLE 3.4<U> BY INTEGRATION AND SIMULATIONSTRUCTURE I, LARGE CAVITY, LJ POTENTIAL

Temperature = 273 °K

LJ Potential Parameters (from Tester et al., 1972)

	<u> x 10<sup>19</sup>, J</u>		
Guest	MDI	ММС	
Argon	-0.2362629	-0.2362453	
Krypton	-0.3205913	-0.3205452	
Xenon	-0.4505324	-0.4503972	
Carbon dioxide	-0.5479374	-0.5479272	
Nitrogen	-0.2494333	-0.2494277	
Oxygen	-0.2302147	-0.2301782	

## TABLE 3.5 COMPARISON OF MDI AND MMC RESULTSSTRUCTURE I HYDRATES, SMALL CAVITY

 $T = 273 \,{}^{\circ}K$ 

Guest	E <sub>MMC</sub>	E <sub>MDI</sub> /E <sub>MMC</sub>	C <sub>MDI</sub> /C <sub>MMC</sub>	$V_{\rm MDI}/V_{\rm MMC}$
Ar	1977.7	1.1646	1.0102	0.8674
Kr	30659.7	1.2151	0.9244	0.7608
Xe	1.58e06	1.3414	· 0.2929	0.2184
CO <sub>2</sub>	3.39e06	1.5847	0.0473	0.0299
N <sub>2</sub>	3120.9	1.2332	1.0151	0.8231
O <sub>2</sub>	1659.2	1.1776	1.0171	0.8637

## TABLE 3.6 COMPARISON OF MDI AND MMC RESULTSSTRUCTURE I HYDRATES, LARGE CAVITY

T = 273 °K

••

Guest	E <sub>MMC</sub>	E <sub>MDI</sub> /E <sub>MMC</sub>	$C_{MDI}/C_{MMC}$	$V_{\rm MDI}/V_{\rm MMC}$
Ar	597.4	1.1317	0.7564	0.6684
Kr	4945.7	1.1424	0.7399	0.6477
Xe	1.55e5	1.1820	0.6659	0.5634
CO <sub>2</sub>	20.60e5	1.3385	0.2397	0.1791
N <sub>2</sub>	748.6	1.1431	0.7553	0.6608
O <sub>2</sub>	449.6	1.1311	0.7553	0.6678

.

Finally both,  $E_{MDI}$  and  $E_{MMC}$ , and  $V_{MDI}$  and  $V_{MMC}$ , could be different. From Tables 3.5 and 3.6, the values of the ratio  $E_{MDI}/E_{MMC}$  show that the approximation 3-4 does not hold. It is possible to modify the Tester *et al.* (1972) method so that  $E_{MDI}$  could be computed directly. For example the averaging summation should be carried out as suggested in the following form,

$$\langle \exp^{-\frac{U}{kT}} \rangle = \frac{\sum_{i} \exp^{-\frac{U-\langle U \rangle}{kT}} \exp^{-\frac{\langle U \rangle}{kT}}}{n},$$
 3-12

where n is any move number, U is the total energy (equation 2-9) computed at move number n, and  $\langle U \rangle$  is the averaged energy computed through Tester *et al.* (1972) method at move number n. Thus there would be no need to make the approximation through equation 3-4. Also the difference in Langmuir constants computed by both the methods is shown to be because of the difference in the computed energy and volume terms by both the methods.

As in Tables 3.1 and 3.2, the Langmuir constants computed by us using the MMC method do not agree with those computed by Tester *et al.* (1972). The MMC method as suggested by Tester *et al.* (1972) is for computing  $\langle U \rangle$ , the Monte Carlo averaged potential energy. It is shown in Tables 3.3 and 3.4 that the values of  $\langle U \rangle$  computed in this work are in good agreement with the MDI method. As such the calculations of  $\langle U \rangle$  using MMC method are not in error. The free volume available for the guest,  $V_{MMC}$ , is influenced by the spatial arrangement of the host molecules and is very sensitive to the cavity asymmetry (Lund, A. 1990). The  $V_{MMC}$ results could not be compared with the results of Tester *et al.* (1972), since they do not report  $\langle U \rangle$  or  $V_{MMC}$  in their computations.

Finally, it is of interest to note that the deviations between the

computed values of Langmuir constants by MMC and MDI methods is significantly high in the case of Xenon and Carbon dioxide. This is especially so in the case of small cavity than for large cavity despite the fact that the large cavity is more asymmetric than the small cavity. For Xenon and Carbon dioxide, unlike Tester et al. (1972), the computed Langmuir constants by us through the MMC method is always higher than the constants computed using MDI method. One possible reason for these large differences in the case of carbon dioxide and xenon between the Langmuir constants computed by MDI and MMC methods is because the LJ potential model may not apply for the polarizable xenon and for the rod-like quadrupolar carbon dioxide. Consequently the energy function is inadequate to model these two molecules and this inadequacy might manifest itself differently in the volumes  $V_{\text{MDI}}$  and  $V_{\text{MMC}}$  sampled. Another reason could be because of restricted translation of the guest molecule owing to the size of the guest molecules which could affect the guest free volume computations and hence the methodology suggested by Tester et al. (1972) is probably unsuited for restricted translation arising from large sized guest molecules. The computation of guest free volume, V<sub>MMC</sub>, is obtained as a sum of two volumes (Tester et al. 1972) as written below.

$$V_{MMC} = V_{Uncond} + V_{diff}$$
 3-13

The unconditionally accepted volume,  $V_{uncond}$ , is which is based on the actual physical size of the guest molecule. The volume,  $V_{diff}$ , is the sum of differential volumes added to obtain  $V_{MMC}$  and is obtained during the Monte Carlo averaging process by dividing the cavity into several concentric spherical shells and adding the contribution of a spherical shell volume to the guest free volume in a discrete fashion suitably weighted by the ratio of the number of times the guest enters that particular shell volume successfully as compared to the number of times the guest molecule attempted to enter that shell (Tester *et al.* 1972, Lund, A. 1990). For carbon dioxide in structure I small cavity, since we know the value of  $\langle U \rangle$  either by MMC or MDI

(Table 3.3), we can compute the value of Langmuir constant taking  $V_{MMC}$  as the same as  $V_{uncond}$ . This has the effect of setting  $V_{diff}$  equal to zero as seen in equation 3-13, and would yield a lower Langmuir constant (see equation 3-7) than that expected if  $V_{diff}$  is not equal to zero. The volume,  $V_{uncond}$ , is computed as follows,

$$V_{uncond} = \frac{4}{3} \pi b^3$$
 3-14

where 'b' is the radius of guest molecule. For Carbon dioxide, b could be taken as 1.1615 °A (Tester et al. 1972). The computed value of Langmuir constant for carbon dioxide, using equations 3-7, 3-9 and 3-13, taking  $\langle U \rangle$  from Table 3.3 (MDI or MMC) and setting  $V_{MMC}$  to be the same as  $V_{uncond}$  is calculated to be approximately 373 (atm<sup>-1</sup>). So if the MMC methodology as suggested by Tester et al. (1972) were to apply, then the minimum Langmuir constant that could be computed for Carbon dioxide is approximately 373 (atm<sup>-1</sup>) and the actual MMC computed Langmuir constant could be higher depending on  $V_{diff}$  (>0). It is noted that in Table 3.1, the Langmuir constants computed by Tester et al. (1972) as well as by the MDI method are lower than 373 (atm<sup>-1</sup>). Since we did see that the MMC and MDI methods agree in  $\langle U \rangle$  computations, we could say that the MMC method as suggested by Tester et al. (1972) for the Langmuir constant computations breaks down, especially for large guest molecules as compared to cavity size. The calculation of guest free volumes needs to be addressed and Kvamme et al. (1993) suggest that molecular dynamics simulations would probably give better results for different guest molecules.

### **3.3 Conclusions**

The computation of the Langmuir constants for the gas hydrate equilibrium calculations involves the evaluation of a multi dimensional configurational integral. It has been shown that in the evaluation of the configurational integral by MMC method, an approximation in energy term made in earlier works, does not apply as a result of hydrate cavity asymmetries. Also the computation of guest free volume, could be affected and as a result the methodology for Langmuir constant computations as suggested by Tester *et al.* (1972) is not recommended.

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### **CHAPTER 4**

#### **Nucleation Kinetics - Gas Hydrates**

### 4.1 Introduction

The kinetics of hydrate formation is an important aspect of research on hydrates that is not as well understood as the thermodynamics of hydrates. The reason for this is that it has not received much attention in the early hydrate research as most researchers focused on the thermodynamics of hydrates. When gas hydrates were found to form in gas pipelines and block the pipelines (Hammerschmidt, 1934) for gas transport with potentially serious consequences research on hydrates was directed towards calculating the thermodynamic conditions of hydrate formation. Subsequently, as further research showed that hydrates could be used for other applications like separating gas mixtures (Barrer and Ruzicka, 1962), storing and shipping natural gas or that their vast reserves could be exploited (Makogan, 1981) for generating energy the kinetics of hydrate formation began to attract interest in hydrate circles. The kinetics of hydrate formation is still a challenging research area today despite growing amount of work. The reason is that the process of hydrate formation is little understood so far and only recently experiments have begun probing the hydrate formation process.

In this work on hydrate nucleation the hydrate formation kinetics is studied in detail from both, an experimental and theoretical, point of view. In this chapter, the relevant literature is reviewed first followed by the presentation of experimental work. In the next chapter a model for nucleation kinetics in gas hydrates is developed and presented. This model has been shown to explain the amount of gas consumed during nucleation and the induction time for hydrate nucleation.

### 4.2 Hydrate Formation - Comparison with Crystallization

The process of hydrate formation and growth is closely related to crystallization process. The hydrate formation process leads to the formation of stable hydrate nuclei. During the hydrate growth process the stable hydrate nuclei grow as solid hydrates. Kinetic data obtained so far (Dholabhai *et al.*, 1993; Englezos *et al.*, 1987a, 1987b; Falabella, 1975; Vysniauskas and Bishnoi, 1983, 1985) includes the 'nucleation' stage as this is a pre-requisite for the 'growth' stage.

As the hydrate formation process has been suggested to be similar to crystallization process, it is interesting to compare the formation process of gas hydrates and salt crystals. Such a comparison between the two processes was not possible earlier since the hydrate formation process was not well understood. However as a result of this work, the comparison of the two processes could now be made as shown In Table 4.1. Some similarities between hydrate nucleation and salt crystal nucleation are that they both require supersaturation to form stable crystals. In the case of both processes, the driving force for nucleation is the degree of supersaturation. Hydrate nucleation phenomena is, however, more difficult to study than salt nucleation as it is complicated by the hydrodynamics, mass transfer of solute from the gas phase to the liquid phase and the possibility of localized supersaturation that could lead to hydrate formation.

### 4.3 Nucleation Studies - Literature Review

The literature on nucleation processes is not very old despite the practice of crystallization for a long time, beginning with the manufacture of common salt or sodium chloride since the dawn of civilization. Crystallization was more of an art rather than science as it was little understood for a long time. However this picture rapidly changed as more and more investigators studied the crystallization processes and the transition of crystallization from being an art to a science is a real possibility today despite its yet unresolved complexities. Needless to add that the nucleation process, which is a fundamental process in crystallization and leads to the formation of stable crystal nuclei, has also been barely understood till recent times. Experimentally, nucleation studies require carefully controlled conditions and are to be studied at low supersaturations over a longer period. On the theoretical side nucleation is not much understood despite several successful crystallization theories. The reason for this low level of understanding is that nucleation is a complex process which can be affected by several factors about many of which we have only a cursory understanding, thus making nucleation a very challenging research area.

The concept of nucleation is based on the formation and decomposition of clusters or aggregates of molecules of the dissolved substance as a result of local concentration fluctuations (Nyvlt *et al.*, 1985). For each supersaturated solution, there exists a critical cluster (also called the critical nucleus) that is in equilibrium with the surrounding medium and has the same probability of growth as of disintegration. For a cluster of size less than the critical size, the probability of decomposition is very high while clusters larger than the critical size grow spontaneously. Thus the critical size represents a size barrier which the growing clusters must attain before spontaneous growth as solid crystal commences.

The classical theory of nucleation states that clusters of particles are formed in solution according to the following scheme of step-wise atomic collisions (Frenkel 1946, Turnbull 1956, Melia 1965, Nielsen, 1964)

$$a + a \leftrightarrow a_2$$
 4-1

$$a_{i-1} + a \leftrightarrow a_i$$
 4-3

SALT CRYSTAL NUCLEATION	GAS HYDRATE NUCLEATION
Leads to the formation of crystalline salt	Leads to the formation of crystalline gas hydrate
Requires Supersaturation with respect to equilibrium	Requires Supersaturation with respect to three phase hydrate equilibrium
The driving force for nucleation is the degree of supersaturation	The driving force for hydrate nucleation is the degree of supersaturation $(f_g^L - f_{eq})$
Nucleation is believed to be the growth of solute clusters in solution to critical size	Nucleation is believed to be the growth of gas - water clusters to critical size
Computation of critical size of nuclei is in agreement with experimental findings	Computation of critical size of nuclei seem to be in agreement with experimental findings. Needs further work for confirmation
Local supersaturation could affect the nucleation process	Local supersaturation could affect the nucleation process
Nucleation process is stochastic in nature	Nucleation process is stochastic in nature
Relatively simple to study experimentally and analyze the results.	Relatively difficult to study experimentally and analyze. Account should be taken of hydrodynamics and mass transfer from gas to liquid

### Table 4.1 Comparison of Hydrate and Salt Nucleation

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As soon as these clusters attain a critical size the inter molecular forces of the particles within the cluster dominate over the intermolecular forces of surrounding particles and the cluster becomes stable. A number of authors (as mentioned in Nyvlt *et al.*, 1985) have derived the following relationship for the rate of nucleation

$$R_n = A \, \Theta^{\frac{-\Delta G^*}{kT}}, \qquad 4-4$$

where  $R_n$  is the rate of nucleation, A is the pre-exponential factor and  $\Delta G^*$  is the free energy of formation of the critical sized nucleus. It should be noted that the rate expression is similar to the Arhenius type rate expression used for chemical kinetics.

During cluster formation, particles of a given substance in the bulk of original phase form new phase 2. The process is accompanied by a change in the Gibbs free energy,

$$\Delta G = \Delta G_s + \Delta G_v, \qquad 4-5$$

where  $\Delta G_s$  is the surface free energy change which is a positive quantity and  $\Delta G_v$  is the volume free energy change which is a negative quantity. According to the classical homogeneous theory of nucleation (Nielsen 1964)

$$\Delta G = -\alpha L^3 \frac{\Delta \mu}{V} + \beta L^2 \sigma_{12} \qquad 4-6$$

where  $\sigma_{12}$  is the interfacial tension between the two phases, 1 and 2,  $\alpha$  and  $\beta$  are constants and L is the size of the nucleus. A typical plot of  $\Delta G$  against L is shown in Figure 4.1. It is important to note that  $\Delta G$  goes through a maximum as L is increased. The maximum value of  $\Delta G$  is obtained at L\*, which corresponds to the critical nucleus. For L greater than L\* the process is accompanied by a decrease in
the Gibbs free energy and hence thermodynamically favourable and spontaneous for the critical nucleus to grow. For L less than  $L^*$ , owing to higher cluster decomposition as compared to its formation, the cluster growth process is thermodynamically unfavourable and can only occur as a result of chance fluctuations.

Thus  $\Delta G^*$  represents some sort of Gibbs free energy barrier for the growing nucleus to cross. The rate of nucleation in equation 4-4 is thus determined with  $\Delta G^*$  obtained from equation 4-6 at L=L\*. However, the magnitude of the proportionality constant or the pre-exponential factor in equation 4-4 cannot be obtained from the thermodynamic theory of nucleation and is determined from the kinetic model of nucleation. In fact, most work done on the kinetic model of nucleation differ in the approach for the derivation of the pre-exponential factor.

In the kinetic model of nucleation, the model assumes the formation of an n atom cluster according to a scheme of step-wise atomic collisions as follows

$$a_1 + a_1 \leftrightarrow a_2$$
 4-7

$$a_2 + a \leftrightarrow a_3$$
 4-8

Reactions of the type and,

$$n a_1 \rightarrow a_n$$
 4-9

$$a_i + a_i \leftarrow a_{i+i}$$
 4-10

where i, j are both greater than 1, are neglected as they are not very likely and hence unimportant. In a supersaturated solution the cluster growth rate is greater than the disintegration rate, hence, the cluster size increases with time. If clusters of super critical size are removed from the solution, separated into their individual components and then returned to the solution, a dynamic equilibrium is attained characterized by a cluster size distribution and a stable cluster size growth through all the sizes. In such a system the stationary nucleation rate is given by the rate of growth of clusters to a size above the critical size.

Quantitatively, then for the kinetic theory of nucleation

where  $k+_{i}k_{i}$  are the rate constants for the growth and disintegration of clusters of i atoms. At dynamic equilibrium,  $dc_i/dt$  is equal to zero which means that the cluster concentration is constant with time

$$\frac{dc_i}{dt} = (k_{+i-1} c_{i-1} + k_{-i+1} c_{i+1}) - (k_{+i} c_i + k_{-i} c_i) \qquad 4-12$$

Thus the rate of growth of clusters over size i is given by

$$j_{i} = k_{+i-1} c_{i-1} - k_{-i} c_{i} \qquad 4-13$$

hence from equation 4-12

$$\frac{dc_i}{dt} = j_i - j_{i+1}$$
 4-14

Using the kinetic theory of nucleation Nielsen (1964) derived the following equation for the case of supersaturated solutions.



Fig. 4.1 Free Energy Change of Growing Particles

$$R_n = \frac{2D}{d^6} \, \Theta^{\frac{-\Delta G_*}{kT}}$$
 4-15

In a recent paper Rita *et al.* (1990) have derived the kinetics of nucleation from an aqueous solution with modifications of Nielsen (1964) development. They have developed a dimensionless parameter which permits the comparison of the rate of nuclei formation with that of growth.

In summary it is seen that the rate of nucleation as obtained from purely thermodynamic or a mixed kinetic-thermodynamic relationship is identical (equations 4-4, 4-15). However the validity of the classical nucleation theory is limited by certain implicit assumptions (Nyvlt *et al.*, 1985) given below.

- a) It is assumed that thermodynamics is applicable for small systems (clusters of several dozen particles) and the macroscopic values of the thermodynamic quantities can be applied to small species. This is a questionable assumption since the classical theory is derived from the thermodynamics of a continuum, i.e the size of particles is much greater than the inter molecular distances. However, this condition is not fulfilled in the case of small clusters and so it cannot be assumed apriori that thermodynamics is applicable to describe nucleation. The macroscopic values of quantities like interfacial tension may not be applicable to small clusters.
- b) The concentration of all cluster sizes are constant during nucleation. This assumption also known as the stationary state assumption cannot be made as the nucleation rate cannot attain this stationary state instantaneously. Thus the time taken to reach the stationary state should be taken into account. The

non-stationary nucleation rate has been derived by Kaschiev (1969).

c) Classical nucleation theory also neglects the translational and rotational contributions to the free energy of the cluster. These contributions are accounted for in a statistical mechanics view of the nucleation process.

The classical nucleation theory despite its several limitations, described above, is still a successful theory as it has not been conclusively disproved. The success of the classical nucleation theory comes from the fact that despite its shortcomings it is derived from fundamental considerations. There are other models widely used in nucleation studies that are not as fundamentally based as the classical nucleation theory but are also very successful. One such very popular model is the power law form (Mullin, 1972) of expressing the rate of nucleation as below.

$$R_n = k (S - 1)^n$$
 4-16

where S is the supersaturation and k and n are constants. This is one of the widely used models for nucleation. A derivation of this model from classical nucleation theory has been suggested by Nyvlt (1968). This model is adapted for application to hydrate nucleation processes as discussed in detail in the next chapter.

## 4.4 Hydrate Nucleation - Literature Review

The hydrate nucleation process leading to the formation of hydrate nuclei has little published experimental data so far. The experimental study of hydrate nucleation phenomenon is difficult as the phenomenon is microscopic in nature involving tens to hundreds of molecules. However, the hydrate nucleation process has become one of the focal points of current research as shown by increasing work in this area recently both in terms of modelling and interpreting nucleation kinetic data available (Sloan *et al.*, 1991; Skovborg *et al.*, 1993) so far, as

well as obtaining more data by sophisticated experimental studies involving laser scattering experiments (Nerheim *et al.*, 1992).

## The Clustering Process in Hydrate Nucleation

The clustering process has been suggested to be the pre-cursor of hydrate nuclei formation (Makogan, 1981; Vysniauskas and Bishnoi, 1983, 1985; Englezos and Bishnoi, 1988b). The experimental mole fractions of the solute molecules (methane) dissolved at the nucleation point were found to be substantially higher than the two phase vapour-liquid equilibrium value by Englezos and Bishnoi (1988b), which was also attributed to the clustering mechanism. The critical size of a hydrate nuclei, which is the stable nuclei size, that continues to grow as a solid hydrate crystal was first computed by Englezos *et al.* (1987a). They derived an expression for the free energy of a hydrate nucleus, as a part of the model they proposed for the growth of hydrate particles after the nucleation stage. The size of the critical nuclei for methane hydrates were computed from their hydrate growth experiments to be of the order of 100 - 300 °A. In a more recent work, Nerheim *et al.* (1992), used a laser light scattering technique and experimentally studied the hydrate nucleation process. They determined the size of the critical hydrate nuclei to be of the order of 50 - 300 °A.

Although the clustering mechanism has been suggested to explain the nucleation process the structure of water and the effect of dissolved solute gas molecules on the water structure are also important in the hydrate nucleation process as explained below.

## Structure of Water

The induction period for hydrate nucleation, could be a function of the structure of water. Vysniauskas and Bishnoi (1983) measured the mean induction

periods in a series of experiments with water of different qualities. On Table 4.2, the mean induction times shown by water of different qualities used for hydrate formation as mentioned by Vysniauskas and Bishnoi (1983) are shown. The mean induction period in their study was found to be much less in the case of thawed ice and water obtained after hydrate dissociation than in the case of hot tap water. Since thawed ice or cold water would have a tendency to maintain a more ordered structural arrangement owing to limited molecular activity as compared to pre-heated water, the results of Vysniauskas and Bishnoi (1983) do suggest a possible effect of water structure on induction period. The same effect (of structuralized water) has also been suggested recently by Nerheim *et al.* (1992) from their laser scattering studies on hydrate nucleation.

There are a number of models in the literature for the structure of water, supported by computer simulations and experiments, as water is a widely used solvent. A popular model of interest especially for understanding of hydrate formation is the "flickering cluster" (FC) model for liquid water. In accordance with the FC model for water, developed by Frank and Co-workers (1945, 1957, 1961) and Nemethy and Scheraga (1962), water consists of an equilibrium mixture of short-lived hydrogen bonded clusters, with a non-hydrogen bonded dense phase. The number of such clusters increases rapidly as the temperature is decreased. A third model for water, of particular interest to hydrates, is the "water-hydrate" (WH) model suggested by Pauling (1959, 1960). Earlier Claussen (1951) and Pauling and Marsh (1952) had shown that water molecules can form structures which are looser than ice with relatively large cavities, while retaining the bond angles and intermolecular distances that are characteristic of ice. These structures are energetically stable despite their looseness owing to the hydrogen bonds that holds them together. The WH model was analyzed by Frank and Quist (1961) using a statistical mechanical approach. In addition to the models discussed above there are other numerous models for water in the literature (reviews by Chadwell, 1927; Malenkov, 1962; Hall, 1948; Grunberg and Nissan, 1949; Haggis et al., 1952; Eck et al., 1958; Ginell, 1961; Namiot, 1961;

## Table 4.2. Induction Time and Water Quality (Average and Pickage and Pickage)

(Vysniauskas	and	Bishnoi,	1983)
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Water Quality	Mean Induction Time, (min)
Cold Tap Water	4.95
Hot Tap Water	18.13
Double Distilled	11.75
Thawed Ice <sup>*</sup>	0.75
Dissociated Hydrate**	2.50
Dissociated Hydrate***	0.0

\* - Sample used immediately after ice melted

\*\* - Dissociated hydrate water sample left overnight before using

\*\*\* - Sample used immediately after hydrate dissociation

Wada, 1961; Berendsen, 1962; Fisher, 1962). All the models discussed above, have been able to account for a number of distinctive features of liquid water but are contradictory in many respects. Hence the problem of liquid water structure is still considered not conclusively resolved.

## Effect of Dissolved Solute Molecules on Water Structure

The structuring of the bulk water molecules around a dissolved apolar solute molecule (Frank and Evans, 1945) is an important aspect in understanding hydrate nucleation phenomena. Evidence for this local structuring around the solute molecule comes from molecular simulation studies (Geiger, Stillinger and Rahman, 1979; Dang, 1985; Owicki and Scheraga, 1977; Swaminathan et al., 1977; Anders Wallquist, 1991) as well as from experimental evidence collected for aqueous solutions of alcohols where the apolar portion of the alcohol molecule has been suggested to affect the water solvent in much the same manner as strictly apolar solutes (Alexander and Hill, 1963; Arnett et al., 1969; Krishnan and Friedman, 1969). The Monte Carlo molecular simulation for the methane and water system by Owicki and Scheraga (1977) and Swaminathan et al. (1977) show the average co-ordination number of water molecules around the dissolved methane to be about 23 and 20 respectively, which is closer to the co-ordination number of 21 for a small Structure I clathrate cavity. In fact the water network arrangement around the dissolved solute molecule is identified as similar to a clathrate type cavity (Rahman, 1974). From thermodynamic considerations, the Gibbs free energy of the solution of natural gas hydrate components is small and positive in accordance with a small solubility, and is primarily characterized by a negative entropy of the solution (Franks and Reid, 1973). The large negative entropy of solution is considered evidence of the creation of a structure within the body of water. Also the heat of solution for ten hydrate formers was found to be the same as the heat of hydrate formation from gas and ice, thereby suggesting the co-ordination of the aqueous solute with surrounding water molecules (Glew, 1962). Albeit the experiments of Vysniauskas are preliminary in understanding hydrate nucleation, the induction time could be a function of the quality of water structure and the dissolution phenomena of hydrocarbons owing to interactions between the dissolved apolar solute and surrounding water molecules.

Although the literature presented so far on the structure of water and of structural changes that occur locally around a dissolved solute molecule indicates substantial work in this area, very little work is carried out to understand nucleation of hydrates. The work by Falabella (1975) represents some of the earliest work on hydrate induction. In his experiments, Falabella (1975) used a low temperature reaction vessel in which ice crystals in contact with a hydrate forming gas were bombarded with metallic balls. The amount of gas consumed in his experiments were supplied by a volumetric system which also allowed the consumption to be monitored. Experimentally, it was observed by Falabella (1975) that some hydrates exhibited induction times during their formation. In particular Falabella (1975) observed that induction time was observed in methane and krypton and did not observe any induction time in the case of other hydrates he studied like xenon, acetylene, ethane, ethylene and carbon dioxide.

Also Falabella's (1975) data showed no induction time for a 90 % methane and 10 % ethane mixture hydrate. On the basis of Falabella's (1975) data Sloan *et al.* (1991) proposed that the induction time for a hydrate could be dependent of the ratio of size of the guest molecule to the size of the small cavities of structures I and II (size ratio). For example in the case of methane hydrate formation Sloan *et al.* (1991) observed, the methane hydrate could have an induction period which is proportional to a periodic oscillation between the small cavities of the two structures I and II, before the small cavity of structure I achieves the critical nuclei radius stability. Krypton was also showing induction phenomena owing to periodic oscillations between the small cavities of both structures before finally forming a stable structure II hydrate. Sloan *et al.* (1991) proposed that a size ratio of 0.81 to 0.89 was responsible for the hydrate to exhibit induction phenomena. Since the induction phenomena was as a result of non-discrimination of the two structures resulting in a periodic oscillation during the hydrate formation, Sloan *et al.* (1991) argued that an addition of little ethane to methane should do away with the induction phenomena as was supported by Falabella's (1975) data for 90 % methane and 10 % ethane hydrate. In order to verify the proposed mechanism for induction, Sloan *et al.* (1991) also conducted experiments and studied the formation kinetics of cyclo-propane hydrates, in an apparatus similar to that used by Falabella (1975) for his experiments. Cyclo-propane can occupy either of the large cavities of structures I or II depending on the experimental conditions. Thus if their proposed mechanism was correct, then they expected cyclo-propane hydrate to exhibit induction during formation. The induction times they measured were too short to be quantified. They also modelled kinetically the proposed molecular mechanism for nucleation with three kinetic constants.

There are some limitations in the work by Sloan *et al.* (1991). There is no direct experimental evidence for the molecular mechanism that they have proposed. The three kinetic constants in their model, were regressed from the experimental hydrate growth data and could well be co-related. As will be discussed later in this work the induction phenomena reported in the literature so far including ALL the supporting data cited by Sloan *et al.* (1991) could be explained by the approach taken in this work.

In summary, there is not much information about hydrate nucleation in the literature. Hence in this work, we focus on modelling hydrate nucleation with the available kinetic data collected in this laboratory. Also the proposed modelling approach is compared with other approaches in the literature for modelling hydrate nucleation.

## 4.5 Experimental Objectives & Design

The main objectives of this work is to model the amount of gas consumed during nucleation and induction time of nucleation. There are some experimental data already available from part of the systematic study of hydrate nucleation and growth conducted over many years (Bishnoi *et al.*, 1985, 1986, 1989b; Vysniauskas and Bishnoi, 1983, 1985; Englezos *et al.*, 1987a, 1987b, 1990; Dholabhai *et al.*, 1993). The available experimental kinetic data includes data for hydrate formation with pure and mixed gas hydrates, hydrate formation in the presence of inhibitors like salts and methanol, and hydrate formation in the presence of surfactant additives and other solvents like heptane. In addition to these existing experimental data, new experiments were performed in this study to investigate the effect of water structure and these new experiments are discussed in the remaining portion of this chapter.

The quality of water used for hydrate formation has an important effect on hydrate formation as seen in Table 4.2 (Vysniauskas and Bishnoi, 1983). Let 'structured water' be defined as the water that was used to form hydrates before and obtained after decomposing the formed hydrates, and 'structuralization' of water be defined as the process of making structured water. It is believed that the structured water could form hydrates easily, probably as a result of trace evidences of hydrate structures in solution, as compared to fresh water and this effect is called the 'memory effect' (Makogan, 1981; Vysniauskas and Bishnoi, 1983; Nerheim *et al.*, 1992). Since the basic objective of this work was to model the earlier experimental data collected in this lab, it was decided to conduct more new experiments to specifically investigate the possible role of water structuralization, if any, in the kinetics of hydrate formation. This was necessary to incorporate any possible effect of structuralization in the modelling work, if required. Also of interest was the role of mass transfer effects, if any, in the induction phenomena observed. The experimental objectives were thus defined as follows

- a) To study the effect of structuralization of water, if any, on the induction time for hydrate formation
- b) To see if mass transfer plays a role in deciding the induction time for hydrate formation

In this study the experiments were carried out at three different experimental pressures, 500, 1000 and 1500 kPa above the corresponding equilibrium pressures. Very high or very low experimental pressures above the hydrate equilibrium pressures could complicate studying nucleation phenomena by introducing possible local supersaturation effects in aqueous solution or take a very long time for nucleation respectively. Hence it was decided to limit the maximum studied experimental pressure for nucleation to 15 bars over the corresponding hydrate equilibrium pressure. Methane was used as the hydrate forming gas at 1 degree Celsius keeping the RPM of stirrer at 400 and the volume of the solution at 300 cm<sup>3</sup> for all the runs.

## 4.6 Experimental Apparatus

The experimental apparatus used in this study is essentially the same as used by Vysniauskas and Bishnoi (1983), Kim *et al.* (1985) and modified later (Bishnoi *et al.*, 1985, 1986). A schematic diagram of the experimental set-up is shown in Figure 4.2. It can be seen that the principal components of the experimental set-up are a semi-batch agitated reactor system, the pressure and temperature measuring systems, the DORIC data acquisition system and several supply and reference gas reservoirs.

The semi-batch agitated reactor system comprises of a stainless steel reactor with a design working pressure of about 140 bars and with an internal volume of  $500x10^{(-6)}$  m<sup>3</sup>. The reactor is fitted with two marine type lucite windows to observe the presence of gas hydrates in the reactor. In order to avoid the formation of vortices baffles are placed in the reactor.

A magnetic stirrer bar coupled to a ceramic magnetic stirrer mounted on a driver outside the reactor was used to agitate the liquid solution. The stirring rate could be controlled by a RPM controlled DC motor.

The gas reservoir R1 was used to pressurize the hydrate reactor to the desired experimental pressure. The reservoir R3 was used to supply the necessary gas, as the hydrate formation ensued, in order to maintain constant reactor pressure. The reservoirs R2 and R4 were used to provide reference pressures for different Differential Pressure or DP transmitters.

The differential pressure transmitters DP1, DP2, DP3 and DP4 were used to measure the pressures in the reservoirs R1, R3 and reactor respectively. The bias sides of DP1, DP2 and DP4 were connected to the reference reservoirs R2, R4 and R5, while the bias side of DP3 was open to the atmosphere. The pressure of the reactor was controlled by a controlling system consisting of a pneumatically activated pressure control valve, a three mode controller, a pneumatic activator and a pressure transmitter. The reactor was initially pressurized from the supply cylinder. As the pressure in the reactor decreases due to gas consumption in the reactor owing to hydrate formation, the control valve opens to admit the gas from the reservoir R1 until the pressure in the reactor is restored to the desired set pressure.

Temperatures inside the reactor were measured by copper-constantan thermocouples, which were inserted into the reactor at different locations to measure the bulk gas temperature, gas-liquid interfacial contact and the bulk liquid temperature. The entire array of reservoirs and the reactor were kept immersed in a glycol bath whose temperature was controlled using an auxiliary glycol refrigerator. The glycol refrigerator had a control sensitivity of  $\pm 0.02$  °C in the temperature range from -29 to 70 °C.

The temperature and pressure measurements were recorded using a DORIC





data logger and a COMPAQ DESKPRO 8086 personal computer. The on-line computations of the cumulative moles of the gas consumed were also executed on the personal computer.

Research grade methane gas (Matheson, Research Purity (99.9995 %) was used in the experiments.

## **4.7 Experimental Procedure**

As the objective was to investigate the structure of water effect, the procedure followed in the earlier hydrate formation and growth experiments (Bishnoi *et al.* 1985, 1986) was modified. The experimental procedure employed in this work is divided into three parts. It is similar to the experimental procedure followed in earlier hydrate formation experiments by Bishnoi *et al.* (1985, 1986) with respect to the first two parts but differs in the third part. In the first part, the procedure for the calculation of moles of gas consumed during hydrate formation is mentioned. As this calculation of the amount of gas consumed needs the volume of the gas supply reservoir, in the second part the Ruska Pump experiment which was used to obtain the volume of the gas supply reservoir is mentioned. And finally in the third part, the new procedure employed to investigate the structure of water effect is elaborated.

## Calculation of the number of moles consumed

The cumulative amount of moles of gas consumed at any time t, is computed during the course of the experiment as the change in total moles in the reactor and the supply cell combined. Thus if n(t) is the moles of gas consumed upto time t then,

$$n(t=0) = 0$$
 4-17

$$n(t > 0) = (n_R + n_S)_{t=0}^{-} (n_R + n_S)_{t=t}$$
 4-18

which could be written as

$$n(t>0) = V_{R}(\frac{P}{ZRT})_{S,t=0} + V_{S}(\frac{P}{ZRT})_{S,t=0} - V_{R}(\frac{P}{ZRT})_{R,t=t} - V_{S}(\frac{P}{ZRT})_{S,t=t} 4-19$$

where subscripts R and S stand for the reactor and the supply cell respectively. The volume of gas phase in the reactor including tubing is denoted by  $V_R$ , which is equal to the empty reactor volume less the injected water volume during the experiment. The volume of the empty reactor and the supply cell is determined from the Ruska pump experiment. The compressibility factor, Z, was determined from an on-line computer program based on the Peng-Robinson equation of state.

## Ruska Pump Experiment

The Ruska Pump Experiment is an experiment performed to determine the volume of the supply reservoir needed for the calculations of amount of gas consumed in moles, during a hydrate forming experiment. In the Ruska pump experiment a known volume of mercury is pumped into the reservoir and the pressure is measured before and after the mercury is pumped in. Since the number of gas molecules within the reservoir remain constant, the pressure and volume of the reservoir have the following relation

$$\frac{P_i V_{s,i}}{P_f V_{s,f}} = \frac{Z_i T_i}{Z_f T_f}$$

$$4-20$$

Hence the volume of gas in the reservoir,  $V_s$  is given by the relation

$$V_{s} = V_{s,f} = \frac{(V_{s,f} - V_{s,f})}{(\frac{P_{f} Z_{f} T_{f}}{P_{f} Z_{f} T_{f}} - 1)}$$

$$4-21$$

where i and f denote the initial and final equilibrated states before and after the mercury injection into the reservoir respectively. The compressibility factor Z was obtained from the Peng-Robinson equation of state and the volume difference,  $V_{s,i}$  -  $V_{s,p}$  was measured during the experiment.

## Modified Procedure to investigate Structure of Water effect

This modified experimental procedure was divided into two main steps. In the first step of the experiment, the water used in the kinetics experiment was structuralized. For this, the reactor was charged always with 300 c.c of fresh water and the reactor was pressurized to a pressure of about 25 bars over the equilibrium pressure while stirring at the prescribed RPM. Also the contents of the reactor were monitored continuously for visual observation of turbidity in the liquid phase. Turbidity is said to have appeared when the solution becomes translucent owing to the emergence of hydrate particles. After the appearance of turbidity point, the experiment was stopped by isolating the gas supply to the reactor, when the number of moles of gas consumed after turbidity point is 10 to 15 % more than the number of moles of gas consumed at turbidity point. Then the decomposition of the formed hydrates was carried out by reducing the reactor pressure to atmospheric pressure. The decomposition was continued keeping the stirrer on till no more gas bubbles were seen in the liquid. After this point of time the reactor was left in the same state for 4 hours, with stirring, before beginning the second part of the experiment.

In the second step of this experimental procedure, before starting the experiment, it was visually verified to see if the structuralized water was clear and a

record of the observation was made. The experiment was started by pressurizing the reactor to the specified experimental pressure. The moles of gas consumed with time was monitored until the appearance of the turbidity point. After the appearance of turbidity point a record of it was made and the experiment was stopped by depressurizing the reactor.

#### 4.8 Experimental Results - Discussion

The gas consumption data during hydrate formation as obtained in the experiments conducted in this study are like those typically obtained in earlier studies (Bishnoi *et al.* 1985, 1986). Such a typical gas consumption data are shown schematically in Figure 4.3. The "hydrate growth" region is shown in the plot after the "turbidity time",  $t_{tb}$ , when the solid hydrates grow in solution. The moles of gas consumed at turbidity is denoted as  $n_{tb}$ . If  $P_{exp}$  and  $T_{exp}$  denote the experimental pressure and temperature respectively and  $P_{eq}$  represents the three phase hydrate equilibrium pressure at the temperature  $T_{exp}$ , then the moles of gas  $n_{eq}$  shown in Figure 4.3 corresponds to that dissolved at  $P_{eq}$ ,  $T_{exp}$ . The region before the time  $t_{eq}$  is the "solubility region", where the phenomena is one of gas dissolution into the liquid and the aqueous solution is not yet saturated. The region between  $t_{eq}$  and  $t_{tb}$ , is the "nucleation region" and  $t_{tb} - t_{eq}$  is defined as the induction period (Figure 4.3).

The raw results obtained from the experiments conducted to investigate the structure of water effect are summarized in Tables 4.3, 4.4, 4.5, 4.6 and 4.7. All "structured water" runs reported in these Tables have run numbers ending with a "B" and all "unstructured water" runs have run numbers ending with or without an "A". For each run, the experimental pressure  $P_{exp}$ , the average experimental temperature,  $T_{avg}$  and the maximum temperature  $T_{max}$  are shown. The  $T_{avg}$  is the average of the solution temperatures measured during the course of the experiment. In these tables,  $P_{eq}$ , is the equilibrium pressure at 274.15 K and  $n_{tb}$  is the moles of gas dissolved at turbidity. Also  $n_{tb}(f)$  is the final value of moles of gas dissolved in the experiment before decomposing the hydrate in order to begin a structured water run in the second part of the experiment. It is usually about 10 % higher than  $n_{tb}$ . The induction time defined as  $t_{tb} - t_{eq}$  (see Figure 4.3),  $t_{ind}$  are also shown in the tables. Approximately three runs were performed for both structured and unstructured water at each pressure. The experimental results were well reproducible for the runs performed. The key experimental results are discussed as follows.

## Effect of water structuralization

Establishing the effect of water structuralization if any, on hydrate formation was one of the objectives of the study. After structuralizing the water by forming hydrates in the first part, the hydrates were decomposed by depressurizing the reactor to atmospheric pressure with continuous stirring. It was important to ensure that the hydrates were totally decomposed after the first part of the experiment so that no hydrate particles (below the visual size) in solution could make it possible to form hydrates again easily. Hence at the decomposed state, the water was kept for 4 hours with stirring before it was used to form hydrates again. Identical results were obtained when in one experiment the water after the first part, was kept overnight with stirring instead of the usual 4 hours. Thus it is reasonable to say that 4 hours was sufficiently long enough to permit decomposition of all hydrates produced in the first part of the experiment.

The results shown in the Tables 4.3 to 4.7 could be viewed in two separate parts. At high enough pressures (higher than 35 bars) both structured and unstructured water were found to behave in the same way and all the induction time results were reproducible as could be seen by comparing runs at similar pressures. For example, Runs MNK-N01A, MNK-N02A, MNK-N03A and MNK-N04A were with unstructured water and their induction times are quite in agreement within



experimental bounds. The same agreement is seen in structured water runs as well as seen from Runs MNK-N01B, MNK-N02B and MNK-N03B. Further, it could also be seen at high enough pressures both unstructured and structured water have similar induction times as could be seen from the Runs MNK-N17, MNK-N18, MNK-N04B and MNK-N05B. Thus it is seen that at high enough pressures there is good agreement between unstructured water runs, structured water runs and between unstructured and structured water runs when considered together. On the other hand, at low enough pressures (lower than 35 bars) the differences in induction time results are larger between unstructured water runs (MNK-N26 and MNK-N23), between structured water runs (MNK-N25B and MNK-N27B) and between unstructured and structured water runs considered together (MNK-N23, MNK-N27B, MNK-N25B and MNK-N26). Thus it is seen that the induction time results at low enough pressures seem to vary within each other for unstructured and structured water runs carried out at the same pressure. The greater variation in induction time results at lower pressures (or at pressures closer to equilibrium pressures) could be expected since at these pressures the induction time would by and large be characterised by nucleation processes which are inherently stochastic. At high enough pressures, there is little variation in induction time results because at these pressures, the chances of achieving the necessary supersaturation of the gas in the solution (even locally) is increased as a result of higher mass transfer driving force for the transport of gas into the aqueous solution. The variation of induction times with experimental pressures as discussed here is also apparent from the plot of induction time against the experimental pressure as shown by Figure 4.4. One key finding in these results are that there does not seem to be a trend in induction time variations for structured water alone when compared to unstructured water (see Figure 4.4). This could mean that the structuralization as carried out in this work has no effect on induction time, or the dynamics of structuralization is very fast compared to that of nucleation process itself or that the structure of water was destroyed by keeping the solution stirred for 4 hours before beginning the structured water portion (second step) of the experimental procedure. Thus to be conclusive about the effect of structuralization more studies might be needed. However, the results also show that the hydrate nucleation modelling of the already available data (Bishnoi et al. 1985, 1986) and the data collected in this work could proceed without regard to structuralization effects. It is noted that some earlier studies (Vysniauskas and Bishnoi, 1983; Makogan, 1981; Nerheim et al., 1992) have found that structuralization affects hydrate induction times. However the experimental procedures of all these studies were different. Most of Vysniauskas results involve cooling water of different qualities (hot water, tap water) to the desired test temperature, increasing the pressure to test pressure with stirring. In our case the starting water was invariably of the same quality all the time and was R.O (Reverse Osmosis) water followed by distillation. The only results of Vysniauskas and Bishnoi (1983) that could be compared to this work would be those for which the water was obtained after hydrate dissociation. The mean induction time in Vysniauskas and Bishnoi (1983) study using water obtained from hydrate dissociation are indeed low and it is not clear if hydrate dissociation was carried out completely and with stirring during hydrate dissociation. The experiments of Nerheim et al. (1992) have been performed without stirring and therefore it is difficult to conclude whether the memory effect they claim to have observed is after complete dissociation of hydrates formed earlier. It should be said that the structuralization study is complex and the phenomena could only be verified conclusively if one can detect sub-critical nuclei and other sub-structures in solution, using a suitable technique like laser light scattering studies.

There was no definite effect of structuralization of water on the moles consumed at turbidity, within experimental errors, for the experimental pressures studied as seen in Figure 4.5. This is somewhat expected since  $n_{tb}$  represents an averaged amount (in moles) of gas in solution it should be nearly the same if there are no local supersaturation effects. Since local supersaturation effects are not expected in low to moderate pressure experiments the amount of moles of gas consumed at turbidity does not show much variation with pressure in these experiments. It is also interesting to see that the  $n_{tb}$  values are the same for both

	Table 4.3	Nucleation Kinetics Data - Methane Hydrate
(Only 'B' rur	ns - Structu	red Water runs. All other runs - Unstructured Water runs)

Run #	P <sub>exp.</sub> bars	T <sub>avg.</sub> °C	T <sub>max</sub> °C	P <sub>eq</sub> bars	n <sub>tb</sub> moles	n <sub>tb</sub> (f) moles	Ind. Time Minutes
MNK-N01A	54.15	1.166	1.240	29.1	0.0211	0.0234	2.0
MNK-N01B	43.15	1.160	1.180	29.1	0.0175		2.5
MNK-N02A	54.14	1.089	1.140	29.1	0.0194	0.0215	0.6
MNK-N02B	43.14	1.153	1.180	29.1	0.0206		0.5
MNK-N03A	54.14	1.067	1.130	29.1	0.0189	0.0212	0.2
MNK-N03B	43.14	1.152	1.180	29.1	0.0187		2.5
MNK-N04A	54.15	1.065	1.150	29.1	0.0180	0.0200	0.0
MNK-N04B	38.15	1.096	1.140	29.1	0.0212		5.7
MNK-N05A	54.14	1.051	1.090	29.1	0.0172	0.0189	0.0
MNK-N05B	38.14	1.085	1.110	29.1	0.0183		0.5

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Run #	P <sub>exp.</sub> bars	T <sub>avg.</sub> °C	T <sub>max</sub> °C	P <sub>eq</sub> bars	n <sub>tb</sub> moles	n <sub>tb</sub> (f) moles	Ind. Time Minutes
MNK-N06A	54.14	1.049	1.080	29.1	0.0136	0.0153	0.0
MNK-N06B	38.14	1.076	1.080	29.1	0.0205		4.9
MNK-N07A	54.14	1.065	1.130	29.1	0.0187	0.0209	0.0
MNK-N07B	38.14	1.068	1.080	29.1	0.0201		3.4
MNK-N08A	54.14	1.127	1.170	29.1	0.0198	0.0219	0.0
MNK-N08B	33.14	1.163	1.180	29.1	0.0213		11.5
MNK-N09A	54.14	1.124	1.180	29.1	0.0210	0.0236	0.0
MNK-N09B	33.14	1.180	1.210	29.1	0.0204		9.0
MNK-N10	33.14	1.162	1.180	29.1	0.0175		0.0
MNK-N11	32.14	1.085	1.170	29.1	0.0205		16.5

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Table 4.4Nucleation Kinetics Data - Methane Hydrate(Only 'B' runs - Structured Water runs. All other runs - Unstructured Water runs)

## Table 4.5 Nucleation Kinetics Data - Methane Hydrate

Run #	P <sub>exp.</sub> bars	T <sub>avg.</sub> °C	T <sub>max</sub> °C	P <sub>eq</sub> bars	n <sub>tb</sub> moles	n <sub>tb</sub> (f) moles	Ind. Time Minutes
MNK-N12	26.63	1.145	1.18	29.1			
MNK-N13	26.64	1.153	1.18	29.1			
MNK-N14	33.64	1.176	1.18	29.1			
MNK-N15	33.14	1.042	1.10	29.1	0.0193		6.8
MNK-N16	38.14	1.124	1.18	29.1	0.0213		10.2
MNK-N17	38.14	1.062	1.13	29.1	0.0211		5.7
MNK-N18	38.14	1.114	1.18	29.1	0.0202		4.0
MNK-N19A	54.14	1.089	1.16	29.1	0.0209	0.0238	2.0
MNK-N19B	26.64	1.171	1.18	29.1			
MNK-N20	43.14	1.101	1.16	29.1	0.0217		5.4

(Only 'B' runs - Structured Water runs. All other runs - Unstructured Water runs)

## Table 4.6 Nucleation Kinetics Data - Methane Hydrate

(Only 'B' runs - Structured Water runs. All other runs - Unstructured Water runs)

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Run #	P <sub>exp.</sub> bars	T <sub>avg.</sub> °C	T <sub>max</sub> °C	P <sub>eq</sub> bars	n <sub>tb</sub> moles	n <sub>tb</sub> (f) moles	Ind. Time Minutes
MNK-N21	33.15	1.051	1.08	29.1	0.0212		11.7
MNK-N22	31.15	1.155	1.18	29.1	0.0228		22.6
MNK-N23	30.15	1.023	1.08	29.1	0.0196		34.9
MNK-N24A	54.15	1.052	1.11	29.1	0.0128	0.0142	0.0
MNK-N24B	30.14	1.084	1.16	29.1	0.0201		33.2
MNK-N25A	54.14	1.067	1.14	29.1	0.0207	0.0233	0.0
MNK-N25B	30.14	1.091	1.15	29.1	0.0202		40.8
MNK-N26	30.14	1.024	1.08	29.1	0.0158		0.0
MNK-N27A	54.14	1.057	1.13	29.1	0.0221	0.0247	0.0
MNK-N27B	30.14	1.106	1.18	29.1	0.0208		27.0

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# Table 4.7Nucleation Kinetics Data - Methane Hydrate(Unstructured Water runs)

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Run #	P <sub>exp.</sub> bars	T <sub>avg.</sub> °C	T <sub>max</sub> °C	P <sub>eq</sub> bars	n <sub>tb</sub> moles	n <sub>tb</sub> (f) moles	Ind. Time Minutes
MNK-N28	43.15	1.185	1.27	29.1	0.0220		2.5
MNK-N29	43.15	1.141	1.18	29.1	0.0210		3.5

structured and unstructured water. This could also be expected since structuralization was not playing a role in induction time observations and the amount of gas supersaturation needed for formation of critical hydrate nuclei is unaffected by structuralization.

## Role of mass transfer in induction time observations

The role of mass transfer could complicate the interpretation of induction phenomena in hydrate studies. Rapid mass transfer to the solution from the gas phase could create local supersaturations of the gas in solution which could trigger spontaneous nucleation. This would result in obtaining a lower value of  $n_{tb}$  at turbidity as the moles of gas consumed is obtained by calculating the moles of gas lost (and thereby dissolved ) from the gas phase during an experiment. Also for situations involving rapid mass transfer of the gas to the solution the turbidity time would be lower thereby resulting in an artificially lower induction time. In particular the role of mass transfer should be examined for its effect on induction time.

Two different stirrers with different  $k_i$  (product of the liquid side mass transfer coefficient " $k_i$ " and the interfacial area per unit volume "a") values were used to study the effect of mass transfer on hydrate induction. In Figure 4.6, solubility experiments performed for these two stirrers (MNK-N13 and MNK-N30) clearly reveal the different  $k_i$  values as seen by the different initial slope of the cumulative moles dissolved curve. The plot of two nucleation runs conducted with these two different stirrers (with two different  $k_i$ as, same RPM) are shown in Figure 4.7. It was observed that the induction time is less in the case of the stirrer with the higher  $k_i$ a as opposed to the one with the stirrer with the lower  $k_i$ a. Thus especially for cases when the stirring could be inadequate (or low  $k_i$ a values) the possibility of local supersaturation is increased. Hence mass transfer phenomena need to be taken into account when interpreting induction phenomena observations, because the mass transfer process does affect the concentration of gas in the solution.

## **4.9 Conclusions**

Based on a review of the literature on crystallization and in particular about hydrate nucleation, it was decided to investigate the effect of structuralization of water used for hydrate formation and the role of mass transfer on induction time analysis. There was no difference observed in terms of moles dissolved at turbidity or in induction time between structured and unstructured water at high enough pressures (higher than 35 bars). Some differences were observed in induction time results for structured and unstructured water separately, as a result of the stochastic nature of hydrate nucleation. There was no systematic trend between the induction time results for structured and unstructured water at low enough pressures (lower than 35 bars). The experimental results also suggest that mass transfer could play an important role in the in the study of hydrate nucleation, especially in the case of rapid mass transfer of gas into the solution. The model for hydrate nucleation is developed in the next chapter based on mass transfer and nucleation considerations and the model is applied to predict the amount of gas consumed and the induction time for several hydrate forming gases in the experiments.

## Fig. 4.4 Induction Time vs Experimental Pressure



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## **CHAPTER 5**

## NUCLEATION KINETICS MODELLING

## **5.1 Introduction**

Despite the similarity of hydrate formation processes with crystallization processes and given that the crystallization processes have all been reasonably well studied, there are not many models of the hydrate nucleation processes in the literature. As noted in the last chapter, the lack of models for hydrate nucleation is partly owing to the insufficient published literature data on this subject. Secondly, the nucleation processes are complex to study both theoretically and experimentally. However, this picture is rapidly changing thanks to the growing interest in this area.

The first model for hydrate nucleation processes based on a molecular mechanism was presented by Sloan *et al.* (1991). The limitations of Sloan's model was discussed earlier in the previous chapter. This model will again be discussed in comparison with the model developed in this Chapter.

## **5.2 Modelling Objectives**

Over the past several years, extensive data on the nucleation and growth of hydrates have been obtained in this laboratory. The objective is to utilise these nucleation and growth data (Vysniauskas and Bishnoi, 1983, 1985; Bishnoi *et al.* 1985, 1986, 1989b; Dholabhai *et al.*, 1993) as well as the data obtained in this work (Chapter 4) to model the gas consumption during nucleation along with the induction time. More specifically, the objectives are as follows

a) To model the moles of gas (n in Figure 4.3) consumed with respect to time, between  $t_{tb}$  and  $t_{eq}$ , and

b) Model the 'induction time' ( $t_{tb}$  -  $t_{eq}$  in Figure 4.3).

## 5.3 Development of the nucleation model

The nucleation of gas hydrates is considered in this model to be the result of a series of sequential steps given below.

a) Dissolution of the solute gas molecule from the gas phase into the aqueous phase,

b) Incorporation of the solute gas molecule into a sub-critical hydrate nuclei,

c) Growth of sub-critical hydrate nuclei to a stable (critical) nuclei size and

d) Growth of stable (critical) nuclei to solid hydrates of atleast visual size.

The dissolution of a gas molecule from the gas phase into the aqueous phase is the key first step in the entire process and precedes the nucleation process in solution. The dissolution process continues when the nucleation process begins in the solution. The process of hydrate nucleation is considered to begin in the solution when the concentration of the dissolved gas in the solution just exceeds the amount that would dissolve at the experimental temperature and corresponding hydrate equilibrium pressure. When the nucleation process is operative in solution, the formation and growth of sub-critical hydrate nuclei take place. The nucleation process is terminated when stable hydrate nuclei form in solution.

Thus it is seen that the moles of gas consumed during the nucleation region is a result of two simultaneously occurring processes, namely, the dissolution of the gas from the gas phase to the liquid phase and the nucleation process in the liquid solution. The dissolution process is a process of mass transfer of gas molecules from the gas phase to liquid phase. The nucleation process is that which occurs in solution and leads to formation and growth of clusters of gas and water molecules to stable hydrate nuclei size. The effect of mass transfer on hydrate formation could be significant as this process is directly responsible for the generation of necessary
supersaturation in solution. Hence a suitable mass transfer model should be used to model the transfer of gas molecules into the aqueous phase. It is noted that the nucleation process occurring in the aqueous solution could affect the gas consumption curve. The onset of nucleation in solution would deplete the bulk liquid of gas molecules as these molecules get incorporated into the growing hydrate nuclei. Thus the nucleation process should aid in the transfer of more gas molecules to bulk liquid from the gas phase.

#### Modelling gas consumption during nucleation - Assumptions

Certain assumptions are made in the derivation of kinetic model for hydrate nucleation. These assumptions are discussed as below. Although both the gas to liquid mass transfer and nucleation in the aqueous solution occur together, as a first approximation it is assumed that the nucleation process in solution does not affect the consumption of gas from the gas phase during nucleation. This means that the transport of gas molecules from the gas phase to the liquid phase is independent of nucleation process in solution. There are several reasons for this approximation. Firstly, the amount of maximum supersaturation of the gas in the liquid phase prior to the hydrate formation is not large (about 10 % for methane). Since the nucleation process is entirely based on the supersaturation (being non-existent at zero supersaturation), the process only affects a fraction of the total gas concentration in the bulk solution as it proceeds. On a molecular level, a commonly accepted nucleation mechanism is one via growing clusters of sub-critical hydrate nuclei. The concentration of clusters is much less when compared to the concentration of the solute molecules in un-clustered form. Thirdly, it would give us an idea of the extent to which the nucleation process affects the gas consumption. The task of modelling the gas consumption would be much simplified by this assumption and would permit decoupling of modelling the mass transfer and nucleation processes. The film theory of mass transfer is applicable to describe the gas to liquid mass transfer occurring in the system. Both the gas phase and the liquid solution are considered well mixed and

uniform. In a vigorously agitated batch reactor system, this assumption is commonly made and considered reasonable. The water concentration change as a result of the nucleation process is considered negligible, since the amount of water consumed for the process is negligible as compared to the total water used in the experiments

Based on the above assumptions, when there is no reaction on the liquid side, the mass balance for the gas for a slice of thickness dy and unit cross-sectional area in the liquid film will give,

$$\frac{\partial^2 C}{\partial y^2} = 0 5-1$$

where C is the concentration of the gas in the film assumed uniform between y and y+dy. If the number of moles of water is assumed constant and far greater than the moles of solute, then the fugacity, f, of the gas is related to its concentration from Henry's law as below

$$f = \frac{HC}{C_w}$$
 5-2

where H is the Henry's constant and  $C_w$  is the concentration of water. From equations 5-1 and 5-2, it can be written

$$\frac{\partial^2 f}{\partial y^2} = 0$$
 5-3

Equation 5-3 can be integrated with respect to the boundary conditions, at y = 0,  $f = f_g - f_{eq}$ 

at 
$$y = y_1$$
,  $f = f_b - f_{eq}$ 

and,

where  $y_1$  is the film thickness. Integration of equation 5-3 leads to,

$$f = \frac{f_g - f_b}{y_l} y + f_g - f_{eq}$$
 5-4

It is to be noted that,

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4

$$\left(\frac{\partial f}{\partial y}\right)_{y=0} = \left(\frac{\partial f}{\partial y}\right)_{y=y_{f}}$$
 5-5

The rate of change of gas consumption from the gas phase, is given as the flux times area as follows,

$$\frac{dn}{dt} = \frac{DC_w}{H} \left(\frac{\partial f}{\partial y}\right)_{y=0} A_{gl}$$
 5-6

where  $A_{gl}$  is the area of gas liquid interface. From a mass balance of gas moles in the bulk we get,

$$\frac{df_b}{dt} = D a \left(\frac{\partial f}{\partial y}\right)_{y=y_l}$$
 5-7

where a is the area of mass transfer per unit volume. It can be seen from equations 5-5, 5-6 and 5-7 that

$$\frac{dn}{df_b} = \frac{C_w A_{gl}}{a H}$$
 5-8

Integrating equation 5-8, from the initial number of moles at zero time  $n_0$ , to moles at any time t denoted by n, we get

$$n - n_o = \frac{C_w A_{gl}}{a H} (f_b - f_{bo})$$
 5-9

where  $f_{bo}$  is the bulk fugacity corresponding to  $n_o$  at zero time. If  $n_w$  denotes the moles of water in solution, then equation 5-9 could be modified as,

$$n - n_o = \frac{n_w}{H} \left( f_b - f_{bo} \right)$$
 5-10

The expression for the bulk fugacity with respect to time could be obtained from integrating equations 5-4 and 5-7 as follows

$$f_b = f_g + (f_{bo} - f_g) e^{\frac{-De}{y_l}t}$$
 5-11

Since the diffusivity of the hydrate forming gas and the film thickness are related as follows,

$$y_l = \frac{D}{k_l} = \frac{D a}{k_l a}$$
 5-12

In the above equation the mass transfer coefficient  $k_1$  times the area a, denoted by  $k_1a$ , is determined from a solubility experiment discussed later. With equation 5-12, we can simplify equation 5-11 as given below.

$$f_b = f_g + (f_{bo} - f_g) e^{-k_f a t}$$
 5-13

Thus the use of equations 5-10 and 5-13 allow us to predict the gas consumption in moles as denoted by n with respect to time. If we take the moles dissolved at zero time,  $n_o$ , as zero then  $f_{bo}$  is also zero. In such a case, the equations

$$n = \frac{n_w f_b}{H}$$
 5-14

and equation 5-13 becomes,

$$f_b = f_g \left( 1 - \Theta^{-k_{\beta} t} \right)$$

Combining equations 5-14 and 5-15, we get

$$n = \frac{n_w}{H} f_g \left(1 - \Theta^{-k_f a t}\right)$$
 5-16

If  $n^*$  is the corresponding moles of gas that would be dissolved, at two phase equilibrium corresponding to experimental pressure,  $P_{exp}$ , and temperature,  $T_{exp}$ , then equation 5-16 could be written approximately as,

$$n = n^* (1 - e^{-k_{\mu} t})$$
 5-17

It is to be noted that equation 5-17 is an equation used to model the gas solubility in water and it predicts that the amount of gas dissolved in the solution, n, would approach n<sup>\*</sup> at infinite time. In order to use this equation we need to know the value of  $k_ia$ , which is the liquid side mass transfer coefficient times the interfacial area per unit volume of the solution for the gas in solution. The  $k_ia$ , is obtained from a solubility experiment conducted at a pressure below the three phase hydrate equilibrium pressure at the experimental temperature. It is assumed that  $k_ia$  is independent of pressure when used for modelling gas consumption during hydrate nucleation. This assumption is justified as the hydrate forming pressures for an experiment are not very much above the three phase hydrate equilibrium pressure

at the experimental temperature. The procedure for determining  $k_la$  is discussed below.

### Solubility Experiment - Determination of ka

A solubility experiment, is carried out at a pressure,  $P_{sol}$ , slightly below the three phase equilibrium pressure and at the experimental temperature,  $T_{exp}$ , of interest. As no hydrates would form, the phenomenon that occurs in this experiment is simply the dissolution of gas in the aqueous solution. The model equation, 5-17, developed in the preceding section would apply for this experiment as well where n<sup>\*</sup> is the amount of gas that would be dissolved in solution at two-phase gas liquid equilibrium corresponding to pressure  $P_{sol}$  and temperature  $T_{exp}$ . So for this experiment,

$$n = n^* (1 - e^{-k\mu t})$$
 5-18

The values of n<sup>\*</sup> and  $k_la$  are regressed from the experimental moles consumed, n, versus time, t, data of this experiment. Also, from the volume of solution  $V_{sol}$ , the equilibrium molefraction x<sup>\*</sup> corresponding to n<sup>\*</sup> is known. Hence from the conditions of the solubility experiment ( $P_{sol}, T_{exp}$ ) the fugacity of the dissolved gas at two phase gas-liquid equilibrium could be computed which when divided by x<sup>\*</sup> gives the Henry's constant.

### 5.4 Modelling moles of gas consumed with time during nucleation - Results

As assumed earlier during model development, the effect of nucleation kinetics on the gas consumption during nucleation has been neglected as a first approximation. Consequently, if only mass transfer of gas molecules into the aqueous phase is responsible for gas consumption during nucleation then the maximum number of moles, n, of the gas molecules that could ever be transferred (without

forming hydrates) to the liquid phase is that corresponding to the two-phase (gasliquid) equilibrium conditions at pressure  $P_{exp}$  and temperature  $T_{exp}$ . However, as discussed later (Figure 5.7) the moles of gas dissolved at hydrate nucleation point or turbidity point,  $n_{tb}$ , could be less than or greater than n<sup>\*</sup>. Hence it is noted that mass transfer considerations alone could not help in predicting the actual gas consumption during hydrate nucleation. Also, the precise mechanism of kinetics of nucleation process occurring in the liquid is not established from data collected in this lab or in the literature to permit taking it into account for modelling. In view of the above, it is noted that the application of the model developed in the previous section for consumption of gas during nucleation (between times  $t_{tb}$  and  $t_{eq}$ ) yielded good agreement between computed and experimental (Bishnoi *et al.* 1985, 1986, 1989b; Dholabhai *et al.*, 1993) moles consumption for methane hydrate formation as shown typically in Figures 5.1, 5.2 and 5.3. Hence the assumption made to neglect the effect of the nucleation process ocurring in the solution on the moles of gas consumed during nucleation is justified as a first approximation.

The applicability of the model to compute the moles of solute gas consumed for hydrate formation in the nucleation region was further checked against the experimental data for other pure hydrates like ethane and carbon dioxide. Plots of the results of the model against experimental data are shown in Figure 5.4 for ethane and in Figure 5.5 for carbon dioxide. The experimental procedure for carbon dioxide was slightly modified. For  $CO_2$  hydrate formation, the reactor was pressurized first to a pressure slightly below the three phase hydrate equilibrium pressure at the experimental temperature. After equilibrium was established, the reactor pressure was increased to the desired experimental pressure for the kinetic experiment. Hence the initial number of moles dissolved for  $CO_2$  hydrate formation is not zero but some value corresponding to that dissolved at a pressure slightly below the three phase hydrate equilibrium pressure at the experimental temperature as could be seen on Figure 5.5. It is seen that the model also applies reasonably well in view of the assumptions made, for ethane and carbon dioxide hydrates.

0.05 P = 5 MPa, T = 274 K0.04 Methane Consumed, moles 0.03 0.02 MH100-09 0.01 -Model 0 20 40 0 60 80 100 Time, min

Fig. 5.1 Gas Consumption Curve - Nucleation Kinetics Methane Hydrate

0.05 P = 3.74 MPa, T = 274 K0.04 Methane Consumed, moles 0.03 0.02 ---- MH100-10 0.01 Model 0 20 40 0 60 80 100 Time, min

Fig. 5.2 Gas Consumption Curve - Nucleation Kinetics Methane Hydrate



Fig. 5.3 Gas Consumption Curve - Nucleation Kinetics Methane Hydrate

# Fig. 5.4 Gas Consumption Curve - Nucleation Kinetics Ethane Hydrate

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# Fig. 5.5 Gas Consumption Curve - Nucleation Kinetics Carbon dioxide Hydrate



In summary, it could be said that with an assumption that the moles of gas transferred to the solution from the gas phase is unaffected by the nucleation processes ocurring in the solution, the model predicts the gas consumption curve in in reasonable agreement with experimental data in the nucleation region.

### **5.5 Induction Time**

The induction phenomena take place until the formation of critical sized stable hydrate nuclei. Once stable hydrate nuclei are formed, the hydrate nuclei grow as solid hydrate particles and the phenomena now is one of "hydrate growth". Strictly speaking, the time of appearance of stable hydrate nuclei should be prior to the visually observed turbidity time,  $t_{tb}$ . If  $t_{ind}$  is the true induction time and  $t_{gwh}$  is the time taken for the critical hydrate nuclei to grow to the visual size, then the induction time is given as,

$$t_{ind} = t_{tb} - t_{og} - t_{gwh} \, . \qquad 5-19$$

It was observed during the experiments that the appearance of the turbidity was quite sudden. It is identified by a sudden switching from a clear solution to a translucent one. Although the size of a critical hydrate nucleus is smaller than the particle size visible to the naked eye, the number of the critical sized stable hydrate nuclei is very large. Because of this large number, the turbidity can be visible even before an individual nucleus becomes visible. If indeed the critical sized nuclei had formed much earlier, and  $t_{gwh}$  was significant then the turbidity change in solution would likely not be so swift. Besides, there are other observations that coincide with the visual observation of the turbidity. There is a slight dip in the reactor pressure at the onset of turbidity owing to the sudden loss of supersaturation in the liquid. Also the discontinuity in the gas curve (moles of gas consumed with time) before and after the turbidity is sharp. Furthermore the temperature of the solution registers a slight but detectable rise at the turbidity point because of the heat released due to sudden formation of the stable hydrate nuclei. Based on the above observations, it is reasonable to assume that  $t_{gwh}$  is negligible and hence, equation 5-19 reduces to,

$$t_{ind} \simeq t_{ib} - t_{og} \, . \qquad 5-20$$

#### **5.6 Discussion of Results**

#### Supersaturation and Driving Force for Hydrate Nucleation

The hydrate nucleation process is similar to salt crystal nucleation. In Table 4.1, a comparison was made between the processes of hydrate nucleation as visualized in this work and salt crystal nucleation. As in salt nucleation, the supersaturation of the aqueous solution by the dissolved gas is responsible for the hydrate nucleation. Since the minimum fugacity of a hydrate forming gas in the hydrate phase at which the hydrates could exist is the three phase equilibrium fugacity, we define the supersaturation for hydrate nucleation as the concentration of the dissolved gas over that corresponding to the three phase equilibrium. In Figure 4.3, the supersaturation just prior to the turbidity is related to  $n_{tb}$  -  $n_{eq}$ . In this work the driving force for hydrate nucleation is defined as the difference between the fugacity of the dissolved gas in the liquid,  $f_g^L$ , and the three phase equilibrium fugacity,  $f_{eq}$ , both at the experimental temperature,  $T_{exp}$ . This definition of the driving force is consistent with the definition of the supersaturation in the nucleation region (Figure 4.3) and is similar to the driving force defined by Englezos et al. (1987a) for hydrate growth. Although there are similarities between hydrate and salt crystal nucleation, the hydrate nucleation is a more complex process and therefore it is important to examine the implications of the supersaturation at turbidity with respect to the hydrate metastable region.

A partial phase diagram of the methane and water system at 274 K was computed using the Trebble-Bishnoi Equation of State (Trebble and Bishnoi 1987,





1988) and is shown in Figure 5.6. In the figure  $L_w$  denotes aqueous solution, H denotes hydrate phase and G denotes the gas phase. The curve AE represents two phase gas-liquid equilibrium curve. The composition of methane corresponding to point E, Xeq, is the equilibrium composition at the three phase equilibrium pressure Peq. At pressures above  $P_{eq}$  and overall compositions above  $X_{eq}$ , only two phases can coexist in stable equilibrium - one of which has to be the hydrate phase. In this region vapor and liquid can coexist only in a metastable equilibrium state. The computed metastable equilibrium states for the liquid aqueous solution are shown as curve EC in the figure. The metastable states for the gas phase are not shown on the diagram as they are very close to the stable gas phase represented by the curve BF. Thus, the shaded region above and to the right of point E shows schematically the metastable region from the point of view of the hydrate nucleation.

Since the metastable region and its implications for hydrate kinetic experiments is of interest in this work, the metastable and other relevant regions are expanded and shown schematically in Figure 5.7, at a constant temperature. The composition of the dissolved gas, corresponding to  $P_{eq}$  is denoted by  $X_{eq}$ . At turbidity, the mole fraction of the dissolved methane is denoted by  $X_{tb}$ . The thermodynamic limit for the maximum composition of the dissolved methane in liquid without hydrate formation is represented by  $X_{ml}$ . The precise location of the thermodynamic metastable limit  $X_{ml}$  is not known. We are, however, convinced that it is greater than the maximum experimentally observed dissolved gas composition in the liquid solution, and far less than the gas composition in the hydrate phase.

All the kinetic experiments could be summarized schematically by the three paths shown in Figure 5.7a. These paths represent the possible course of a kinetic hydrate formation experiment over a period of time. The change of X with time is shown for each path in Figures 5.7b, 5.7c and 5.7d. The course of an experiment, in which the experimental pressure  $P_{exp}$  is lower than  $P_{eq}$ , is shown as path I. As a result of gas dissolution in liquid, X increases after the start of the experiment



Fig. 5.7 Schematic of Metastable Region for Hydrate Nucleation

○ - Possible Hydrate Nucleation Point (PHNP)

(Figure 5.7b) until the attainment of an equilibrium when  $X = X^*$ . Since the experimental pressure and temperature are kept constant throughout, path I is a straight line parallel to the X - axis, in Figure 5.7a, and is terminated at the point where  $X = X^{*}$ . When P is greater than  $P_{eq}$ , it is possible to obtain X greater than  $X_{eq}$ and thus there is a driving force for hydrate nucleation as defined before. Consequently, the metastable region for hydrate nucleation starts after the point where  $X = X_{eq}$ . The upper limit for X in the metastable region is  $X_{ml}$ . At this point  $(X = X_{ml})$  the appearance of hydrate phase is spontaneous if it has not occurred earlier. A typical hydrate formation experiment, is shown along path II for which the pressure P is constant and greater than  $P_{eq}$ . For this path, as seen in Figure 5.7c, X continues to increase even beyond  $X_{eq}$  and into the metastable region as time proceeds. Once in the metastable region the hydrate formation could occur randomly at any point of time. The "Possible Hydrate Nucleation Point" (or PHNP) which could be identified with turbidity points  $(X = X_{tb})$  are marked in Figure 5.7a for path II as small open circles. Along path II, while it is easy to see that  $X_{tb}$  could be less than X<sup>\*</sup>,  $X_{tb}$  could also be greater than X<sup>\*</sup>. The reason for a higher  $X_{tb}$  than X<sup>\*</sup> has been suggested before for methane hydrates as the clustering of water molecules around a dissolved methane molecule which causes the depletion of methane molecules in the bulk liquid thereby causing more gas to dissolve in the liquid beyond the two phase equilibrium value (Englezos and Bishnoi, 1988b). Since hydrate formation is basically a random phenomena occurring as a result of chance fluctutations amongst the growing sub-critical clusters of water and gas molecules, there is a distribution of PHNPs on either side of the line defined by  $X = X^*$ , along path II in the nucleation region. After hydrate formation, X falls quickly to  $X_{eq}$  owing to the release of supersaturation as a result of new (hydrate) phase formation as shown in Figure 5.7c for path II.

### Effect of Local Supersaturation

For the formation of stable hydrate nuclei all that is needed is the necessary

supersaturation in solution. The upper limit of the necessary supersaturation is the thermodynamic metastable limit. The supersaturation could manifest locally in the solution, when the gas is coming into the solution at a high mass transfer rate and when the mixing provided in the solution is not vigorous enough to destroy the localised concentration gradients in the solution. So the net effect would be for the hydrate formation to occur as determined by a higher local supersaturation rather than the measured (lower) bulk concentration. In cases where the local supersaturation effect is strong, it is possible to obtain hydrates even when bulk X is lower than  $X_{eq}$ . The effect of local supersaturation is expected at high pressure experiments and the possible course of one such experiment is shown in Figure 5.7d as path III. As seen along path III, the PHNPs could even occur apparently outside the metastable region (or when X is less than  $X_{eq}$ ). The reason for such an occurrence of PHNPs before the metastable region is the local supersaturation, where X is higher than  $X_{eq}$  locally near the gas-liquid interface while the overall bulk X is lower than  $X_{eq}$ . The local supersaturation effect should be taken into consideration when analysing hydate nucleation data. In Figure 5.7d, it is seen that local X rises quite rapidly with time and crosses into the metastable region quickly whereas the bulk X rises very slowly. A distinct point to be noted is that for path III in Figure 5.7d, the X never reaches a steady value unlike as in path II, before the formation of hydrates. If the experimental pressure  $P_{exp}$  is very high then hydrate formation could occur instantaneously at the gas-liquid interface since the concentration of the gas near the interface on the liquid side could be near that corresponding to X<sub>ml</sub>.

#### Nucleation Driving Force and Induction Time

In Figure 5.8, the experimentally obtained  $X_{tb}$  points are shown along with the metastable region. The computed two phase gas-liquid equilibrium curve defined by  $X = X^*$  is shown as a solid line before the metastable region and as a dashed line in the metastable region. The computations of the two phase gas-liquid

Fig. 5.8 Methane Hydrate at 274K - Experimental Hydrate Nucleation Point





0.002

Х

0.003

0.004

0.005

0 L 0

0.001

Fig. 5.9 Methane Hydrate - Experimental Hydrate Nucleation Point





Fig. 5.11 Carbon Dioxide Hydrate - Experimental Hydrate Nucleation Point



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equilibrium curve both inside and outside the metastable region were done using the Trebble-Bishnoi Equation of State (Trebble and Bishnoi 1987, 1988). As it was discussed through Figure 5.7, it is seen that the  $X_{tb}$  points distribute on either side of the line given by  $X = X^*$ . Quite a few  $X_{tb}$  points are observed before the metastable solution region, especially at higher experimental pressures suggesting the possibility of local supersaturation in these experiments. The same behaviour is also observed for methane at other temperatures and for ethane and carbon dioxide as shown in Figures 5.9 to 5.11.

Since the experimental  $X_{tb}$  points are distributed on either side of the twophase gas liquid metastable equilibrium line, for modelling hydrate nucleation,  $X^* - X_{eq}$ , or equivalently  $f_g^V - f_{eq}$ , is taken as the driving force rather than  $f_g^L - f_{eq}$ .

As in crystallization studies, the rate of hydrate nucleation, R, can be expressed in a power law form given below,

$$R = k (S - 1)^n$$
, 5-21

where k and n are constants. Since induction time is inversely related to the rate of nucleation (Mullin, 1972), we can write,

$$t_{ind} = \alpha / R^{r}, \qquad 5-22$$

where  $\alpha$  is another proportionality constant. Since in general the dependence of induction time on the nucleation rate could be non-linear, r may not be unity. From equations 5-21 and 5-22, we obtain

$$t_{ind} = \beta (S-1)^{-m}$$
, 5-23

where  $\beta$  is a constant and equal to  $\alpha/k$ , and m is equal to nr.

Replacing (S-1), by  $(f_g^{V}/f_{eq} - 1)$ , in equation 5-23, the following equation for hydrate induction time (Bishnoi *et al.* 1993) is obtained

$$t_{ind} = K \left( \frac{f_g^V}{f_{oq}} - 1 \right)^{-m}, \qquad 5-24$$

where "K" and "m" are constants.

As discussed in the previous chapter with respect to Figure 4.3, the available experimental data consists of moles of gas consumed with time during nucleation and a record of turbidity time for each experiment. The hydrate formation pressure,  $P_{eq}$ , was computed at the experimental temperature,  $T_{exp}$ . Then the fugacities of the hydrate forming gas were computed using an equation of state (Trebble and Bishnoi, 1987, 1988). The fugacity computed at  $P_{exp}$ ,  $T_{exp}$  is denoted by  $f_g^{V}$  and at  $P_{eq}$ ,  $T_{exp}$  by  $f_{eq}$ . The mole fraction of the dissolved gas,  $x_{eq}$ , corresponding to  $P_{eq}$ ,  $T_{exp}$  ( $f_{eq}$ ) was then computed using a suitable model (Henry's law or an equation of state). Then,  $n_{eq}$ , the dissolved moles of hydrate forming gas was computed from mole fraction  $x_{eq}$  and the volume of solution  $V_{sol}$ . If  $n_{eq}$  is thus obtained, the time,  $t_{eq}$ , when the moles of gas consumed in the experiment is  $n_{eq}$  is determined. This complete set of data was then used for the analysis of the induction times. A complete list of all the experimental data used for analysis in this work is shown in tabular form in Appendix III and is also made available in a database form on the computer.

The experimentally obtained induction times for methane are plotted against the driving force expressed as  $(f_g^{V}/f_{eq} - 1)$ , in Figure 5.12. Similar results are shown for ethane and carbon dioxide hydrates in Figures 5.13 and 5.14. The fugacities shown in Figures 5.12 to 5.14 were calculated using the Trebble - Bishnoi Equation of State (Trebble and Bishnoi, 1987, 1988). The experimental results show an







exponential dependence of induction time on the driving force. The induction time goes up very sharply for a low driving force and decreases quite rapidly as the driving force is increased. The exponential dependence of induction time data with respect to supersaturation suggests that the logarithm of the induction time should be examined. The solid line represents the expected values of induction times as computed by a regression model discussed below.

Based on equation 5-24, a plot of logarithm of  $t_{ind}$  against the log of supersaturation ( $f_g^{V}/f_{eq}$  - 1) should give a straight line relationship of the form,

$$ln(t_{ind}) = ln(K) - m ln(\frac{f_g^V}{f_{eq}} - 1)$$
 5-25

As suggested by Equation 5-25, a linear regression was performed on the induction time data for methane at all the experimental temperatures. Confidence interval analysis on the regressed parameters, K and m, at each temperature showed that within 95% interval limits, the regressed parameters, K and m, could be treated as independent of temperature. Hence, the induction time data at different temperatures were combined to estimate the model parameters, K and m. Similarly, the model parameters for ethane and carbon dioxide were obtained and all the values of the regressed parameters, K and m, are listed in Table 5.1 for the three gases. As shown in Figures 5.15 and 5.16, the induction time data for the three gases can be represented in a linear fashion with a negative slope as expected from equation 5-25. Also in Figures 5.15 and 5.16, the 95 % interval limits are shown for the predicted induction times obtained from the regression model. With 95 % confidence, it can be said that the values of experimental induction times would lie within the limits shown from the predicted induction times and is seen to include most experimental data points (Figures 5.15 and 5.16). However, as the induction times are in logarithmic coordinates (Figures 5.15 and 5.16) it is important to note

# Fig. 5.15 Log Plot - Induction Time vs Driving Force Methane Hydrate





Fig. 5.16 Log Plot - Induction Time vs Driving Force Ethane and Carbon Dioxide Hydrates

Guest Gas Species	K, s	m
Methane	311.64	-1.21
Ethane	42.85	-1.38
Carbon Dioxide	189.56	-0.91
Methane 25 % + Ethane 75 %	1448.59	-0.80
Methane 75 % +		
Ethane 25 %	989.45	-0.76
Methane + 3 % NaCl	407.29	-1.07
Methane + 3 % KCl	509.83	-2.46
Methane + 5 % KCl	76.67	-7.21
Methane + 8 % KCl	339.42	-2.31
CO <sub>2</sub> + 3 % KCl	62.30	-2.30
CO <sub>2</sub> + 5 % KCl	188.14	-1.87

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## **Table 5.1. Induction Model Parameters**

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that the deviations from the model could be significant at lower supersaturations.

Since there are a large number of data points available for methane, a standard model adequacy test was performed using the f-distribution. In particular the variance obtained by the regressed model was tested to see if it is equal to the variance computed from independent replicate experiments. The model was found to be adequate with greater than 95 % confidence.

#### Supersaturation and Supercooling

Supercooling is a long recognised process of creating supersaturation in solution and the degrees of supercooling could be used to express the driving force for nucleation (Mullin, 1972). As described before, in our experiments the aqueous solution was supersaturated with the hydrate forming gas at a temperature  $T_{exp}$  by the mass transfer of gas from the gas phase to the aqueous solution to a higher dissolved gas concentration (corresponding to pressure  $P_{exp}$ ) than that of equilibrium concentration (corresponding to  $P_{eq}$ ). In other words, the supersaturation was achieved by "super-pressurizing" the reactor well above the corresponding hydrate equilibrium pressure at the experimental temperature. It is possible to create this supersaturation by a process of supercooling as well, at a constant pressure. For instance, if we let T<sub>eq</sub> to denote equilibrium temperature corresponding to experimental pressure  $P_{\text{exp}}$  then at a temperature higher than  $T_{\text{eq}}$  and at  $P_{\text{exp}}$  there would be no hydrates. We can slowly then cool the system at constant pressure  $P_{exp}$ to a final temperature of  $T_{exp}$ . The degrees of supercooling then would be  $T_{eq}$  -  $T_{exp}$ , which would correspond to the same supersaturation that was obtained earlier by super-pressurizing at  $P_{exp}$  and  $T_{exp}$ . Consequently, in terms of driving forces, the degrees of supercooling would be the driving force for hydrate nucleation. This driving force expressed in terms of degrees of supercooling corresponds to the driving force expressed earlier in terms of fugacities. Hence we could expect the hydrate induction time data could also be interpreted with respect to the degrees of



Figure 5-17. Induction Time vs Supercooling Driving Force Methane Hydrate Formation

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supercooling. A detailed derivation of the induction time model in terms of degrees of supercooling as the driving force is given in Appendix II. As shown in Figure 5.17 for methane hydrate formation, we find that our hydrate induction data are supported by our analysis based on degrees of supercooling ( $T_{eq} - T_{f}$ , see appendix) as well.

### Application of Induction Time Model to Mixtures

The induction time model has been developed and shown to model the induction times observed in the kinetic data of pure hydrate formation. However, such a model would apply only to hydrate formation from a pure gas. In order to extend the model, the kinetic data for a hydrate forming gas mixture was analysed to see if the induction times observed could also be represented by a driving force similar to that defined earlier. The induction time for a mixture is again defined as the difference between the turbidity time,  $t_{tb}$ , and the time,  $t_{eq}$ , when the moles of gas mixture consumed,  $n_{eq}$ , corresponds to the three phase equilibrium pressure,  $P_{eq}$ , at the experimental temperature. If the composition of the gas mixture is given in terms of its molefraction, y, then  $n_{eq}$  for a mixture is obtained from the following relation.

$$n_{eq} = \sum_{i} y_{i} \hat{n}_{eq,i}$$
 5-26

where  $n_{eq,i}$ , is the moles dissolved of the component i in the mixture, at  $P_{eq}$  and  $T_{exp}$  and  $y_i$  is the mole fraction of that component. The summation in equation 5-26 is performed for all the components in the gas mixture. Similar to the form of dependence suggested by equation 5-24, the modified driving force for a gas mixture is taken as  $f_g^V/f_{eq} - 1$ , where the fugacities now represent the fugacities of the component in the gas mixture. It is to be noted that the representation of the driving force in the form of component fugacity ratio, takes into account implicitly the

# Fig. 5.18 Induction Time vs Driving Force Methane 25 % Ethane 75 % Mixture


Fig. 5.19 Induction Time vs Driving Force Methane 75 % Ethane 25 % Mixture



composition of the mixture. The induction time data for the case of two gas mixtures analysed are shown in Figures 5.18 and 5.19 with respect to the driving force for methane (*i.e*  $f_g^{V}/f_{eq}$  - 1 for methane) and the corresponding model parameters are given in Table 5.1. The dependence of induction time on the defined driving force seem to follow the same type of exponential dependence as discussed in the case of hydrate formation by single gas species.

## Application of Induction Time Model to Systems Containing Electrolytes

The induction time model as in equation 5-24, was also applied to examine the dependence of the induction time with the nucleation driving force for gas hydrate formation from aqueous electrolyte solutions. The three phase equilibrium pressure,  $P_{eq}$ , is higher for the case of hydrate formation derived from electrolyte solutions, as compared to formation from pure water at the same temperature. The increase of the thermodynamic three phase equilibrium pressure by electrolytes enables them to act as inhibitors of hydrate formation. On a molecular level, dissociated electrolytes are known to interact with the hydrogen bonding water molecules in solution. Since hydrate nucleation requires the hydrogen bonding water molecules to form clusters with gas molecules in solution thereby leading to stable critical sized nuclei, addition of electrolytes could be expected to make hydrate formation more difficult from a kinetic viewpoint as well. The induction time, for methane hydrate formation from aqueous electrolyte solutions with compositions 3, 5 and 8 weight percent KCL and 3 weight percent NaCl were analysed. Also the induction times of carbon dioxide hydrate from 3 and 5 weight percent aqueous NaCl solutions were examined. The dependence of the induction times against proposed driving force (equation 5-24) are shown in Figures 5.20 to 5.25. It is seen that the induction time dependence on the nucleation driving force is similar to the form of dependence observed in the cases before for non-electrolyte aqueous solutions. The parameters of the model for these electrolytes are also given in Table 5.1.





# Fig. 5.21 Induction Time vs Driving Force Methane + 3 % KCl



# Fig. 5.22 Induction Time vs Driving Force Methane + 5 % KCl



# Fig. 5.23 Induction Time vs Driving Force Methane + 8 % KCl



# Fig. 5.24 Induction Time vs Driving Force CO<sub>2</sub> + 3 % KCl



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# Fig. 5.25 Induction Time vs Driving Force CO<sub>2</sub> + 5 % KCl



## 5.7 Factors Affecting Nucleation

In this work, the nucleation driving force is defined and identified as a key factor affecting hydrate nucleation. The induction time data are dependent on the nucleation driving force as seen in the preceding section. However, in addition to the driving force the hydrate nucleation phenomena could be affected by other factors like surface heterogeneities of the reactor wall and stirrer, presence of impurities and thermal histories of water. Hence the experimental observations only serve to isolate the key factors that affect hydrate nucleation and the model parameters 'K' and 'm' shown in Table 5.1, could be equipment dependent. Most of the available information on hydrate nucleation are at a macroscopic level and very little is known experimentally about the sub-critical nuclei in solution. As such a detailed molecular modelling of hydrate nucleation is at present difficult and the mechanism of hydrate nucleation needs to be studied experimentally and understood before any modelling at a fundamental level could be accomplished.

Skovborg *et al.* (1993) have measured induction times for methane, ethane and their mixture hydrates. The experiments reported by them are very limited in number (total of 11) and the definition of induction times as suggested by them includes the solubility region as well. It was not possible to extract the information on induction times, defined here, from their (Skovborg *et al.*, 1993) presented data for the application of the model developed in this work. Hence the model developed in this work could not be applied to explain the limited experimental data measured by Skovborg *et al.* (1993).

Recently Sloan and Fleyful (1991) proposed a model based on the experimental data of Falabella (1975). It was observed from the data that methane and krypton hydrates exhibited induction times during their formation, whereas other gases like xenon, acetylene, ethane, ethylene and carbon dioxide did not show any induction times. Also Falabella (1975) data showed no induction time for a mixture

Gas	f <sub>g</sub> <sup>v</sup> , kPa	T <sub>exp</sub> , K	f <sub>eq</sub> , kPa	$f_g^{V}/f_{eq}$	Remarks
Methane	100.04	183	54.71	1.830	Induction Observed
Krypton	99.79	183	39.17	2.548	Induction Observed
Xenon	12.96	183	0.782	16.578	Induction Not Observed
Acetylene	80	183	4.405	18.160	Induction Not Observed
Ethylene	78.44	183	2.70	29.063	Induction Not Observed
Ethane	97.88	183	1.87	52.454	Induction Not Observed
CO <sub>2</sub>	78.62	183	10.74	7.322	Induction Not Observed
Methane 90 %	90.05 (CH <sub>4</sub> )	183	12.15 (CH <sub>4</sub> )	7.411	Induction Not Observed
+ Ethane 10 %	9.84 (C <sub>2</sub> H <sub>6</sub> )	183	1.35 (C <sub>2</sub> H <sub>6</sub> )	7.289	

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 Table 5.2
 Fugacity Ratios for Induction Time Observations

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As was shown with our induction data, the driving force, expressed as the difference of  $f_g^V$  and  $f_{eq}$  at the experimental temperature, affects hydrate nucleation. Hence, qualitatively we can expect to observe induction if the ratio of  $f_g^V/f_{eq}$  is low and observe practically no induction time if the ratio is very large. In Table 5.2, we have calculated and shown the  $f_g^V/f_{eq}$  values along with the experimental observations made by Falabella in the remarks column in the same table for methane, krypton, xenon, acetylene, ethylene, ethane and carbon dioxide. From the table, it is seen that the observations of Falabella (1975) regarding the presence or absence of induction is in agreement with what we could expect based on computed values of the  $f_g^V/f_{eq}$  ratios. It should be noted that Falabella (1975) studied hydrate formation from ice whereas our study is confined to hydrate formation from aqueous solutions.

The data obtained by Falabella (1975) show that the mixtures of methane and ethane do not show induction whereas pure methane exhibits induction during hydrate formation. As we have only modelled the induction exhibited by single hydrate formers in this work, the driving force proposed here cannot be directly applied to the mixture data. In a preliminary sense, however, we have computed  $f_g^{V}/f_{eq}$  ratios for methane and ethane in the mixture studied by Falabella (1975), where the  $f_g^{V}$  and  $f_{eq}$  now represent fugacities of a component in a mixture. Thus it is seen from Table 5.2 that the addition of even 10% of ethane to pure methane increases substantially the  $f_g^{V}/f_{eq}$  ratio for the components, and therefore induction is not expected for the methane-ethane mixture.

Sloan and Fleyful (1991) suggested that a guest:cavity size ratio between 0.81 and 0.89 for the small cavities is responsible for exhibiting the induction phenomena. Accordingly, carbon dioxide should not exhibit induction as the size ratio for carbon

Gas Hydrate Nucleation Mechanism				
Proposed by E.D.Sloan <i>et al.</i>	This Work			
AIChE, Sept. 1991	Model			
Proposed for nucleation from ice	Proposed for nucleation from ice and aqueous solutions			
Key nucleation parameter is size of the guest gas molecule to cavity diameter ratio (size ratio)	Key Nucleation parameter is $f_g/f_{eq}$ corresponding to experimental hydrate kinetic run temperature (fugacity ratio)			
Size ratio between 0.81 and 0.89 for	Low values of fugacity ratio could			
small cavities is susceptible to the	result in the observance of induction			
induction time	time			
Could explain the observance of	Could explain the observance of			
induction time in Falabella's kinetic	induction time in Falabella's kinetic			
data (Falabella, 1975) for methane and	data (Falabella, 1975) for methane			
krypton	and krypton			
Could explain the non observance of	Could explain the non observance of			
induction time in Falabella's kinetic	induction time in Falabella's kinetic			
data for xenon, acetylene, ethylene,	data for xenon, acetylene, ethylene,			
ethane and carbon dioxide and	ethane and carbon dioxide and			
mixture of ethane and methane	mixture of ethane and methane			
Could not be applied to explain the induction time exhibited by carbon dioxide hydrate nucleation from aqueous solutions	Could explain the induction time observed for carbon dioxide hydrate nucleation from aqueous solutions			

# Table 5.3. Comparison of model and Sloan et al. (1991) model

dioxide is clearly outside the prescribed range. However, as discussed before in the present work for low values of the  $f_g^{V}/f_{eq}$  ratio carbon dioxide hydrate could exhibit induction. In Figure 5.14, our experimental data for carbon dioxide hydrate kinetics does show observed induction time as high as 185 minutes. A summary of the comparison of the model proposed in this work with Sloan *et al.* (1991) model is shown in Table 5.3.

In summary, it is shown that the nucleation model satisfies the objectives set out for modelling as elucidated in the beginning of this chapter. However, although the model is successful in modelling the nucleation region data collected in the laboratory, it does not provide much insight into the nucleation process itself. At this juncture it is felt there is need for more microscopic data on nucleation phenomena for developing a more fundamental nucleation model.

### 5.8 Unified Treatment of Hydrate Nucleation, Growth and Decomposition

It is possible to provide a unified approach to understanding the kinetics of hydrate formation and decomposition in aqueous liquid solutions including the phenomenon of hydrate nucleation. The approach is based on the fact that the hydrate formation or decomposition kinetics depends on the conditions like pressure and temperature relative to the hydrate equilibrium curve. The driving force based on the difference between the dissolved gas fugacity and its equilibrium value is used for the formation and decomposition kinetics. A partial schematic three phase (hydrate-liquid water-gas) equilibrium curve, B-A-C-F, is shown in Figure 5.26. A hydrate formation experiment would need to be conducted above the equilibrium curve, whereas a hydrate decomposition experiment would be conducted below the curve, after initially forming the hydrates. Let E and D denote the conditions of a hydrate formation experiment ( $P_{ty}T_{exp}$ ) and a hydrate decomposition experiment ( $P_{dy}T_{exp}$ ) respectively. Since the minimum fugacity at which the hydrates can exist is the three phase equilibrium fugacity, the conditions at the particle surface move



along the equilibrium curve during its growth or decomposition. If the experiment is conducted isothermally and the particle is maintained at the experimental temperature  $(T_{exp})$ , point A represents the conditions of the growing or decomposing hydrate particle. In a hydrate formation experiment, if the heat transfer resistance around a particle is significant the temperature of the particle would move on the equilibrium curve to point C which is higher than  $T_{exp}$ . In a similar manner, for a hydrate decomposition experiment if the heat transfer resistance is significant the temperature of the particle would move to point C which is higher transfer resistance is significant the temperature of the particle would move on the equilibrium curve to point B which is lower than  $T_{exp}$ .

The kinetics of hydrate nucleation has been discussed in detail before in this chapter and the induction times of several hydrates were shown to be dependent on the proposed nucleation driving force  $(f_1^g - f_{eq})$ . The kinetic models of hydrate growth and decomposition are reviewed very briefly, below, to illustrate the similarity of the driving force in them.

#### Hydrate Growth Model

The kinetics of hydrate growth has been successfully modelled for hydrate formation from pure gases and gas mixtures by Englezos *et al.* (1987a, 1987b). The model considers the difference in fugacities of the dissolved gas in the liquid and the equilibrium fugacity at hydrate surface temperature as the driving force. The hydrate formation is visualized as a two step process. In the first step, the dissolved gas diffuses from the bulk of the solution to the crystal-liquid interface through the laminar diffusion layer around a particle. In the next step, an adsorption 'reaction' occurs at the interface that incorporates the gas molecules into the clustered water molecule network and subsequently stabilizes the network. The gas consumption rate for hydrate growth is given as follows,

140

$$\frac{dn}{dt} = \sum_{1}^{N_h} \frac{dn_j}{dt} = \sum_{1}^{N_h} K_j^* A_p (\hat{f}_g^L - f_{eq})_j$$
 5-27

where  $K_j^*$  and  $(\hat{f}_g^{L}-f_{eq})_j$  are the individual rate constants and driving forces. The fugacity  $(\hat{f}_g^{L})_j$  is the dissolved gas fugacity of the component in the solution and  $f_{eq,j}$  is the fugacity of the component j at the three phase equilibrium pressure for the gas mixture. In equation 5-27,  $N_h$  is the number of hydrate forming gases. With  $N_h$  equal to unity, Equation 5-27 could be used to model hydrate formation from pure gases. The rate constants  $K_j^*$ s, are obtained from modelling experimental data for hydrate formation from pure gases and have been determined for methane, ethane and carbon dioxide hydrates. Using these rate constants, Equation 5-27 was successfully applied by Englezos *et al.* (1987b) to predict the hydrate growth kinetics for mixtures of ethane and methane. Recently, Dholabhai *et al.*(1993) have shown that Equation 5-27 could be also applied for methane hydrate formation in the presence of electrolyte solutions, using the rate constant for methane as determined before from pure water data.

#### Hydrate Decomposition Model

The decomposition of hydrates were studied by Kim *et al.* (1985). The process was visualized as the destruction of the clathrate host lattice at the surface of the particle followed by the desorption of the guest gas molecule from the surface. As a result of decomposition occurring at the surface of the particle the particle shrinks as decomposition proceeds. As their system was well stirred the driving force for hydrate decomposition becomes the difference in fugacities of the gas at three phase equilibrium pressure and the value in the bulk gas phase. This driving force for hydrate decomposition is shown in Figure 5.27. For an isothermal decomposition kinetics experiment the driving force for decomposition would correspond to the



Fig. 5.27 Hydrate Decomposition Driving Force

fugacity difference between points A and D ib Figure 5.26. The rate of decomposition for a hydrate particle is given by,

$$-\frac{dn_H}{dt} = K_q A_p (f_{eq} - f_g^V) . \qquad 5-28$$

The kinetic constant  $K_d$ , was obtained by fitting experimental methane hydrate decomposition data and was found to have an Arrhenius type temperature dependence.

## **5.9 Conclusions**

In conclusion, it is said that the nucleation model was developed to satisfy the modelling objectives set out earlier. Specifically, the gas consumption during nucleation and the dependence of induction time on supersaturation are modelled. It is also shown that the approach proposed by the model could successfully account for the induction phenomena observed by Falabella for hydrate nucleation from ice. The proposed nucleation model could also be looked at in a unified perspective with other hydrate models for hydrate growth and decomposition. Such a unification is shown possible due to the similarity of the driving forces defined for hydrate nucleation, growth and decomposition. It is mentioned that the model, should be considered as a preliminary model for hydrate nucleation based on observed kinetic data available so far. As more and more microscopic experimental nucleation kinetic data for hydrates become available, there would be a possibility of developing a more fundamentally based model for modelling hydrate nucleation.

# **CHAPTER 6**

## CONCLUSIONS AND RECOMMENDATIONS

## **6.1 Conclusions**

a) It is found that Langmuir constants are more reliable indicators of hydrate structure than computed hydrate formation pressure. Constants obtained through simulation of Argon and Krypton as Structure II hydrates using the Metropolis Monte Carlo method are found to be in agreement with experimentally obtained constants.

b) The method of Monte Carlo simulation applied to Langmuir constant computations as suggested by Tester *et al.* (1972) is not recommended as the results obtained using this method are found to be incorrect for guest molecules with a high LJ potential parameter,  $\sigma$ . The direct numerical multi-dimensional integration should instead be used for computing Langmuir constants.

c) In this experimental study of hydrate formation kinetics conducted with a well stirred system, it is found that the structure of water has no noticeable effect on hydrate induction times.

d) It was observed that there is a greater variation in induction times at lower supersaturation than at higher supersaturation for hydrate formation kinetics experiments with both structured and unstructured water.

e) The induction time model proposed in this work based on hydrate formation data from aqueous solutions also qualitatively explains the observed induction times for hydrate formation from ice reported in the literature. f) The proposed induction time model also accounts for induction time variation with the driving force expressed in terms of supercooling rather than supersaturation.

g) As a result of this work, it is now possible to view the modelling of hydrate nucleation, growth and decomposition processes in a unified manner through the similarities in the driving force for all these processes.

#### **6.2 Recommendations**

a) The parameters used in the correlation of chemical potential of water needs to be rationalised. Currently one needs a set of consistent parameters in order to obtain the chemical potential of water required in the computation of hydrate equilibrium pressures.

b) Efforts should be focussed on a more rational way of obtaining the inter molecular potential parameters used in the Langmuir constant computations. At present most of the published work have their own set of potential parameters.

c) Hydrate nucleation experiments should be conducted preferably at low supersaturation conditions to suppress mass transfer effects and enhance nucleation effects.

d) Experimental data on sub-critical hydrate nuclei are needed. There is a strong need to make more microscopic experimental observations regarding nuclei particle size distributions, nuclei composition, growth of nuclei in solutions and the memory effect as related to "structures" existing in solution.

e) The induction time model proposed in this work should be extended to hydrate formation from gas mixtures and to formation from electrolyte solutions.

f) Further experimental study is needed to understand the effect of other factors on nucleation. In particular the effect of impurities, thermal history of water, surface heterogeneities of the reactor wall and stirrer should be studied.

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# **APPENDIX I**

#### **APPENDIX I**

## Computed X,Y,Z Co-ordinates of Oxygen Atoms Using Crystallographic Data of Wak and McMullan(1965) Structure II Hydrates

Pentagonal Dodecahedron Centered at (1.125, 1.125, 1.125)

X	Y	Z	Distance from Cell Center, °A
1.0000	1.0000	1.0000	3.7477
0.9077	1.0923	1.0923	3.8457
0.9426	1.0574	1.2449	3.9555
1.2500	1.2500	1.2500	3.7477
1.3423	1.1577	1.1577	3.8457
1.3074	1.1926	1.0051	3.9555
1.0923	0.9077	1.0923	3.8457
1.0574	0.9426	1.2449	3.9555
1.1577	1.1577	1.3423	3.8457
1.0923	1.0923	0.9077	3.8457
0.9426	1.2449	1.0574	3.9555
1.2449	1.0574	0.9426	3.9555

## Computed X,Y,Z Co-ordinates of Oxygen Atoms Using Crystallographic Data of Wak and McMullan(1965) Structure II Hydrates Pentagonal Dodecahedron Centered at (1.125, 1.125, 1.125)

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X	Y	Z	Distance from Cell Center, °A
1.1557	1.3423	1.1577	3.8457
1.1926	1.3074	1.0051	3.9555
1.0574	1.2449	0.9426	3.9555
1.1926	1.0051	1.3074	3.9555
1.3074	1.0051	1.1926	3.9555
1.2449	0.9426	1.0574	3.9555
1.0051	1.3074	1.1926	3.9555
1.0051	1.1926	1.3074	3.9555

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## Computed X,Y,Z Co-ordinates of Oxygen Atoms Using Crystallographic Data of Wak and McMullan(1965) Structure II Hydrates

Hexakaidecahedron Centered at (-0.25, -0.25, 0.75)

X	Y	Z	Distance from Cell Center, °A
-0.0923	-0.0923	0.9077	4.7281
-0.0574	-0.0574	0.7551	4.7157
-0.3074	-0.1926	1.0051	4.6340
-0.0923	-0.4077	0.5923	4.7281
-0.0574	-0.4426	0.7449	4.7157
-0.0574	-0.2449	0.9426	4.7157
-0.1926	0.0051	0.6926	4.6340
-0.2449	-0.0574	0.9426	4.7157
0.0051	-0.3074	0.8074	4.6340
-0.4077	-0.4077	0.9077	4.7281

## Computed X,Y,Z Co-ordinates of Oxygen Atoms Using Crystallographic Data of Wak and McMullan(1965) Structure II Hydrates

Hexakaidecahedron Centered at (-0.25, -0.25, 0.75)

X	Y	Z	Distance from Cell Center, °A
-0.4426	-0.2551	0.9426	4.7157
-0.4077	-0.0923	0.5923	4.7281
-0.2551	-0.0574	0.5574	4.7157
-0.5051	-0.1926	0.8074	4.6340
-0.1926	-0.1926	0.4949	4.6340
-0.4426	-0.4426	0.7551	4.7157
-0.4426	-0.0574	0.7449	4.7157
-0.3074	-0.3074	0.4949	4.6340
-0.1926	-0.3074	1.0051	4.6340

## Computed X,Y,Z Co-ordinates of Oxygen Atoms Using Crystallographic Data of Wak and McMullan(1965) Structure II Hydrates

Hexakaidecahedron Centered at (-0.25, -0.25, 0.75)

X	Y	Z	Distance from Cell Center, °A
-0.0574	-0.2551	0.5574	4.7157
-0.4426	-0.2449	0.5574	4.7157
-0.1962	-0.5051	0.8074	4.6340
-0.3074	-0.5051	0.6926	4.6340
-0.3074	0.0051	0.8074	4.6340
-0.2551	-0.4426	0.9426	4.7157
-0.2449	-0.4426	0.5574	4.7157
-0.5051	-0.3074	0.6926	4.6340
0.0051	-0.1926	0.6926	4.6340

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# **APPENDIX II**

#### **APPENDIX II**

#### Supersaturation and Supercooling

Derivation of Induction Time Model with Supercooling

In this appendix, the induction time model as derived already in Chapter 5 is (Equation 5-24) is expressed equivalently in terms of supercooling as nucleation driving force with the help of the three phase hydrate equilibrium curve.

Let  $P_{exp}$ ,  $T_{exp}$  be the experimental pressure and temperature and  $P_{eq}$  be the hydrate equilibirum pressure at temperature  $T_{exp}$ . Let  $T_{eq}$  be the hydrate equilibrium temperature corresponding to  $P_{exp}$ . Also let  $f_{exp}$  to denote the fugacity of the hydrate forming gas at  $P_{exp}$ ,  $T_{exp}$  and  $f_{eq}$  at  $P_{eq}$ ,  $T_{exp}$ . From Equation 5-24 we have for induction time, t, as below

$$t = K \left(\frac{f_{exp}}{f_{eq}} - 1\right)^{-m}$$
 All-1

where "K" and "m" are constants as defined in Equation 5-24. Now since  $f_{eq}$  is a hydrate equilibrium fugacity computed at  $P_{eq}$ ,  $T_{exp}$  the dependence of  $f_{eq}$  on temperature  $T_{exp}$  could be expressed by the following equation

$$\ln(f_{eq}) = A - \frac{B}{T_{exp}}$$
All-2

in which "A" and "B" are fitted constants using hydrate equilibrium data.

If  $T_f$  be the temperature corresponding to equilibrium fugacity of  $f_{exp}$  then the degrees of supercooling is given by  $T_{exp}$  -  $T_f$  for a fugacity change  $f_{exp}$  -  $f_{eq}$ .  $T_f$  would be higher than  $T_{exp}$  but lower than  $T_{eq}$ . Similar to equation AII-2, since the point  $f_{exp}$ ,

T<sub>f</sub> corresponds to equilibrium we can write,

$$\ln(f_{exp}) = A - \frac{B}{T_f}$$
All-3

Since B is the slope of the linear relationship represented by equations AII-2 or AII-3, combining equations AII-2 and AII-3 we get

$$\frac{f_{\exp}}{f_{eq}} = \Theta^{B(\frac{1}{T_f} - \frac{1}{T_{exp}})}$$
All-4

From equations AII-1 and AII-4 we get for t as given by equation AII-5.

$$t = K \left( e^{B \left( \frac{1}{T_f} - \frac{1}{T_{exp}} \right)} -1 \right)^{-m}$$
All-5

If we expand the term in the exponential in the above equation and drop terms with powers higher than 1, we can write the above equation as

$$t = K \left(\frac{B}{T_f} \left(\frac{T_f}{T_{exp}} - 1\right)\right)^{-m}$$
All-6

Equation AII-6 could then be written in the final form as given below.

$$t = K \left(\frac{B}{T_f}\right)^{-m} \left(\frac{T_f}{T_{exp}} - 1\right)^{-m}$$
All-7

Equation AII-7 represents the necessary model relation between induction time and the nucleation driving force expressed in degrees of supercooling.

## **APPENDIX III**

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Run #	P <sub>exp</sub> bars	°C ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>V</sup> bars
MTH100-01	83.58	8.86	0.0389	0.0242	90.5	14	300	400	63.03	53.87	68.46
MTH100-02	89.03	8.98	0.032	0.0244	35.5	16.5	300	400	63.8	54.44	72.14
MTH100-03	85.9	8.98	0.0439	0.0244	41	9.5	300	400	63.8	54.44	70.04
MTH100-04	80	9	0.0561	0.0253	140	24.5	300	400	63.92	54.53	66.04
MTH100-09	50.5	0.87	0.0236	0.0182	23	13.4	300	400	28.79	26.51	43.91
MTH100-10	37.44	0.87	0.0249	0.0183	56.5	19.8	300	400	28.79	26.51	33.7
MTH100-11	34.87	0.87	0.0211	0.0183	53.5	32.4	300	400	28.79	26.51	31.61
MTH100-12	32.94	1	0.0232	0.0185	15.35	44	300	400	29.16	26.82	30.02
MTH100-14	72.53	6	0.0356	0.0241	45	12.5	300	400	47.46	41.87	60.41
MTH100-15	83.98	5.88	0.0291	0.0242	21	14.8	300	400	46.91	41.44	68.18
MTH100-16	63.95	5.88	0.0329	0.0238	96	22	300	400	46.91	41.44	54.31
MTH100-17	57.94	5.88	0.0321	0.0237	74	18	300	400	46.91	41.44	49.91

Appendix III. Methane Hydrate - Nucleation Data Table

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Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
MTH100-18	53.93	5.88	0.0408	0.0236	498	36.5	300	400	46.91	41.44	46.9
MTH100-21	48.57	2.75	0.025	0.0206	38.5	18	300	400	34.56	31.38	42.58
MTH100-22	48.58	2.75	0.0395	0.0208	300	11.5	300	450	34.56	31.38	42.58
MTH100-23	48.57	2.75	0.0273	0.0208	49.5	23	300	350	34.56	31.38	42.58
MTH100-24	48.57	2.88	0.0233	0.0201	64.5	48	300	300	35	31.75	42.58
MTH100-25	48.57	2.88	0.027	0.0212	30	15.5	300	400	35	31.75	42.58
MTH100-26	48.58	2.75	0.0153	0.0207	28	35	300	400	34.56	31.38	42.58
MTH100-29	93.05	8.86	0.037	0.0243	53.5	14.5	300	400	63.03	53.86	74.77
MTH100-31	89.11	8.86	0.04	0.024	117	23.5	300	400	63.03	53.86	72.17
MTH100-32	84.07	6	0.0352	0.0241	72	18.51	300	400	47.46	41.87	68.27
MTH100-33	66.04	0.87	0.0242	0.0183	21	14	300	400	28.79	26.51	55.19
MTH100-34	50.5	0.87	0.0319	0.0185	75	20.5	300	400	28.79	26.51	43.91

Appendix III. Methane Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
MTH100-35	65.96	1	0.02	0.0187	5.5	4.5	300	400	29.16	26.82	55.15
MTH100-39	37.03	2.75	0.0407	0.0207	1226.5	48.75	300	400	34.56	31.38	33.45
MTH100-40	36.96	2.88	0.032	0.021	415	66	300	400	35	31.75	33.4
MTH100-41	36.96	2.75	0.0391	0.0208	642	31.5	300	450	34.56	31.38	33.39
MTH100-42	36.96	2.75	0.0402	0.0207	1073.5	39	300	425	34.56	31.38	33.39
MTH100-43	36	2.9	0.0133	0.022	202.5	285	300	350	35.06	31.81	32.61
MTH100-44	36.93	3.01	0.0145	0.0136	187.5	95.5	190	550	35.44	32.12	33.38
MTH100-45	36	2.9	0.0236	0.0134	926.5	22	190	525	35.06	31.81	32.61
MTH100-46	36	2.9	0.0216	0.0134	267.5	5.25	190	500	35.06	31.81	32.61
MTH100-47	36	2.9	0.022	0.0134	411	3.75	190	450	35.06	31.81	32.61
MTH100-48	36	2.9	0.025	0.0134	320.5	3.75	190	400	35.06	31.81	32.61
MTH100-49	36	2.9	0.0194	0.0137	226.5	15	190	350	35.06	31.81	32.61

Appendix III. Methane Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
MTH100-50	36.96	2.75	0.0172	0.013	180.75	14.25	190	300	34.56	31.38	33.39
MTH100-51	36.94	2.88	0.0189	0.0134	84.5	3.75	190	550	35	31.75	33.38
MTH100-52	36.87	2.88	0.0217	0.0134	329.5	21	190	525	35	31.75	33.32
MTH100-53	48.49	3.01	0.0173	0.0155	285	2	190	550	35.44	32.12	42.53
M100-103	43.41	1.1	0.0204	0.0188	24	21	300	400	29.64	27.23	38.47
M100-104	38.28	1.1	0.0177	0.0188	21.5	25	300	400	29.67	27.26	34.39
M100-105	32.84	1.1	0.02	0.0188	70	49	300	400	29.67	27.26	29.94
M100-106	35.69	1.1	0.0204	0.0188	61	38	300	400	29.67	27.26	32.29
M100-107	33.97	1.1	0.0201	0.0187	53	39.5	300	400	29,5	27.11	30.87
M100-108	53.83	1.2	0.0174	0.0191	15.1	17	300	400	29.67	27.26	46.43
M100-109	50.71	1.1	0.0179	0.0192	14.5	16	300	400	29.67	27.26	44.08
M100-111	38.33	1.1	0.0209	0.019	26.5	21	300	400	29.67	27.26	34.43

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Appendix III. Methane Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
M100-112	32.81	1.1	0.0216	0.019	107	34	300	400	29.67	27.26	29.91
M100-113	58.82	1.2	0.0156	0.0194	11	14	300	400	29.67	27.26	50.09
M100-114	58.78	1.2	0.0301	0.0193	39.75	16	300	400	30.05	27.58	50.06
M100-115	53.8	1.2	0.0179	0.019	18	20.5	300	400	29.96	27.5	46.4
M100-116	50.77	1.3	0.0235	0.0193	27.5	18	300	400	30.08	27.61	44.14
M100-117	53.88	1.4	0.0236	0.0191	22.5	15.5	300	400	29.99	27.58	46.48
M100-118	53.81	1.2	0.0214	0.0209	23	22	300	400	30.05	27.58	46.41
M100-119	60.7	1.1	0.0294	0.0193	41	14.5	300	400	29.96	27.5	51.43
M100-120	Ġ4.7	1.1	0.017	0.0193	10.5	12	300	400	29.96	27.5	54.28
M100-122	53.76	1.1	0.0194	0.0188	14	13.5	300	400	29.64	27.23	46.37
M100-123	43.8	1.2	0.0227	0.0204	26.5	23.5	300	400	29.38	27.01	38.78
M100-124	43.88	1.1	0.0217	0.0189	25.5	19	300	400	29.38	27.01	38.83

Appendix III. Methane Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> °C	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
M100-125	43.91	1.1	0.0191	0.0187	14.5	14	300	400	29.16	26.82	38.86
M100-126	40.3	1.1	0.0204	0.0186	26.24	22	300	400	29.38	27.01	36.01
M100-127	38.87	1.1	0.0206	0.019	20.5	15.5	300	400	29.38	27.01	34.86

Appendix III. Methane Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
ETH100-02	18.91	8.86	0.0116	0.0108	51.6	37.6	300	400	14.99	12.74	15.41
ETH100-6A	14.92	5.88	0.0071	0.0089	21	28.2	300	400	10.33	9.22	12.66
ETH100-07	12.82	5.88	0.0077	0.0095	45	51.6	300	400	10.33	9.22	11.14
ETH100-08	11.8	5.63	0.0099	0.0087	63	40.8	300	400	10.02	8.97	10.37
ETH100-09	10.83	5.75	0.0124	0.0102	199.2	151.2	300	400	10.17	9.09	9.63
ETH100-11	17.88	2.88	0.0025	0.007	6	18	300	400	7.17	6.62	14.56
ETH100-12	12.83	2.88	0.0076	0.0072	30.6	28.82	300	400	7.17	6.62	11.1
ETH100-13	9.79	2.88	0.0072	0.007	39	38.4	300	400	7.17	6.62	8.78
ETH100-14	8.26	2.75	0.0071	0.0069	63	61.2	300	400	7.06	6.52	7.54
ETH100-15	7.3	3.01	0.0057	0.0071	260	307.8	300	400	7.29	6.72	6.73
ETH100-17	16.83	1	0.0028	0.0028	7.8	13.8	300	400	5.72	5.4	13.83
ETH100-18	12.82	0.87	0.0056	0.006	16.8	18.6	300	400	5.63	5.28	11.06

Appendix III. Ethane Hydrate - Nucleation Data Table

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Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ⁰C	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
ETH100-20	9.86	0.87	0.0044	0.0067	12.6	17.4	300	400	5.63	5.28	8.81
ETH100-21	7.62	1	0.0063	0.0061	34.2	32.4	300	400	5.72	5.4	6.99
ETH100-22	6.36	1	0.0066	0.0076	58.8	72.6	300	400	5.72	5.4	5.92
ETH100-23	5.63	1.12	0.0079	0.0076	240	133.8	300	400	5.8	5.43	5.29

Appendix III. Ethane Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> °C	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>V</sup> <sub>g</sub> bars
RCO2-08	15.88	1.1	0.3016	0.2799	23.4	7	300	400	14.1	12.65	14.07
RCO2-09	14.68	1.4	0.3117	0.2897	13.5	8	300	400	14.6	13.05	13.13
RCO2-10	19.88	1.59	0.302	0.2942	7.2	6.5	300	400	14.9	13.29	17.07
RCO2-11	21.88	1.59	0.2753	0.2753	4.75	9	300	400	14.9	13.29	18.49
RC02-12	23.88	1.5	0.2754	0.2754	5.65	8.5	300	400	14.7	13.13	19.84
RCO2-40	19.88	1.2	0.291	0.2825	9.35	8.5	300	400	14.2	12.73	17.06
RCO2-41	18.88	1.2	0.2826	0.2826	4.25	4.5	300	400	14.2	12.73	16.33
RC02-42	17.88	1.2	0.2857	0.281	12.25	11.5	300	400	14.2	12.73	15.59
RCO2-17	19.88	3.08	0.3413	0.3094	21.5	6.5	300	400	17.7	15.47	17.11
RCO2-18	21.88	3.38	0.3685	0.3685	39.25	8.5	300	400	18.4	16	18.55
RCO2-19	23.38	3.18	0.3789	0.3104	24.75	5.5	300	400	18	15.47	19.57
RCO2-20	24.88	3.18	0.3755	0.3098	12.5	3.5	300	400	18	15.47	20.58

Appendix III. Carbon Dioxide Hydrate - Nucleation Data Table

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
RCO2-38	23.88	3.18	0.3403	0.3109	11.5	6	300	400	18	15.47	19.91
RCO2-39	21.88	3.18	0.3696	0.3094	49.75	5.5	300	400	18	15.47	18.54
RCO2-24	24.38	5.16	0.4163	0.3624	200	13.5	300	400	22.9	19.27	20.33
RCO2-25	26.38	5.16	0.4018	0.3641	49	10.5	300	400	22.9	19.27	21.65
RCO2-26	29.38	5.16	0.3546	0.3642	9.3	11	300	400	22.9	19.27	23.54
RCO2-27	27.88	5.16	0.4088	0.3648	19.5	9	300	400	22.9	19.27	22.61
RCO2-32	26.88	5.86	0.4114	0.391	44.8	14	300	400	25	20.72	22.01
RCO2-33	28.38	5.86	0.3974	0.3916	17.4	15	300	400	25	20.72	22.96

Appendix III. Carbon Dioxide Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars
M25E75-01	23.91	8.11	0.0147	0.007336	155	14.8	300	400	14.67
M25E75-02	21.67	7.99	0.01571	0.007253	97	11.6	300	400	14.47
M25E75-03	19.92	8.11	0.01328	0.007344	212	14	300	400	14.67
M25E75-04	17.83	7.99	0.01448	0.00725	232	19	300	400	14.47
M25E75-07	19.87	1.12	0.01225	0.005552	13	13.8	300	400	6.68
M25E75-08	12.8	1	0.01084	0.005482	21	11	300	400	6.59
M25E75-10	7.29	0.87	0.01021	0.005399	56	17	300	400	6.49
M25E75-11	6.82	0.87	0.01011	0.005403	230	20	300	400	6.49
M25E75-13	19.88	5.01	0.01315	0.005459	13	5.8	300	400	10.351
M25E75-14	16.88	5.01	0.01146	0.005459	24	6.4	300	400	10.351
M25E75-24	9.45	3.01	0.0101	0.005525	163	12.8	300	400	8.267

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Appendix III. Methane 25 %, Ethane 75 % Mixture Hydrate - Nucleation Data Table

Run #	f <sub>g,c1</sub> bars	f <sub>g,c2</sub> bars	f <sub>eq,c1</sub> bars	f <sub>eq,c2</sub> bars
M25E75-01	5.87	13.83	3.61	9.42
M25E75-02	5.32	12.86	3.56	9.32
M25E75-03	4.89	12.07	3.61	9.42
M25E75-04	4.38	11.06	3.56	9.32
M25E75-07	4.87	11.85	1.65	4.65
M25E75-08	3.15	8.31	1.63	4.59
M25E75-10	1.8	5.04	1.61	4.53
M25E75-11	1.69	4.74	1.61	4.53
M25E75-13	4.88	11.96	2.55	6.95
M25E75-14	4.15	10.52	2.55	6.95
M25E75-24	2.33	6.39	2.04	5.67

Appendix III. Methane 25 %, Ethane 75 % Mixture Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars
M75E25-01	61.02	10.86	0.04049	0.009794	78	8	300	400	35.33
M75E25-02	56	11.33	0.02024	0.010286	32	9.4	300	400	37.28
M75E25-03	51.08	11.2	0.01237	0.010149	0.8	6.01	300	400	36.73
M75E25-04	46.04	11.08	0.01414	0.01002	9	6.01	300	400	36.23
M75E25-05	41	11.2	0.02424	0.010149	104.5	10.5	300	400	36.73
M75E25-07	40.9	8.36	0.01953	0.009905	81.4	10.6	300	400	26.78
M75E25-12	28.95	8.11	0.0261	0.00966	693.5	16	300	400	26.06
M75E25-13	35.98	8.11	0.02307	0.00966	34	9	300	400	26.06
M75E25-17	25.89	5.25	0.015	0.008719	130	10.6	300	400	19.16
M75E25-18	23.91	5.13	0.01338	0.008613	47	11.6	300	400	18.92
M75E25-21	21.93	5.13	0.01372	0.008613	35.5	12	300	400	18.92
M75E25-22	20.99	5.25	0.01325	0.008714	41	15	300	400	19.16

## Appendix III. Methane 75 %, Ethane 25 % Mixture Hydrate - Nucleation Data Table

Run #	f <sub>g,c1</sub> bars	f <sub>g,c2</sub> bars	f <sub>eq,c1</sub> bars	f <sub>eq,c2</sub> bars
M75E25-01	40.032	8.692	24.42	6.407
M75E25-02	37.121	8.39	25.67	6.651
M75E25-03	34.182	8.01	25.32	6.583
M75E25-04	31.119	7.56	24.997	6.52
M75E25-05	28.01	7.062	25.32	6.583
M75E25-07	27.853	6.967	18.82	5.222
M75E25-12	20.243	5.527	18.35	5.115
M75E25-13	24.762	6.421	18.35	5.115
M75E25-17	18.191	5.051	13.685	3.991
M75E25-18	16.879	4.755	13.521	3.949
M75E25-21	15.556	4.446	13.521	3.949

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### Appendix III. Methane 75 %, Ethane 25 % Mixture Hydrate - Nucleation Data Table (Continued)

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
MNA03-22	53.98	1.1	0.01021	0.01636	38.5	0	300	400	33.18	30.18	46.44
MNA03-25	47.88	1.2	0.01893	0.01651	97	28	300	400	33.51	30.46	41.87
MNA03-26	47.93	1.1	0.01829	0.01636	28	23	300	400	33.18	30.18	41.9
MNA03-27	40.81	1.2	0.01946	0.01651	198	37	300	400	33.51	30.46	36.37
MNA03-28	53.82	1.3	0.01959	0.01666	26.5	19.5	300	400	33.84	30.74	46.34
MNA03-29	63.95	1.1	0.02315	0.01636	23.5	13	300	400	33.18	30.18	53.63
MNA03-30	58.71	1.1	0.01945	0.01636	24	16	300	400	33.18	30.18	49.9
MNA03-31	43.86	1.1	0.01985	0.01636	29.5	19.5	300	400	33.18	30.18	38.76
MNA03-32	38.83	1	0.01926	0.01621	45.5	22	300	400	32.85	29.91	34.78

Appendix III. Methane Hydrate + 3 % NaCl - Nucleation Data Table

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Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RP M	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>V</sup> bars
MK03-02	52.61	1.02	0	0.02019	0	22.8	300	400	32	29.2	45.5017
MK03-12	48.87	1.02	0.03506	0.02025	246	20.5	300	400	32	29.2	42.6804
MK03-03	62.68	1.02	0.03445	0.02102	52.88	14.22	300	400	32	29.2	52.8383
MK03-11	52.87	1.12	0.02244	0.02092	31	27	300	400	32.32	29.47	45.7043
MK03-10	55.82	1.12	0.02493	0.02077	23	15.5	300	400	32.32	29.47	47.89
MK03-14	50.76	1.22	0.02850	0.02059	100	20.5	300	400	32.65	29.75	44.1287
MK03-06	50.78	3.01	0.03067	0.02243	332.12	31.5	300	400	38.99	35	44.2827
MK03-08	70.79	3.01	0.03548	0.02269	68.5	13.5	300	400	38.99	35	58.7771
MK03-07	60.71	3.11	0.02889	0.02270	56	26	300	400	39.38	35.32	51.658

Appendix III. Methane Hydrate + 3 % KCl - Nucleation Data Table

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ⁰C	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
MK05-01	55.79	1.12	0.0284	0.0197	139	18.5	300	400	34.46	31.24	47.8679
MK05-02	60.78	1.12	0.025	0.0199	38	21.5	300	400	34.46	31.24	51.4929
MK05-03	60.75	1.12	0.0289	0.0197	69.5	17.5	300	400	34.46	31.24	51.4714

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Appendix III. Methane Hydrate + 5 % KCl - Nucleation Data Table

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	fg <sup>∨</sup> bars
MK08-10	50.8	1.22	0.0081	0.02	10	35	300	400	38.57	34.58	44.1588
MK08-09	57.56	1.22	0.0252	0.0203	26	20	300	400	38.57	34.58	49.1739
MK08-11	50.76	1.12	0.0328	0.0198	300	28	300	400	38.18	34.26	44.1208
MK08-12	50.76	1.22	0.0226	0.0202	102	49	300	400	38.96	34.9	44.1287
MK08-13	54.74	1.32	0.026	0.0205	277	34.5	300	400	38.96	34.9	47.1117
MK08-15	70.71	1.12	0.0265	0.02	38	18	300	400	38.18	34.26	58.4513

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Appendix III. Methane Hydrate + 8 % KCl - Nucleation Data Table

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> ℃	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
CO2NA3-4	24.88	1.1	0.3213	0.2764	9.7	5	300	400	16.15285	14.25	20.43
CO2NA3-5	21.88	1.1	0.352	0.2764	31	4.5	300	400	16.15285	14.25	18.42
CO2NA3-6	18.88	1.1	0.3251	0.2764	150	7	300	400	16.15285	14.25	16.3
CO2NA3-7	26.88	1.1	0.3417	0.2764	11.2	5	300	400	16.15285	14.25	21.7
CO2NA3-11	25.88	3.48	0.3751	0.3297	97.5	8.5	300	400	21.86234	18.5	21.19
CO2NA3-12	28.88	3.28	0.3794	0.3227	26.5	8.5	300	400	21.31757	18.11	23.04
CO2NA3-14	22.88	1.1	0.3506	0.2764	27	4	300	400	16.15285	14.25	19.11
CO2NA3-15	20.88	1.1	0.2962	0.2764	7.17	0	300	400	16.15285	14.25	17.73

Appendix III. Carbon Dioxide in 3 % NaCl Hydrate - Nucleation Data Table

Run #	P <sub>exp</sub> bars	T <sub>exp</sub> °C	n <sub>tb</sub> moles	n <sub>eq</sub> moles	t <sub>tb</sub> min	t <sub>eq</sub> min	V <sub>sol</sub> Cm <sup>3</sup>	RPM	P <sub>eq</sub> bars	f <sub>eq</sub> bars	f <sup>v</sup> bars
CO2NA5-4	22.88	1.1	0.3311	0.2741	55	0	300	400	18.79991	16.24	19.11
CO2NA5-5	25.88	1.2	0.3675	0.2772	84	3.5	300	400	19.03816	16.42	21.07
CO2NA5-7	28.88	1.2	0.3533	0.2772	14	3.5	300	400	19.03816	16.42	22.92

Appendix III. Carbon Dioxide in 5 % NaCl Hydrate - Nucleation Data Table