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The Feasibility of Binary and Ternary Hydrate Mixtures of CH₄, CO₂ and C₃H₈ for Metals Removal

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Abstract

The selection of suitable hydrate formers and their respective gas composition for high hydrate formation driving force is critical to achieve high water recovery and metals removal efficiency in the hydrate-based desalination process. This study presents a feasibility analysis on the possible driving force and subcooling temperatures for the binary and ternary mixtures of methane, carbon dioxide, and propane for hydrates-based desalination process. The driving force and subcooling of the gas systems was evaluated by predicting their hydrate formation phase boundary conditions in 2 wt.% NaCl systems at pressures ranges from 2.0 - 4.0 MPa and temperatures of 1 – 4°C using Modified Peng-Robinson Equation of State in the PVTSim software package. The results suggested that the driving force of $CH_4-C_3H_8$ and $CO_2+C_3H_8$ binary systems are similar to their ternary. Thus, the use of binary systems is preferable and simpler than the ternary systems. For binary gas composition $CO_2+C_3H_8$ (70:30) exhibited a higher subcooling temperature of 8.07 °C and driving force of 1.49 MPa in presence of 2wt% salt. In case of ternary system ($CH_4-C_3H_8-CO_2$) composition of (10:80:10) provided a good subcooling temperature of 12.86 °C for hydrate formation. The results favour $CO_2-C_3H_8$ as preferred hydrate formers for hydrate-based desalination. This is attributed due to the formation of sll structure and as it constitutes 136 water molecules which signifies a huge potential of producing more quantity of treated water.

1. Introduction

Freshwater is a basic and key resource for existence and is essential for socio-economic growth. The increasing population and economic development demand more fresh water supply in the world. However, only 0.3% of the 2.5% accessible by humans [1]. Leading to an urgent need to produce freshwater saline water which amounts to about 97.5% of the world water resources and readily accessible. The conversion of saline water to freshwater (known as desalination) via removal of dissolved salts form saline water would positively aim to meet the increasing freshwater demands in the world. Desalination techniques are classified into three main types, namely (i) thermal process systems in which evaporation and condensation processes are used to separate dissolved salts from saline water, (ii) the membrane process systems where either pressure difference or electric field is applied over the saline water to allow it to pass through a permeable membrane, leaving salts behind and (iii) chemically-activated technique[2–4]. These water management techniques are mature and robust techniques to treat saline water but faced with limitations like less water recovery, corrosion, scaling issues and above all they are highly energy intensive processes. Because of these limitations hydrate-based desalination is proposed as a potential method seawater desalination.

Gas hydrates are ice like, crystalline nonstoichiometric compounds consisting of gas as guest molecule and water as host molecule that are together bonded by hydrogen bond. Hydrates requires two main basic requirements for hydrate to form namely water and gas molecule. Thus, the presence of ion in any system could be excluded since only water would engage in the hydrate formation process. The choice of hydrate forming gas is an addition advantage with could allow a simultaneous seawater desalination while utilizing harmful gases such as CO₂. However, challenging kinetics limitation based on the thermodynamic driving force on the gas systems in seawater is an important concern to enhance the process. The presence of a significant temperature and pressure driving force based on different gas mixtures in brine systems would help to determine and develop hydrate desalination processes that could perform well with minimal operating conditions.

The separation efficiency of metal ions from aqueous salt solution is directly related to the amount of hydrate that could be formed and how fast it can form. The fast hydrate formation and amount of hydrate formation is directly related to the pressure driving force and/or subcooling temperature. Subcooling temperature is determined as the difference between the system temperature and the equilibrium temperature at the system pressure Driving force is the difference between the Gibbs free energy of the solution and the crystal phase as considered in this work. Several driving forces for the nucleation and growth process of hydrate formation have been discussed elsewhere in the literature [4-7]. Many significant achievements have been made in gas hydrate thermodynamic, kinetic studies and research is maturely increasingly. So far there has been no study performed in determining the best gas composition that can provide suitable driving force in terms of pressure and subcooling temperature for seawater desalination purpose. Hence, initiating the driving force research in selecting the best gas composition for gas hydrate formation has significant importance to provide guidelines for selecting the best composition hydrate-based desalination applications. The use of gas such as propane, methane, CO₂ and their mixtures has gained much attention as suitable gas compositions for hydrate-based desalination purposes. Theses gas are mostly considered because they provide good driving for and forms sll hydrate stores which yields for water removal. Also, in the case of gases such a CO2, their environmental prohibitive nature in recent times promotes their utilization to produce clean water instead of stored permanently. However, the selection of the best gas systems by researchers for seawater desalination is trial and error or based on the researcher's choice form literature. This kind of method limits the full potentials of the hydrate-based desalination process, leading to driving force challenge and low efficiency. Therefore, uncovering the boundary conditions of driving force for different gas system will be useful to choose the best gas composition for seawater desalination.

The use of hydrate phase boundary conditions is the main properties that could be used to determine the pressure and temperature driving forces for high water recovery. Aside the classical thermodynamic models, software such as CSMGem and PVTSim are well known products used by academicians and industries alike to study hydrate behaviour of gas components. Therefore, in this study the suitable ranges pressure and temperature hydrates driving forces CO_2 , C_2H_4 and C_3H_8 , and their binary and ternary mixtures was evaluated using PVTSim in presence of 2 wt.% salinity (1.6wt% NaCl, 0.2wt% CaCl₂, 0,2 wt % KCl). The pressure and temperature driving force were used to study the suitable gas composition that good to provide high water recovery and metal removal during sea water desalination. The binary mixtures were based on varying concentrations of CO_2 -CH₄, CO_2 -C₃H₈, and CH₄-C₃H₈, while the ternary system was formulated based on CO_2 -CH₄-C₃H₈. The finding in this study would provide the landmarks

for selecting the appropriate gas systems for high water production and metals removal from seawater during desalination process.

2. Methodology

2.1 Gas and Brine systems

The gas system used in this work are CO_2 , CH_4 , and C_3H_8 . The simulated systems were made from binary and ternary mixtures of these gas. They were selected to represent CO_2 utilization applications produced from high CO_2 content natural gas systems. On the other hand, C_3H_8 was selected for its ability to form sll hydrates which consists 136 water molecules, thus could lead to high water recovery. CH_4 is the dominant gas in natural gas, as such its usage in desalination was tested for binary and ternary combination with CO_2 and C_3H_8 to determine the best gas combination that could provide suitable driving force to achieve higher water recovery and metals removal efficiency. Details on the various gas combination compositions used in this work are presented in Table 1.

Composition (wt.%)						
Binary			Ternary			
CH ₄	C0 ₂	C_3H_8	CH_4	C0 ₂	C_3H_8	
100	-	-	10	80	10	
90	10	-	10	70	20	
80	20	-	10	60	30	
70	30	-	10	50	40	
60	40	-	10	40	50	
50	50	-	10	30	60	
40	60	-	10	20	70	
30	70	-	10	10	80	
20	80	-	20	70	10	
10	90	-	20	60	20	
-	100	-	20	50	30	
-	90	10	20	40	40	
-	80	20	20	30	50	
-	70	30	20	20	60	
-	60	40	20	10	70	
-	50	50	30	60	10	
-	40	60	30	50	20	
-	30	70	30	40	30	
-	20	80	30	30	40	
-	10	90	30	20	50	
-	-	100	40	50	10	
10	-	90	40	40	20	
20	-	80	40	30	30	
30	-	70	40	20	40	

Table 1	
Studied gas systems in this	study

Composition (wt.%)						
40	-	60	40	10	50	
50	-	50	50	40	10	
60	-	40	50	30	20	
70	-	30	50	20	30	
80	-	20	50	10	40	
90	-	10	60	30	10	
-	-	-	60	20	20	
-	-	-	60	10	30	
-	-	-	70	20	10	
-	-	-	70	10	20	
-	-	-	80	10	10	

The hydrate formation driving force of the gas systems were predicted in a synthetic brine system. This is the mimic the influence of the salts on the hydrate formation conditions as used in typical desalination process. The synthetic brine systems used in this work consist of 1.6 wt.% NaCl + 0.2 wt.% KCl + 0.2 wt.% CaCl₂ aqueous solution.

2.2. Hydrate Equilibrium Phase Predictions using PVTSim

In this study, PVTSim was initially used to determine the phase behaviour conditions of the gas systems (Table 2). The obtained phase behaviour data for the PVTSim simulations was used to estimate the driving force and subcooling for all the gas systems. PVTSim is used to simulate hydrate formation conditions for gasses and oil mixtures and can deal with the most used thermodynamic hydrate inhibitors like methanol, ethanol, glycols, and salts. To predict hydrate phase behaviour in PVTSim, the desired fluid (gas systems in Table 1) is entered and selected from the PVTSim with their composition and fluid characterisation based on plus fraction. The plus fraction option is used because the molecular weight of chosen alkanes is always higher due to the presence of other compounds. Peng Robinson Penenloux equation of state was used for all the predictions with the desired brine systems as stated earlier. The hydrate equilibrium data for the gas were then predicted by following two stages. The first was determining the hydrate equilibrium temperatures at constant pressures of 20, 25, 30, 35, and 40 bar. This allowed the estimation of the subcooling temperatures. Also, the pressures were selected to select a system that can form hydrates at low pressure conditions for practical applicably with less energy consumptions. Secondly, the pressure driving force was determined by predicting the hydrate equilibrium pressures of the gas systems at 1, 2, 3 and 4°C respectively. Theses temperatures represents suitable conditions to form hydrates for desalination purposes with relatively less energy.

2.3. Estimation of driving force parameters

The driving force measurement in this work was based on pressure and subcooling temperature. Theses parameters were used since they are critical fundamental parameter to hydrate formation kinetics and ensure the possibility of forming a substantial amount of hydrate with less metastability in the system. Generally, the driving force for the formation of hydrate is a function of pressure, temperature, and gas composition. The driving force calculated as the difference between the system pressure and temperature and their respective equilibrium pressure and temperature. The use of this properties to describe the driving force of hydrate formation is well established and acceptable in literature. The subcooling temperatures and driving force in this study was estimated used Equations 1 and 2. For each system, the average values were reported.

$$\Delta T_{avg \, i,j,k} = \frac{\sum_{i,j,k}^{P} (T_{eq} - T_{expt})_{i,j,k}}{n_{i,j,k}}$$
(1)
$$\Delta P_{avg \, i,j,k} = \frac{\sum_{i,j,k}^{T} (P_{expt} - P_{eq})_{i,j,k}}{n_{i,j,k}}$$
(2)

where $\Delta T_{avg \, i,j,k}$ corresponds to the average driving force subcooling temperature at the respective compositions of i,j,k for CH₄, CO₂, C₃H₈ as listed in Table 1 and it's the difference between the equilibrium temperature and experimental temperature at different pressures values of P=20,25,30,35 and 40 bar, $n_{i,j,k}$ corresponds to the number of data points i.e., 5 in this case at compositions of i,j,k for CH₄, CO₂, C₃H₈ as shown in Table 1. Similarly, $\Delta P_{avg \, i,j,k}$ corresponds to the average pressure driving force at the respective compositions of i,j,k of CH₄, CO₂, C₃H₈ as listed in Table 1 and it's the difference between the experimental pressure and equilibrium pressure at different temperature values of T = 1,2,3, and 4°C, and $n_{i,j,k}$ corresponds to data points i.e. 4 in this case at compositions i,j,k for CH₄, CO₂, C₃H₈.

3. Results And Discussion

3.1. HBD feasibility zone in binary gas systems

The feasibility zone for using binary gas systems for hydrate-based desalinations were first evaluated and presenting in this section. Since a decade research in gas hydrate has profoundly focussed at the molecular level using solid state analytical instruments like X-ray diffraction and NMR spectroscopy and Raman spectroscopy to charactise the composition and structure of hydrate formed. Studies based on mixed hydrates using Raman spectroscopy and X-ray diffraction, suggesting that the reaction kinetics of each hydrate system is different and relies on the type of guest molecule and external pressuretemperature conditions [8-10]. ¹³C NMR studies performed for $CH_4+C_3H_8$ during sll hydrate formation was presented by Kini et al., [11]. They observed that the large cages (5¹²6⁴) occupied with C₃H₈ form twice as fast as small cages (5¹²) with CH₄.Generally small molecules like CH₄, CO₂ tend to form s1 hydrates where the small cages are filled by CH₄ and larger cages are filled by CO₂ or C₂H₆, while larger molecules like C₃H₈, C₄H₁₀ form sll hydrates [10]. In the interim the gas molecules occupying different cavities of gas hydrates would also affect the stability of structure. Some of the properties of the various gas hydrate structures are listed below in Table 2[10].

Properties of cage		sl		sll		sH			
Cavity		Small	Large	Small	Large	Small	Medium	Large	
Description		5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴	5 ¹²	4 ³ 5 ⁶ 6 ³	5 ¹² 6 ⁸	
Number per unit cell		2	6	16	8	3	2	1	
Average cavity radius(Å)		3.95	4.33	3.91	4.73	3.91	4.06	5.71	
Coordination number ^a		20	24	20	28	20	20	36	
Lattice type		Cubic Fa		Face cen cubic	Face centered cubic		Hexagonal		
Water molecules per unit cell		46		136		34			
Ratio of diameter of guest molecule to diameter of cage for hydrate former									
Guest	Diameter (Å)								
CH ₄	4.36	0.886*	0.757*	0.889	0.675	75			
CO ₂	5.12	1.041	0.889*	1.044	0.792				
C ₃ H ₈	6.28	1.276	1.090	1.280	0.971*				

Table 2: Structural and cage occupancy characteristics of gas hydrates

^a number of oxygen atoms at the end of each cavity

*Indicate cage occupied by guest species

Zheng et al.,[12] presented a thermodynamic model to enhance the accuracy in the prediction of phase boundary of hydrates of pure components CH_4 , CO_2 and binary mixture CH_4+CO_2 in presence of pure and saline water. They observed that the CH_4+CO_2 binary hydrates pressure phase boundaries decreased with increase in CO_2 concentration. In another communication the clatharate hydrate phase equilibria of CH_4+CO_2 suggested the stable structure for the binary system to be s1 structure [13]. Identical perceptions have been addressed [14-15]. Propane molecule diameter is too large as listed in Table 2 to occupy the small 5¹² cages; so, it occupies the larger cages of 5¹²6⁴ leaving the smaller 5¹² cages empty. [10,16-18]. The small 5¹² cages of sll hydrate can possibly be occupied by the molecules having smaller diameter size like CO2 and CH4 at suitable pressure and temperature conditions. Essentially, these smaller guest molecules often stabilize the sll hydrates more than just the C3H8 molecule. Because there are usually no additional forces available between the host and the guest molecule, Van der Waal forces are thought to be responsible for this stability [10]. Based on the dissociation enthalpy value the mixed hydrate formed from the gas system $CO_2+H_2+C_3H_8$ was confirmed to be a sll hydrate [19]. With the help XRD and NMR spectroscopy it was communicated that the three gas system $CO_2+H_2+C_3H_8$ is composed of sll structure [20].

The three binary systems studied were CO_2+CH_4 , $CO_2+C_3H_8$ and $C_3H_8+CH_4$. To evaluate the feasibility of forming suitable hydrates in the binary systems for the driving force and subcooling temperatures were estimated. The average driving force at 20 bar for 1 - 4 °C were reported, while the average subcooling temperatures for pressure ranging from 2.0 -4.0 MPa at 4 °C was reported. The selection of 2.0 MPa and 4 °C was to ensure the evaluation of the minimum conditions suitable to form more hydrates with less energy and pressure required.

Figure 1 shows the average driving force subcooling temperature for CH₄+C₃H₈ system at 2 wt.%. This system is suitable for the utilization of natural gas constituents for desalination. In Figure 1, the subcooling temperature for pure CH₄ and C₃H₈ at 4°C are -4.7°C and 0.28°C, respectively. The system with 90CH₄ + 10C₃H₈ rises the pure CH₄ systems subcooling temperature by 12°C. Increasing the propane concentration up to 30% increases the subcooling temperature of pure CH₄. Propane concentrations above 30% show a slight negligible impact on the subcooling temperature for CH₄+C₃H₈ systems. The driving force for CH₄+C₃H₈ mixtures behavior is similar as their subcooling temperature, however, pure C_3H_8 exhibits a high driving force than its mixture with CH_4 as all concentrations (Figure 1). The pure C_3H_8 systems have poor subcooling temperature which is a limitation for its application [21-23,17] Therefore, 90CH₄+10C₃H₈ or 10CH₄+90C₃H₈ are suitable systems that could provide a significant driving force and subcooling temperature for hydrate-based desalination/water treatment at minimal/average energy intensity conditions of 4°C and 2.0 MPa This process is evident to show that the small addition of propane there is a pressure increase which is caused by the hydrate crystal change from s1 to sll as propane can only fit into larger $5^{12}6^4$ cavity of sll so more pressure is required to fit into the cage as C_3H_8 is too large to occupy any other cavity as listed in Table 2. However, increasing the C₃H₈ composition in the C₃H₈+CH₄ system increases the subcooling temperature and driving force. The system with 90C₃H₈+10CH₄ exhibits the highest driving force and subcooling temperature of 1.69 MPa and 12.9°C, respectively. This is about 70% and 77.5% high than the driving force and subcooling temperature for $90CH_4+10C_3H_8$ system as shown in Figure 1.

On the other hand, CO₂ and C₃H₈ mixtures also behavior similarly to CH₄+C₃H₈ (Figures 1 and 2). The subcooling temperature for CO₂-C₃H₈ is averagely about 0.39°C lower than CH₄-C₃H₈, but about 0.05 MPa high than the CH₄+C₃H₈ systems. This suggests that the hydrate formation behavior and the water recovery/metals removal in mixing C₃H₈ with CO₂ is highly influenced by the pressure differential driving force. While the subcooling temperature highly controls the hydrate formation behaviour and the water recovery/metals removal efficiency in $C_3H_8+CH_4$ systems. The binary mixtures of C_3H_8 , CH_4 and C_3H_8 , CO₂ at 70-80%:20-30% would averagely provide a suitable subcooling temperature and driving force for metals removal via hydrate-based desalination or water treatment methods at relatively moderate temperature and pressure conditions. Hence the process could occur and run efficiently with low energy intensity. Because CO₂ and C₃H₈ can form hydrates at significantly lower pressures than methane, they have a wide range of potential applications [24-26]. However, increasing the C_3H_8 composition in the $CO_2+C_3H_8$ system increases the subcooling temperature and driving force. $90CO_2+10C_3H_8$ to 50CO₂+50C₃H₈ are suitable systems that could provide a significant driving force and subcooling temperature for hydrate-based desalination/water treatment at minimal/average energy intensity conditions of 4°C and 2.0 MPa. The system with 70-80%CO₂+ 30-20%C₃H₈ exhibits the highest subcooling temperature of 1.495 MPa and 8.07 °C, respectively. This is about 29.45% and 34.1% high than the driving force and subcooling temperature for $90CO_2+10C_3H_8$ system as shown in Figure 2.

Figure 3 the CO₂+CH₄ gas composition exhibits a poor hydrate formation subcooling and driving force at low pressure and temperature conditions. Thus, using CO₂+CH₄ mixed gas systems for desalination or metal removal would require very high pressure and lower temperature conditions. These conditions would increase the energy demand for the process to occur. Increasing the concentration of CH4 in CO₂+CH₄ systems linearly reduces the subcooling and driving force of pure CO₂ by 3 and 8 times, respectively (Figures 3). Generally, in the presence of electrolytes, the hydrate formation is delayed [27]. There is extensive literature [28-32] available with experimental data, models, and simulations of hydrate formation and dissociation in the presence of electrolytes. All of these studies show that the presence of salt in water produces an increase in hydrate equilibrium pressure and/or a drop in the hydrate equilibrium temp. As a result, the formation of water cages is impeded, and the stability of the hydrate structure is decreased [33]. In essence, using pure CO₂ would yield suitable conditions to form hydrate that mixed CO₂+CH₄ systems, however, the driving force and subcooling for pure CO₂ must be at lower temperature condition (< 4°C) and high pressures (< 2.0 MPa). This would be due to the double hydrate formation of CH₄+CO₂, where majority of the large cages might be accommodated by both guest species, though there is less occupancy of CH₄ in the large cages because CO₂ can only occupy the large cage, whereas CH₄ can occupy both the large and small cages. This holds in good agreement with the study performed by few researcher [34-35] using NMR spectroscopy. In this case CH₄+CO₂ significantly higher pressure driving force is required which might not be economical for hydrate based desalination.

The hydrate formation driving force and subcooling behaviour of the ternary system for $CH_4+C_3H_8+CO_2$ was further investigated in this work. Figures 4-6 shows the results on the ternary systems. Generally, all the ternary systems exhibited high subcooling temperatures and driving forces that are suitable for high hydrate formation kinetics at low pressure and high temperature conditions (Figures 4-6). The presence of C_3H_8 in all the ternary systems assisted their increased driving forces, especially for the CH_4+CO_2 systems.

The driving force of the ternary systems in Figures 4-5 are similar to the binary systems in Figure 1 and 2, expect for CH₄-CO₂ systems (Figure 3). This implies that, using binary systems for desalination or metals removal purposes is preferable in terms of driving forces. The subcooling for the ternary systems varied significantly. This provides an added advantage to easy form hydrate when using ternary systems compared to the binary systems. However, the ternary system with constant C₃H₈ (10%) and varying CO₂ and CH₄ exhibited subcooling temperature conditions similar to the systems binary systems of CO₂+C₃H₈ and CH₄+C₃H₈. This might be due to the fact that small addition of C₃H₈ causes an increase in the subcooling temperature and a decrease in the driving force due to structural change from sI to sII and also follows literature [11]. Propane can only occupy larger cages of sll due to its large size as listed in Table 2 and CH₄+CO₂ forms s1 structure. Few researchers [14-15] have made similar observations. For constant 10 % CH₄ and varying C₃H₈+CO₂ the ratio of (10:80:10) exhibits highest subcooling temperature and driving force of 12.86°C and 1.657 MPa at 4°C and 2.0 MPa as shown in Figure 4. From figure 5 with constant 10 % CO₂ and varying concentrations of $CH_4+C_3H_8$ the ratio (10:30:60) exhibits the highest subcooling temperature of 13.22 °C and at (10:10:80) provides a high driving force of 1.6575MPa at 4°C and 2.0 MPa as shown in Figure 5. However, the ternary systems with either constant CO₂ or CH₄ and varying C₃H₈ composition exhibited higher subcooling temperatures up to 4°C high than binary systems. Instead of using binary system CH₄+CO₂ it is better to use a ternary system with small addition of propane as 10 % C₃H₈ addition to this system provides good driving force for hydrate-based desalination system as shown in Figure 6. For the ternary system C₃H₈+CH₄+CO₂ (10:40:50) or (10:50:40) provide a high subcooling of 8.25°C which is about 96.5% increase from pure C_3H_8

4. Conclusion

The hydrate equilibrium pressures and temperatures for binary and ternary gas system are predicted for the given temperatures (1-4°C) and pressures (2.0-4.0 MPa) respectively using PVTSim. From this study the suitable gas composition of mixtures which can provide good driving force in terms of subcooling and pressure is evaluated. From this study the findings are:

- CH₄+C₃H₈ gas combination gave higher subcooling temperature of 12.93°C for gas composition (10:90) provided significant driving force of 16.68 bar.
- $CO_2+C_3H_8$ gas combination gave higher subcooling temperature of 8.07°C and driving force average of 1.495 MPa at the gas composition (70:30). This gas system is appropriate for high water

production and metals removal from seawater during desalination process.

- CO₂+CH₄ gas combination gave higher subcooling temperature of 2.18°C with gas composition (100:0) and driving force of 0.19 MPafor gas composition CO₂-CH₄ (0:100)
- CH₄+C₃H₈+CO₂ gas combination having concentration composition (10:30:60/10:80:10) varying C₃H₈ concentration and keeping CH₄/CO₂ concentration constant at 10 wt% gave higher subcooling temperature averaged at 12.86°C and higher driving force of 1.657 MPa

Based on the findings from this work the suitable gas combination in case of binary or ternary system that provides good driving force can be selected in presence of salt solution.

Declarations

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Supplementary materials

Supplementary material associated with this article is attached.

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Gas concentration (wt.%)



Driving forces vs various CH4-C3H8 gas concentration



Driving force vs various CO2-C3H8 gas concentrations.



Driving force vs various concentrations of CO2-CH4



Driving force vs. concentrations of C3H8+CO2 at 10 wt% CH4 concentration



Driving force vs. concentrations of CH4-C3H8 at 10 wt% CO2 concentration

Driving force vs. concentrations of CH4-CO2 at fixed 10 wt% C3H8 concentration.

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