Is subcooling the right driving force for testing low-dosage hydrate inhibitors?

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Abstract

The degree of subcooling is usually used as the driving force for hydrate formation; however, it does not encompass the effect of pressure. A comprehensive driving force for hydrate formation is a function of pressure, temperature, and gas composition; however, its calculation is not as simple as that of subcooling. In this work, by application of the two latest driving force expressions for hydrate formation, the relationships between subcooling and the true driving force at different conditions for pure gas–water and natural gas–water systems are analysed. The effect of pressure on the induction time in the presence and absence of a kinetic inhibitor have been tested at similar degrees of subcooling.

The results show that for pure gas–water systems subcooling is proportional to the driving force, with a good approximation over a wide pressure range at isothermal conditions. However, for multicomponent systems (e.g., natural gases), the driving force is more than that suggested by subcooling at some pressures. Changes of driving force with pressure at a constant degree of subcooling for the above systems have been presented. The results show that the pressure has no significant effect on the driving force (at a constant degree of subcooling) above a certain pressure range. The experimental results show that in a natural gas–water system at constant degree of subcooling the induction time is not significantly affected by pressure. However, in the presence of the kinetic inhibitor tested in this study, high-pressure conditions decreased the induction time.
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1. Introduction

The term gas hydrates is that generally used in reference to clathrate hydrates, a group of non-stochiometric, ice-like crystalline compounds, which form through a combination of water and suitably sized 'guest' molecules, under low temperature and elevated pressure conditions. Within the clathrate lattice, water molecules form a network of hydrogen-bonded cage-like structures, enclosing the guest molecules, which generally comprise of single or mixed suitably sized molecules (e.g., methane, CO_2) (Sloan, 1998).

In petroleum exploration and production operations, gas hydrates are a serious economic and safety concern. Clathrates can block pipelines, subsea transfer lines, and, in the event of a gas kick during drilling, form in the well bore, risers, blow-out preventers (BOPs) and choke lines (Baker and Gomez, 1989).

Gas hydrates can be prevented in the pipelines by physical methods (e.g., insulation and operating outside the hydrate stability zone, water removal, etc.), or by injection of chemicals. At the present time, gas hydrates are generally prevented by injecting the so-called thermodynamic inhibitors, such as methanol, glycol, etc. However, these inhibitors may not be economical at high water cuts, and may pose many environmental and logistical issues (Phillips and Grainger, 1998). The Petroleum industry has responded to the

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economic and HS&E concerns by identifying and testing alternative low-dosage hydrate inhibitors (LDHIs). These chemicals could be divided into two groups, kinetic inhibitors and anti-agglomerant agents (Sloan, 1998). Kinetic inhibitors delay hydrate nucleation and/or crystal growth for a certain period of time (induction time) exceeding the free water residence time in the section of the pipeline, with operation conditions inside the hydrate stability zone. Anti-agglomerants prevent the agglomeration and deposition of crystals so that a transportable slurry is formed (Behar et al., 1994). Both classes of additives are used in low concentrations, often around 0.3–0.5 mass% compared with 10–60 mass% needed for conventional thermodynamic inhibitors (Kelland et al., 1995).

The performance of kinetic inhibitors is usually evaluated in autoclaves and/or flow loops in terms of induction time. The induction time is defined as the elapsed time from the start of the experiments to the onset of hydrate formation. The experiments are usually conducted at isothermal and/or isobaric conditions to simulate the field operating conditions. For such tests, subcooling is usually considered as the driving force for hydrate formation and a criterion for simulating field conditions. Subcooling is calculated as the difference between the system temperature and the equilibrium temperature (on the hydrate phase boundary) at the system pressure. In many cases, it is a routine industrial practice to scale up the experiments conducted at low-pressure conditions to high pressures based on some similarity principles. Application of subcooling as a driving force and scale-up criterion may be reliable in some cases, while in other cases it may overestimate or underestimate the pressure effect.

A comprehensive driving force for the description of the appearance and growth of gas hydrates is of great importance in the investigations associated with gas hydrates. A number of driving force expressions for hydrate formation have been reported in the literature. Vysniauskas and Bishnoi (1983) introduced subcooling as the driving force for hydrate formation. Skovborg et al. (1993) defined it as the difference of water chemical potentials in the hydrate crystal and liquid water phase. Natarajan et al. (1994) considered $(f_i^{exp}/f_i^{eq} - 1)$ as the driving force, where f_i^{exp} and f_i^{eq} are fugacity of component 'i' in the bulk and in the hydrate interface, respectively. Christiansen and Sloan (1995) presented the total molar change in Gibbs free energy in hydrate formation reaction, Δg^{exp}, as the driving force for hydrate formation. Sloan (1998) has shown that the driving force derived by Christiansen and Sloan, Δg^{exp}, is the general case for all driving forces presented by the previous investigators. The fundamental driving force for crystallization is defined as the difference between chemical potential of the given substance in the transferring and the transferred state, e.g., in solution and in crystal (Mullin, 1997; Garside et al., 2002). Kashchiev and Firoozabadi (2002) considered the hydrate formation as a crystallization reaction and derived the driving force, supersaturation, for hydrate formation in a pure gas–water system on the basis of the differ-

ence between chemical potentials of the old phase (aqueous water with dissolved gas) and the new phase (hydrate).

A comprehensive driving force for hydrate formation in a gas–water system, derived on the basis of thermodynamics principles, should be applicable to any system in the presence of low-dosage hydrate inhibitors. This is because the inhibitors are present in very low concentrations in the aqueous phase, and their effect on the hydrate phase boundary can be ignored.

In this communication, first a brief description of the two latest driving force expressions for hydrate formation (Christiansen–Sloan and Kashchiev–Firoozabadi) is presented. The former method is applied to calculate the variation of driving force with pressure at isothermal conditions, and its relationship with subcooling for methane and natural gas hydrates. The latter is used for calculating the variation of driving force with temperature at isobaric conditions. Next, the effect of pressure on the driving force at a constant degree of subcooling for methane and natural gas hydrate is calculated to find out the conditions where subcooling alone can be considered as a driving force index for up-scaling means. Finally, the results of the experiments in relation to the effect of pressure on the induction time of natural gas–water systems in the presence and absence of a kinetic inhibitor are presented.

2. Background

2.1. Christiansen and Sloan approach

Christiansen and Sloan (1995) derived the driving force for hydrate formation on the basis of molar changes of the total Gibbs free energy of the system when hydrate crystal forms from water and gas. With the application of the isothermal path, Fig. 1, for calculating ΔG of hydrate formation, they obtained the following equation for a multicomponent system:

$$\Delta G^{exp} = n_w(v_w - v_h)(P^{eq} - P^{exp}) + RT\Sigma(n_i)\ln[f_i^{eq}/f_i^{exp}], \tag{1}$$

$$\Delta g = \Delta G^{exp}/n_w, \tag{1a}$$

where ΔG^{exp} is the change in Gibbs free energy at operating conditions, Δg the change in specific Gibbs free energy at operating conditions (The total changes of Gibbs free energy in the above operating path per mole of water consumed); n_w the number of moles of water consumed (hydration number); v_w, v_h the molar volumes for water and hydrate, respectively; and f_i^{eq}, f_i^{exp} the fugacity of component 'i' in the gas mixture at equilibrium and experimental conditions, respectively.

An interesting virtue of the driving force expression of Eq. (1) is that it can be applied to multicomponent gases.
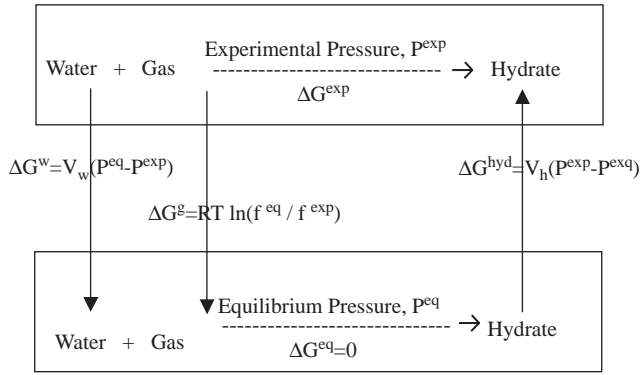
Fig. 1. Isothermal path for calculating driving force for hydrate formation.

For isobaric conditions, Sloan (1998) applied the Gibbs–Helmholtz relation to obtain

$$\Delta g = (-s)\,\Delta T, \tag{2}$$

where $(-s)$, the entropy term, relates Gibbs free energy to the temperature change.

2.2. Kashchiev–Firoozabadi approach

They derived the driving force for the formation of gas hydrate for a system of one gas component and water (Kashchiev and Firoozabadi, 2002). The system was considered at constant pressure and temperature and hydrate formation was assumed to be analogue to a solid precipitation reaction in a solution:

$$G + n_w \mathrm{H_2O} \Leftrightarrow Gn_w\mathrm{H_2O}. \tag{3}$$

One molecule of dissolved gas and n_w (hydration number) water molecules of the solution form one building unit $(Gn_w\mathrm{H_2O})$ of the hydrate crystal. By defining μ_{gs} and μ_w as the chemical potentials of gas and water molecules in the aqueous solution, the chemical potential of a hydrate-building unit (one gas molecule and n_w water molecules) in solution, μ_{hs}, we shall have

$$\mu_{hs} = \mu_{gs} + n_w\mu_w. \tag{4}$$

By definition, the driving force for the new phase formation is the difference between the chemical potentials of the old and new phases. This difference is called super-saturation $\Delta\mu$ and can be calculated by

$$\Delta\mu = \mu_{hs} - \mu_h = \mu_{gs} + n_w\mu_w - \mu_h, \tag{5}$$

where μ_h is the chemical potential of a hydrate-building unit in the hydrate crystal. Nucleation and/or growth of hydrate crystals are possible only when $\Delta\mu > 0$: then $\mu_{hs} > \mu_h$ and the solution is supersaturated.

With expansion of the relevant chemical potential terms in Eq. (5) and with assuming chemical equilibrium between the solution and gas phase, they derived the driving force

at isothermal and isobaric conditions. For isothermal conditions, the driving force was found to be

$$\Delta\mu = kT\,\ln[\varphi(P,T)P/\varphi_e(P_e,T)P_e] + \Delta v_e(P - P_e), \tag{6}$$

where k is the Boltzmann constant, P_e is the hydrate equilibrium pressure at T, and φ is the fugacity coefficient of gas at given P, T. Δv_e is given by

$$\Delta v_e = n_w(P_e,T)v_w(P_e,T) - v_h(P_e,T). \tag{6a}$$

Δv_e is the difference between the volume of n_w water molecules in the solution and the volume of a hydrate-building unit in the hydrate crystal at the equilibrium pressure. v_h can be calculated from

$$v_h = v_{\mathrm{cell}}/n_g, \tag{7}$$

where n_g is the number of gas molecules per unit cell of hydrate crystal lattice and v_{cell} is the volume of the unit cell of the hydrate crystal lattice.

For isobaric conditions, by applying some approximations in the derivations, they determined the driving force as

$$\Delta\mu = \Delta s_e(T - T_e) = \Delta s_e\,\Delta T, \tag{8}$$

where ΔT is subcooling and Δs_e is given by

$$\Delta s_e = n_w(P,T_e)s_w(P,T_e) - s_h(P,T_e) + s_{gg}(P,T_e), \tag{8a}$$

where s_{gg}, s_w and s_h are the entropies per gas molecule in the gas phase, per water molecule in the water phase, and per hydrate-building unit in the hydrate crystal, respectively. Δs_e is the hydrate dissociation entropy per hydrate-building unit at equilibrium temperature, i.e., the entropy change in the transfer of one gas molecule from the hydrate crystal into the gas phase and of n_w water molecules also from the hydrate crystal but into the water-rich phase at given P and T.

For calculating the driving force in the following sections, Eqs. (1) and (8) are used. Some of the subroutines of our in-house hydrate programme (Avlonitis et al., 1994; Tohidi et al., 1995), which is on the basis of Valderrama modification of the Patel and Teja equation of state (Valderrama, 1990), were used for calculating the driving force from Eq. (1).

3. Driving force for simple hydrates

Hydrates formed from a single hydrate former are known as simple hydrates. In this section, the driving force for these systems are discussed.

3.1. Changes of driving force at isothermal and isobaric conditions

Consider an isothermal operating line on the methane hydrate phase boundary (Fig. 2); by increasing the pressure the subcooling will increase. If the changes (increasing) in
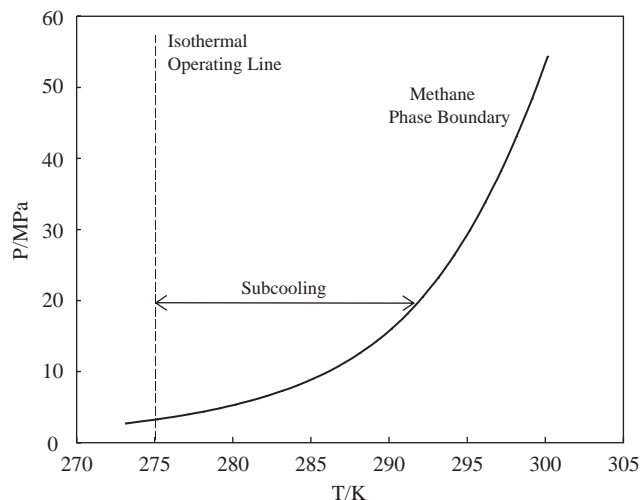
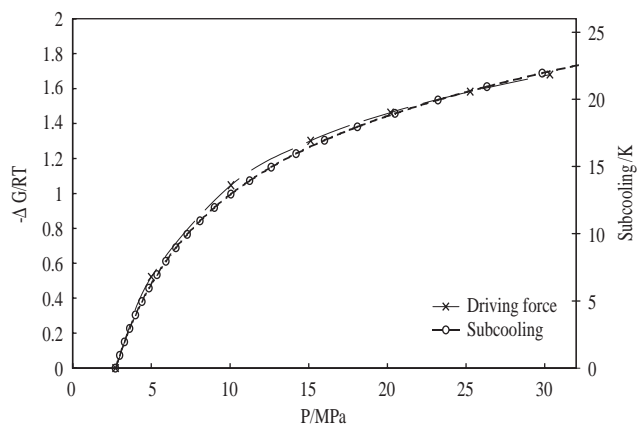Fig. 2. Changes in subcooling with pressure at isothermal conditions.

Fig. 4. Variations in driving force with subcooling at different isobars for a methane–water hydrate system.

Fig. 3. Variations in the driving force and subcooling with pressure at constant temperature, $T = 273.2$ K, for a methane–water hydrate system.

from Eq. (8), all of the isobars are linear, demonstrating a linear relationship between driving force and subcooling, with a slope of $\Delta s_e / RT_e$. Furthermore, there is an increase in the slope with reduction in the system pressure. It is worth noting that the main decrease in the slope of the lines (12.5%) occurs from 5.36 to 19.4 MPa, afterwards up to 43 MPa there is only 7% decrease in $\Delta s_e / RT_e$.

From the above discussions, it can be concluded that for hydrate formation from a single compound, the driving force is proportional to subcooling. In addition, at isothermal and isobaric conditions, the changes of driving force with pressure or temperature can be followed by the change of subcooling.

3.2. Changes of driving force with pressure at constant degrees of subcooling

At a constant degree of subcooling, an increase in the system pressure will result in an increase in the system temperature, as shown in Fig. 5. For methane–water system, the changes of driving force with pressure at constant degrees of subcooling have been calculated and are presented in Fig. 6. In general, at constant degrees of subcooling, the driving force decreases as pressure increases. However, the magnitude of driving force decrease as a function of pressure is not considerable (7–15% decrease after increasing the system pressure from 10 to 75 MPa). It should also be noted that the main reduction in driving force occurs at pressures lower than 20 MPa, above this limit driving force is practically constant. Therefore, in pure gas–water systems, for practical applications, where the operation pressure is higher than 20 MPa, subcooling alone can be representative of the driving force for hydrate formation.

subcooling and the calculated dimensionless driving force $(-\Delta G / RT)$ are plotted against pressure in the same diagram, by adoption of an appropriate scale for subcooling axis, the two curves almost match (Fig. 3). Thus, from Fig. 3, at a constant pressure, one can read the degree of subcooling and the driving force at the same time from different axes and relate them to each other. The driving force for hydrate formation in methane–water system is found to be proportional to the degree of subcooling at isothermal conditions. Comparing the axes of Fig. 3, for methane the following relationship between driving force and subcooling can be concluded:

$$- \Delta G / RT \cong 0.08 \Delta T \quad \text{at constant temperature;}$$
$$T = 273.2 \text{ K and given } P. \tag{9}$$

At isobaric conditions, Eqs. (2) and (8) show that driving force is also proportional to subcooling. Using Eq. (1) the variation of driving force with subcooling at different isobars has been calculated and is shown in Fig. 4. As expected
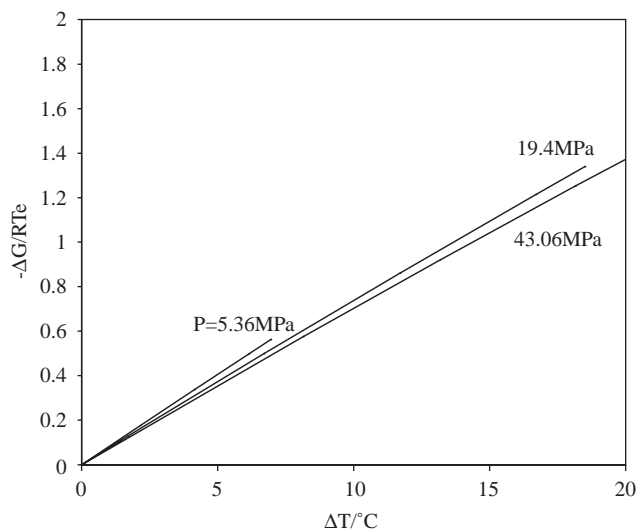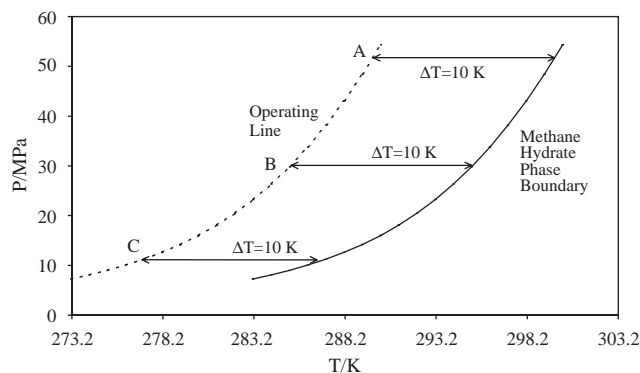
Fig. 5. Constant degrees of subcooling at different pressures and temperatures; points A, B and C.

Fig. 7. Driving force and subcooling for NG1 as a function of pressure at a constant temperature of 273.2 K.

Fig. 6. Driving force versus pressure in a methane–water system at various constant degrees of subcoolings.

Table 1
Composition of the natural gases used in this work

Component	NG1 (mol%)	NG2[a] (mol%)
C_1	86.49	87.26
C_2	5.71	7.57
C_3	1.63	3.1
$n-C_4$	0.35	0.79
$i-C_4$	0.2	0.49
$n-C_5$	0.08	0.2
$i-C_5$	0.08	0.2
C_6^+	0.1	—
N_2	3.86	0.39
CO_2	1.5	—

[a]Natural gas used by Christiansen and Sloan (1995) and Yousif (1994).

Fig. 8. Driving force as a function of pressure for two different types of natural gases at a constant temperature of 273.2 K.

4. Driving force for double hydrates

When two or more compounds take part in hydrate formation, the resulting hydrate is called double hydrate. In this section, the driving force for these systems is discussed. We have chosen a natural gas system for this purpose due to availability of experimental data, but the approach is applicable to any multicomponent systems.

4.1. Isothermal and isobaric conditions

As shown in Fig. 7, if the degree of subcooling and the calculated driving force for natural gas are plotted against system pressure (by adoption of an appropriate scale for subcooling axis), it is not possible to get a good match at all pressures (unlike the pure gas system as shown in Fig. 3). The composition of this natural gas 1 (NG1) is presented in Table 1. As demonstrated in Fig. 7, at some pressure ranges, the degree of subcooling could be a good measure of the driving force. However, at $P = 4$–20 MPa, the subcooling

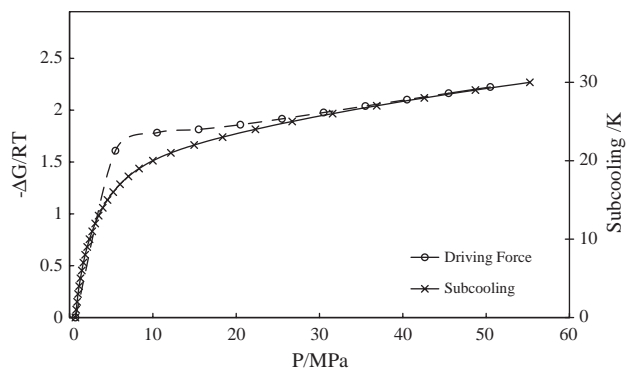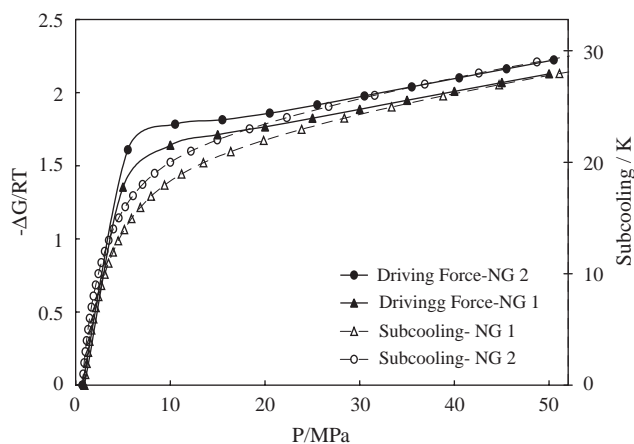underestimates the real driving force. It should be mentioned that the deviation in the driving force curve changes with the composition of the natural gas. Fig. 8 shows that for a different natural gas (NG2) with higher concentration of propane and butane, the deviation in the driving force curve is larger than that of low propane content natural gas (NG1). The composition of NG2 is also presented in Table 1.
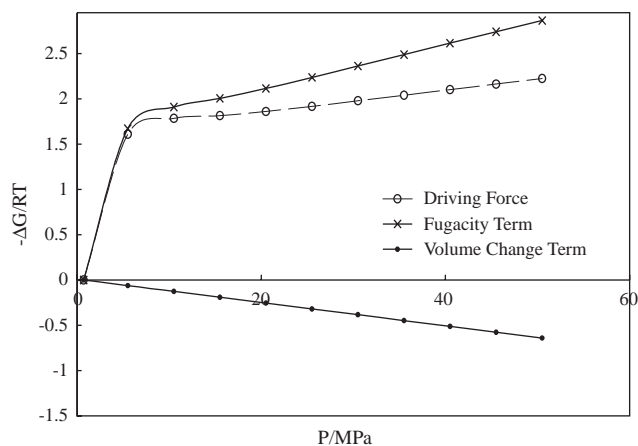
Fig. 9. The changes of different terms in Eq. (1) as a function of pressure for NG1 at a constant temperature of 273.2 K.
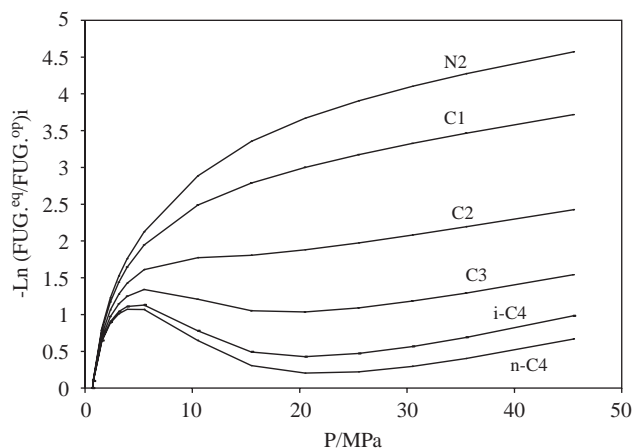

Fig. 11. Driving force versus subcooling at isobaric conditions for NG2.

Fig. 10. The logarithm of fugacity ratios as a function of pressure at 273.2 K for different components in NG2.

Fig. 12. The variation of driving force for hydrate formation in an NG2–water system at constant degrees of subcooling.

The reason for such changes in the driving force with pressure in multicomponent systems can be found by studying different terms in the driving force equation (Eq. (1)). Fig. 9 presents the plot of different terms of Eq. (1) (all the terms are divided by RT to be dimensionless) for NG1. As shown in the figure, the fugacity term in Eq. (1) causes the deviation in the driving force curve for the natural gases.

Plotting the logarithm of the fugacity ratios for each component of natural gas versus pressure (Fig. 10) shows that mainly propane and butane cause the difference in the driving force curve and subcooling versus pressure at isothermal conditions. The equilibrium composition of the components in the hydrate structure (n_i in Eq. (1)) can increase or decrease the effect of each component in the overall driving force curve. At isobaric conditions, and applying Eq. (1), the changes of driving force with subcooling can be calculated, as presented in Fig. 11.

As shown in Fig. 11, the isobars are almost linear and in the pressure range of 0–20 MPa the slope of isobars de-
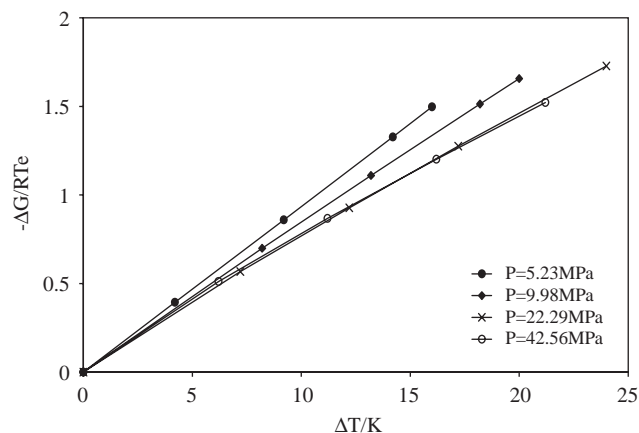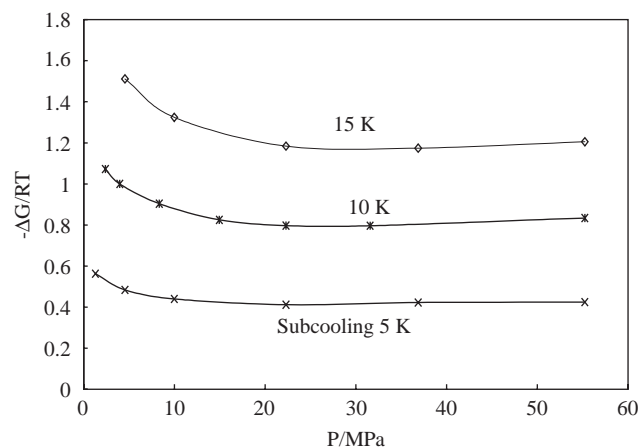
creases at higher pressure values. However, after 20 MPa, the isobars coincide. Though Eq. (8) has been derived for a pure gas and water system only, by analogy it may also be used in a multicomponent system and the slope of the lines in Fig. 11 may be considered as $\Delta s_e / RTe$ for natural gas.

When comparing Figs. 4 and 11, it can be seen that in 0–20 MPa pressure range the changes in the slope of isobars in the natural gas case are more pronounced than that of methane; however, for both cases at isobaric conditions the changes of driving force can be followed by changes of subcooling with a good approximation.

4.2. Constant degree of subcooling condition

The variation of driving force with pressure at different degrees of subcooling for NG1 is presented in Fig. 12. As shown in the figure, up to 20 MPa, by increasing the pressure the driving force decreases (approximately 20% drop in the driving force). After that the driving force is not a

strong function of the system pressure (e.g., 1–2% increase in driving force within 20–55 MPa).

In other words, for the natural gas in the pressure range of $P > 20$ MPa, with a good approximation, a constant degree of subcooling is equivalent to a constant driving force (Fig. 5).

5. Subcooling at different gas systems as driving force criterion

The above discussions are true for driving force of hydrate formation in various systems (pure gas or natural gas). It is common practice to test a low-dosage hydrate inhibitor in different laboratories to assure its performance and the repeatability of the tests. Different natural gases with different compositions may be used in the laboratories for testing the same inhibitor. The results of the tests are comparable only when the reported driving forces for hydrate formation are comparable. In practice, the degree of subcooling is generally reported with little attention to the potential effects of pressure and gas composition.

Since the experiments are usually conducted at isothermal conditions, Eq. (1) can be used for calculation of driving force. In Fig. 13, the changes in driving force with the degree of subcooling at different isobars for the two above-mentioned natural gases have been illustrated. It shows that the compositions of the natural gases have a negligible effect on the isobars and subcooling is representative of real driving force. At a constant degree of subcooling, as expected from the discussion in Section 5.1, the effect of pressure on the driving force is mainly between 5 and 20 MPa (about 20% decrease) for both natural gases.

In the case of testing a low-dosage hydrate inhibitor with two differently synthesised gas mixtures (e.g., methane–ethane or methane–propane), again the driving forces for the systems must be similar. Considering two different systems, from Eq. (8) and by analogy, the driving force for hydrate formation in each system at isobaric conditions may be written as

$$\Delta G_1^{\text{exp}} = \Delta s_{e1} \, \Delta T_1, \qquad (10)$$

$$\Delta G_2^{\text{exp}} = \Delta s_{e2} \, \Delta T_2. \qquad (11)$$

If $\Delta G_1^{\text{exp}} = \Delta G_2^{\text{exp}}$, then

$$\Delta T_2 = [\Delta s_{e1}/\Delta s_{e2}]\Delta T_1, \qquad P = \text{constant.} \qquad (12)$$

In addition, we know that $\Delta s_e = \Delta h_e/T_e$, where Δh_e is the enthalpy of dissociation of 1 mol of hydrate, by substitution we obtain

$$\Delta T_2 = [\Delta h_{e1}/\Delta h_{e2}][T_{e2}/T_{e1}]\Delta T_1, \qquad P = \text{constant.} \qquad (13)$$

From the above equation, at isobaric conditions, the subcooling in System 2, which will lead to an identical
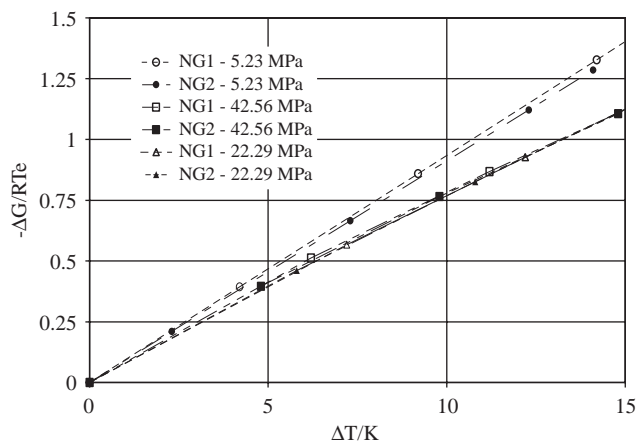

Fig. 13. The comparison of driving forces for hydrate formation in the two different natural gas systems (NG1 and NG2) at different degrees of subcooling and pressures.

driving force as that of System 1 with ΔT_1 subcooling, can be calculated. The enthalpies of dissociations can be obtained from phase equilibria via Clapeyron equation.

6. Induction time and pressure effect

In the light of the above analysis, we shall now consider the impact of pressure on the induction time in the absence and presence of a kinetic inhibitor when the driving force $(-\Delta G/RT)$ for hydrate formation or subcooling is constant. Two series of experiments were conducted to study the pressure effect, which will be discussed in the following sections.

6.1. In the absence of kinetic inhibitors

A total of four experiments were carried out in a kinetic rig to measure the induction times for hydrate formation in the NG1–water system, at similar degrees of subcooling and different pressures to investigate the effect of pressure on induction time. The kinetic rig set-up (Fig. 14) consists of a jacket vessel (500 ml, internal diameter of 78 mm), a mixer with magnetic motor and a temperature control system. During the tests, pressure and temperature inside the rig were recorded by a computerized data-logging system. In the experiments, the required water volume was first loaded into the test cell, and then the gas was charged into the cell up to the required pressure. The system was then heated up to 307.15 K and left for 3–4 h to remove any possible water history. To form hydrates, the system was cooled down to a set point of temperature and at a specified stirring rate (600 rpm). The system was then left to form hydrates. The hydrate formation could be detected by a sudden pressure drop and temperature rise. The reference point for calculating the induction time was considered the time when the system pressure and temperature were stabilized in the rig.
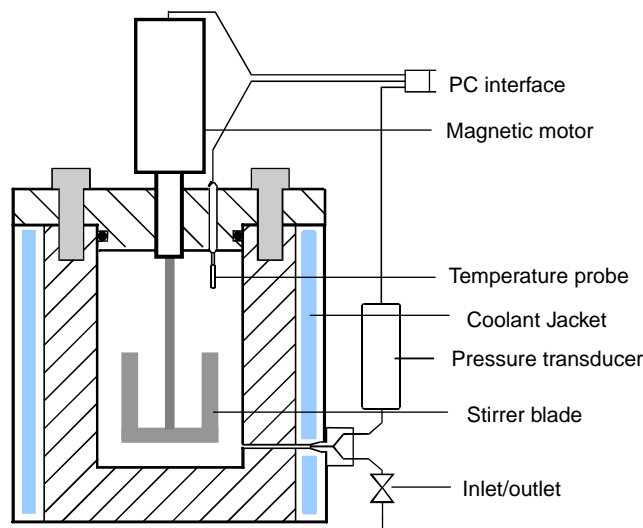
Fig. 14. Schematic diagram of the hydrate kinetic rig.

Table 2
Summary of the tests with NG1–water system

Test no.	Testing T/P (K/MPa)	Subcooling (/K)	Induction time (min)	$-\Delta G/RT$
1	287.35/17.4	7.1	60	0.586
2	287.35/17.4	7.1	65	0.586
3	281.65/6.3	7.1	60	0.651
4	281.65/6.3	7.1	65	0.651

Table 3
The induction times for an NG2–water system reported by Yousif (1994)

Test no.	Testing T/P (K/MPa)	Subcooling (/K)	Induction time (min)	$-\Delta G/RT$
1	280.46/6.89	13	17.5	0.987
2	282.47/9.65	13.2	25	0.932
3	283.71/6.89	9.7	32	0.679
4	286.05/9.65	9.6	43.5	0.615

Two sets of experiments were carried out in two different pressure ranges but at the same degree of subcooling. As shown in Table 2, tests 1–2 were conducted at 17.4 MPa and tests 3–4 at 6.3 MPa. The change in the system pressure had no significant effect on the induction times at a constant degree of subcooling (as the effect on the driving forces is not significant, as detailed above).

Yousif (1994) has reported the results of the tests conducted on the NG2–water system. The result of the tests, which were carried out at similar degrees of subcooling and different pressures, have been selected and are presented in Table 3. As shown in Table 3, at similar degrees of subcooling, the pressure does not have a significant impact on the driving forces and induction times. This is an expected result and in line with the trend predicted in Fig. 12.

Table 4
Summary of the tests with an NG1–water system–0.5 mass% PVCap at 6.3–6.9 MPa pressure range

Test no.	Testing T/P (K/MPa)	Subcooling (/K)	Induction time (h)	$-\Delta G/RT$
1	275.15/6.9	14.2	0	1.34
2	274.65/6.3	14.2	0	1.35
3	275.65/6.9	13.7	17	1.29
4	275.75/6.9	13.6	> 12	1.28
5	276.15/6.9	13.2	> 36	1.24
6	276.15/6.9	13.2	> 36	1.24
7	276.85/6.9	12.5	> 60	1.18

Table 5
Summary of the tests with an NG1–water system–0.5 mass% PVCap at 30–31 MPa pressure range

Test no.	Testing T/P (K/MPa)	Subcooling (/K)	Induction time (h)	$-\Delta G/RT$
1	284.35/30	13.3	0	1.05
2	286.45/30.8	11.2	0	0.9
3	286.65/30.3	11.0	5	0.88
4	286.55/30	10.9	6	0.88
5	288.4/31	9.5	60	0.76

6.2. In the presence of kinetic inhibitor

The induction times for hydrate formation in the system of NG1 and 1.25 mass% of a kinetic inhibitor (containing 40 mass% poly vinyl caprolactam (PVCap) and 60 mass% ethylene glycol as solvent) in water were measured in the above kinetic rig. Two series of tests were conducted in two different pressure ranges and the summaries of the tests have been presented in Tables 4 and 5. Table 4 shows the results of the tests in the pressure range of 6.3–6.9 MPa. As shown, at that pressure and at 14.2 K, subcooling hydrate formed without any induction time. By decreasing the degree of subcooling to 13.7 K, an induction time of 17 h was observed. At 12.5 K subcooling the induction time was longer than 60 h. Table 5 shows the results of the tests in pressure range of 30–31 MPa. As shown in the table, at high-pressure conditions, even at 11 K subcooling, there was no induction time for hydrate formation. For observing 60 h induction time, the degree of subcooling needed to be reduced to 9.5 K. On comparison of the driving forces and the induction times in Tables 4 and 5, it can be seen that for the tests carried out at high-pressure conditions, in spite of lower driving forces than those in low-pressure tests, shorter induction times are observed. This shows that the performance of the kinetic inhibitor tested, at constant driving force conditions, is affected by pressure. The results of the tests show the importance of considering the full operational envelope of the production system (e.g., initial high-pressure operation with depletion to low pressure) for testing LDHIs.

7. Conclusions

In this work, the driving force models for hydrate formation in the literature were reviewed. Two of the latest approaches for derivation of driving force were applied for further analysis in a pure gas and multicomponent gas system. The following conclusions could be drawn:

- The relationship between the driving force and the degree of subcooling for methane demonstrated that subcooling is a good representative of driving force for pure compounds at a wide pressure range.
- For natural gas systems at isothermal conditions, between 5 and 20 MPa, subcooling underestimates the real driving force for hydrate formation; however, above 20 MPa, variation in driving force with pressure can be estimated by subcooling.
- Constant degree of subcooling is an appropriate criterion for up-scaling the tests with pure gas and natural gas.
- A relation was developed for calculating the required degree of subcooling in various hydrocarbon systems to achieve identical driving forces, when determining the induction time for LDHIs.
- For natural gas–water system at constant driving force/subcooling conditions, the induction time does not seem to be a function of pressure, while in the presence of the kinetic inhibitor tested in this study, increasing the system pressure had a negative effect on the induction time. Therefore, it is recommended to test LDHI at similar pressure conditions.

Acknowledgements

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