



Review Paper

Study on equilibrium conditions of methane gas hydrates

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Abstract

Methane gas hydrates are nonstoichiometric crystalline form of solids which are formed by the amalgamation of molecules of methane gas with the molecules of water at low temperature and high pressure. For oil, gas, chemical and other industries, the formation of MGHs has been a problem for many years because hydrate may block the pipelines or valves. Hydrate formation in a pipeline may also cause a blowout in the drilling operations. The knowledge of the equilibrium conditions of gas hydrate is obligatory for the economical and safe plan of operations in oil, gas, chemical industries where hydrate nucleation/formation occurred. It becomes important to measure the incipient conditions of hydrate formations for the system containing different inhibitors, promoters, salts, porous materials. The conditions of stability for MGHs in pure and seawater will be different because of the existence of ions and salts in seawater. The stability pressure of MGHs in seawater is higher than pure water, but the temperature for the gas hydrate can be lower in seawater than pure water. The stability conditions of MGHs can be disturbed by the simple addition of salts, electrolytes in the host sediments or water of MGHs. The co-existence of all dissolved ions in seawater depresses the dissociation temperature for the stability of methane hydrate ranges between pressures of 2.75-10 MPa. For seawater with a salinity of 33.5%, the observed offset in dissociation temperature was 1.1°C in comparison to pure water. Various researchers have done various experiments to find the stability conditions of MGHs at different temperatures and high pressure. The equilibrium curves for the methane MGHs in porous media has been shifted to the high pressure and lower temperature as compared to the equilibrium curves for the bulk MGHs.

Keywords:

Introduction

A non-stoichiometric type of crystalline solids has been formed by the enclathration of gaseous molecule inside the cages of molecules of water, which is called as Methane Gas Hydrates (MGH). The formation/stability condition of these MGHs is low temperature and high pressure¹. Clathrates are a natural source of vast quantity of energy which may fulfill the future energy requirement of all over the world. The structure of MGH has the capacity to store a huge amount of methane gas^{2,3}. There are huge quantities of naturally formed hydrate deposits in the earth's crust containing methane mostly^{4,5}. Kvenvolden predicted that 10¹⁶m³ of methane gas encaged inside the MGHs⁶. The MGHs can be formed in the deep oceans and permafrost regions both at desired stability conditions. There is 164 m³ of gas at standard stability condition (P-T) inside the 1m³ of MGHs. The quantity of methane in the hydrate is greater than the total combined fossil fuel, and hence it may become a great potential source of energy for the future⁷. A rich quantity of methane gas has been generated in polar regions and offshore continental margins of the world and hence it is the most abundant component of MGHs⁸. There are various research studies that are based on the formation phenomenon of MGHs and their dissociation approach to release methane gas from natural deposits of MGHs⁹. The formation of hydrate is one of

the major issues for the oil & gas industry. It may plug the pipelines or valves and erode the surface of the equipment also¹⁰. The formation of MGHs may also change the viscosity of the oil. The dissociation of naturally formed MGHs leads to the leakage and damage in the pipelines because of the uncontrolled release of gas and wellhead blowouts etc¹¹. The dissociated methane gas contributes to the greenhouse effect. Knowledge of the equilibrium condition of hydrate formation is an attractive research topic because of these devastating and costly consequences of hydrate formation in oil and gas, chemical industries. There is a need to develop some new approaches for the determination of phase equilibrium data to avoid the problems related to hydrate formation and also for the economic exploitation of MGHs as one of the major sources of energy in the future. In this study, we tried to gather incipient equilibrium hydrate formation data from various research studies and their comparison. An infinitesimal quantity of the hydrate phase is always in equilibrium with the fluid phase in the incipient hydrate formation process. Hence, understanding the formation conditions of hydrate is required for the safe and economic plan of processes in oil, gas, chemical and other industries⁷. The reserved methane gas and water in a porous media can be extracted after the formation of MGHs. Water present in the pores and dissolved methane in water can form clathrate at suitable conditions. This formation of MGHs in sediments will

enhance the sediments strength and as a result it lowers the permeability and porosity of porous media¹². Various studies are going on for the study of the occurrence of MGHs formed in marine sediments and porous media. To perform the research in the formation and exploitation of MGHs, Stability and solubility of MGHs are crucial parameters¹³. The stability conditions of MGHs depend upon some major parameters i.e. in situ pressure, temperature and salinity (P-T-S). These parameters have been applied for the estimation of temperature by the extrapolation of result findings of shallow heat studies to the deep down at Bottom Simulating Reflector(BSR)¹⁴⁻¹⁶. There are numerous experimental data are available on the stability conditions(P-T) of MGHs formed in pure water¹⁰, but very little experimental data are available for the stability conditions (P-T) of MGHs in sea water¹⁷. The direct computation of solubility of MGHs in seawater is not available, but numerous studies describe the thermodynamic approaches for the stability calculation¹⁸⁻²⁰ and methane MGHs solubility in seawater by applying the Vander Waals and Plateau Model²¹. But the experimental data for pure water can be used for the prediction of properties of MGHs in sea water^{17,22}.

Very few studies are present, which describes the phase equilibria of MGHs under conditions relevant to marine environments. Various papers describe the three-phase equilibrium conditions between seawater, hydrate and free gas²³. The stability conditions (P-T) of hydrate in seafloor depend upon the composition of the gas, composition of salts and some other additives present in seawater. The suitable stability conditions for MGH are located over various parts of the ocean floor even though the formation of hydrate is confined to continental margins.

The MGHs will normally form where adequate availability of gas has been found. There are huge natural deposits of MGHs are located in the whole world. Fig 1 shows the locations of MGHs deposits in the world. The physical properties of natural gas hydrate reservoirs all over the world are listed in Table-2.

Progress of gas hydrate expedition in India

In India, gas hydrate expedition program was initiated under National Gas Hydrate Program (NGHP) with the collaboration of Oil and Natural Gas Corporation of India (ONGC), Gas Authority of India Limited (GAIL), Oil India Limited (OIL) and Government research Institutions such as National Institute of Ocean Technology (NIOT), National Institute of Oceanography (NIO) and National Geophysical Research Institute (NGRI). The NGHP is coordinated by the Directorate General of Hydrocarbons (DGH).

In India, First BSR was reported in 1984, and the Oil and Natural Gas Corporation of India started the analysis of all available seismic data. About 80000 km² areas in Indian seep offshore were observed which are favorable for the occurrence of MGHs. The ministry of petroleum and Natural Gas (MOPNG) initiated the NGHP in 1997 and the study started in Krishna Godavari (KG), Cauvery offshore and Gulf of Mannar. In 2000-2001, a 460 km line of data pertaining to the Gulf of Kutch, Deep Continental Shelf, Kerala Laccadive, Bengal, and Mahanadi offshore areas were analyzed as the potential areas for the exploration of MGHs. DGH collaborated with the United States Geological Survey (USGS) for the scientific studies during and after the coring and drilling program of MGHs in Indian offshore (NGHP-01). In 2006, the first milestone was achieved and they confirmed the presence of hydrate in the central part of Krishna Godavari offshore area. The National Gas Hydrate Program Expedition 02 (NGHP-02) was initiated off the eastern coast of India in 2015. The main aim of the NGHP-02 was to logging while drilling at identified sites and coring and wire line logging program at 20 sites in the deepwater Mahanadi and Krishna-Godavari basins. The drilling and coring task was assigned to ONGC. The aim of Expedition 03 (NGHP-03) is to execute a pilot production trial of at least one location/site in the Indian deep-water environment. Under the NGHP-02, ONGC is appointed as the nodal agency for central KG offshore and Reliance Industries Limited (RIL) for the northern KG offshore, Cauvery and Mahanadi basin⁵⁴⁻⁶¹.

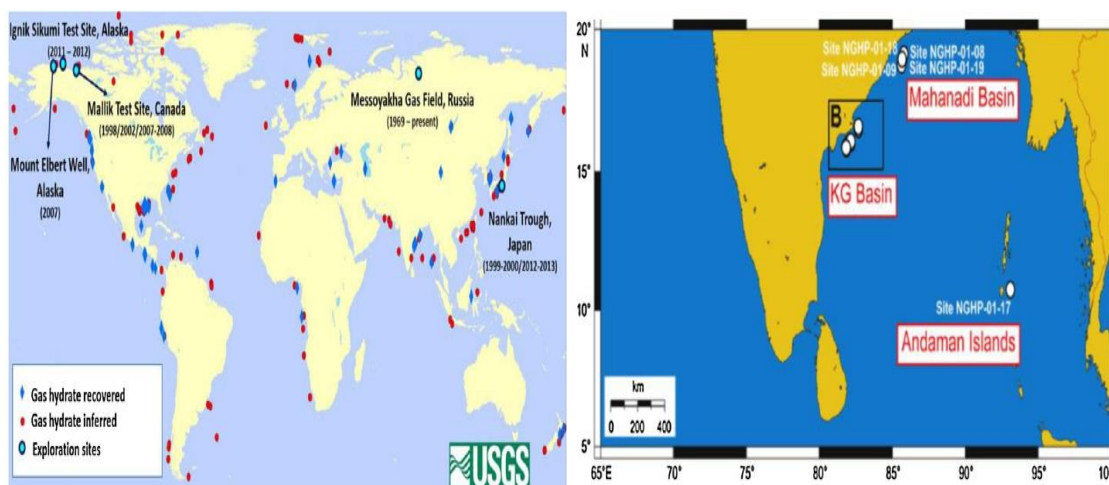


Figure-1: Locations of natural reserves of MGHs in the World and India²⁴.

Table-1: Properties of Natural reserves of MGHs (expedition program) in the world.

Exploitation country	T (K)	P (Mpa)	Saturation	V (trillion m ³)	Porosity	Water Depth (m)	Type of Sample	Exploitation Technique	Ref
Canada	283	9.795	80	0.088	30-45	885-1150	Permafrost and gas-hydrate-bearing core samples	Depressurization Thermal Stimulation	25
Canada	277	6.89	72	2.49	10-40	682.752	Permafrost	Depressurization CO ₂ -CH ₄ exchange	26
Russia	283	2				1300	Sand Reservoirs		27, 28
Russia			57-75		20-80	278.70912	Sand, Clay, Precipitated Slit, Crushed Slit,		27, 28
Russia	281-285	7.92	29-50	36.81	16-38	945-5070	Permafrost	Depressurization methanol injection	29
Korea	>293	5		0.000252	60-80	2092	Sand, basal silt-sand, volcanoclastic and siliciclastic sand reservoirs	Pressurized drilling	30-32
US & Canada	276.5	2	23-65			47-123 mbsf	Marine sediments (microbiological)	Depressurization thermal stimulation	34-36
China	275	7	13-53			885-1530 mbsf		Fugro pressure Cores	37
Germany	281	6.7	35-65		42-60	720	Microbial		38-43
Japan	286-288	13.4		1.195e ⁻⁷		1000	Sandy turbidite type sediments at 300m below the seafloor	Depressurization	44-53
India	278.5-2283.1	16	<20	1900		500-1500			54-61

Table-2: Locations of Gas Hydrate (NGHP-01)⁵⁴⁻⁶¹.

Program	No of Sites Located	Water Depth (mbsf)	Depth to base of MHSZ (mbsf)	Sediment Type	Reservoir Type
KG	15	895-1285	126-203	Clay with limited silt/sand beds	Possible fracture/ pore-filling
Mahanadi	04	1374-1935	210-220	No Core / Clay with limited silt/sand beds	Possible pore/fracture filling
Kerala Konkan	01	2663	360	Carbonate Rich	No MGHs
Andaman	01	1344	620	Clay/silt (nanofossil ooze) with volcanic ash beds	Pore-filling (dispersed to highly saturated hydrate in ash beds)

Phase Diagram of MGHs

Figure-1 depicts the phase diagram of MGHs in terms of pressure-temperature and water depth. Fig depicts the geothermal gradients with depth. The intersection point of the solid phase boundary, and geothermal gradient lines give the lower boundary depth of the stability of MGHs. In this region, MGHs are stable with only one other phase¹⁰.

Discussion

Effect of Salinity: The pressure-temperature (P-T) data for the dissociation and formation of MGH will depend upon the salinity of water in which MGHs will form. The pressure at which the MGH will dissociate is increased as the salinity of seawater enhances. The induction time for the formation of MGH will depend upon the degree of sub cooling and salt concentration⁶². There are three reasons due to which the stability conditions of MGH at the BSR's are different than the stability conditions of MGH of pure water and pure methane. i. The diffusion and advection of dissolved/liquefied salts that are removed upon the formation of MGH may decrease the total

salinity of the hydrate system. ii. inclusion of several other gases such that hydrogen sulfide, carbon dioxide, ethane and propane will increase the stability of MGH as compared to pure MGH⁶³. Iii. presence of sediments will increase the stability of MGH^{17,64}. The addition of simple salts such that NaCl, KCl, CaCl₂, and mixtures of these salts in water can decrease the stability of MGH such that for a definite range of pressures and the temperature of dissociation can be decreased by a constant amount as compared to pure water systems^{23,65-67}. This decrease occurs because dissolved ion inhibitors have no effect on the formation enthalpy but lower the entropy of water molecules. It means that the water activity is the only one parameter related to the equilibrium conditions of MGH that is influenced by the inclusion of dissolved/liquefied species^{68,69}.

The combined form of all dissolved ions of seawater also decreases the temperature of dissociation for MGH by a constant value between pressures ranges 2.75-10 MPa. Figure-3 shows the shift in P-T conditions of MGH in seawater in comparison with pure water and after the injection of different salts (data taken from⁷⁰⁻⁷⁶).

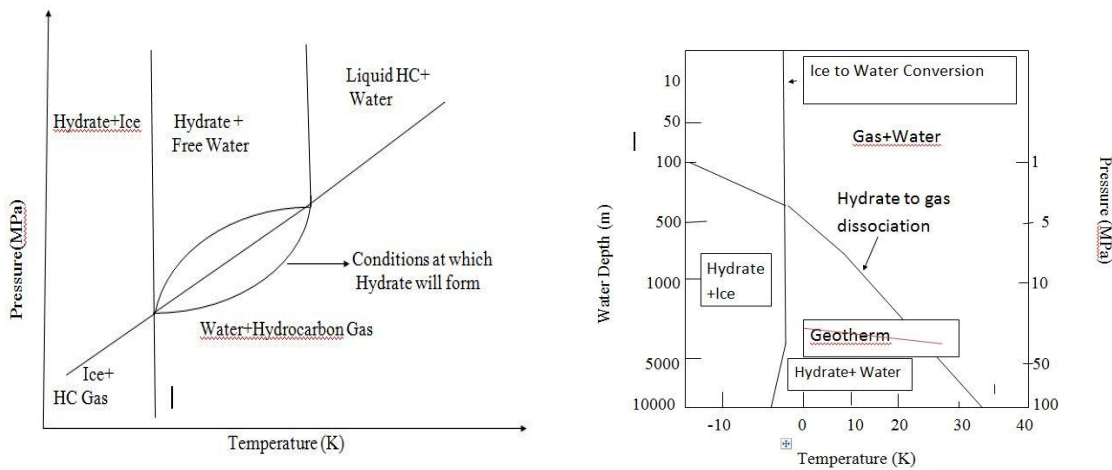


Figure-2: Phase diagram of MGHs.

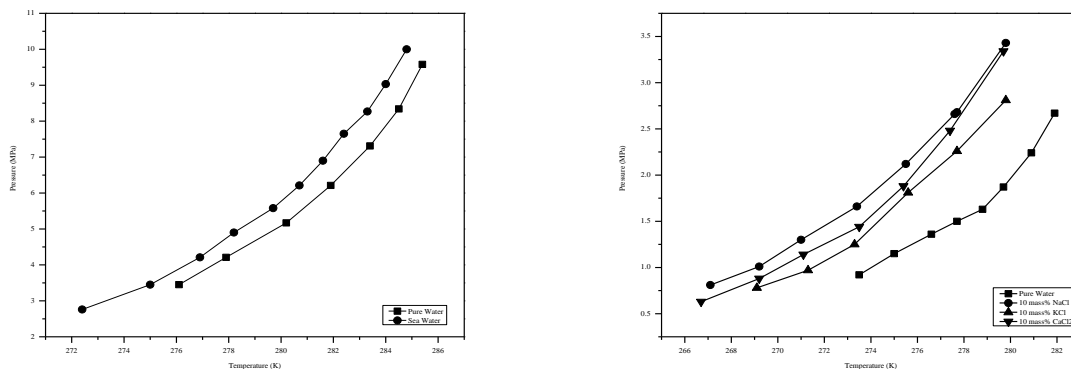


Figure-3: Shift in equilibrium(P-T) conditions of MGHs formed in Pure Water, Seawater, and after the injection of salts.

Effect of Inhibitors: The hydrate formation in gas pipelines creates large pressure drop or censorious safety issues. Hence, prevention from the hydrate blockage is a major research area for the oil and gas industry. Depressurization, dehydration and insulation can be applied to prevent the formation of MGHs. But there some drawbacks to these methods such as dehydration is not possible between the well and dehydration units. Insulation is too inconvenient and economically expensive in the deep sea and depressurization will decrease the transportation capability of pipelines. Hence the most applicable method to avoid the blockage due to hydrate formation is the injection of chemicals that can decrease/inhibit the aggregation of MGHs inside the pipelines. The base of the hydrate inhibition is to keep the pressure and temperature of the hydrate system out of the formation region⁷⁷. A practical method to prevent the formation of MGHs is the injection of the chemical agents into the hydrate system to prevent the formation of MGHs. These chemical agents are called as hydrate inhibitors. Hydrate inhibitors are divided into two categories such as thermodynamic hydrate inhibitors (THI), low dosage hydrate inhibitors (LDHIs). These inhibitors shifts curve for the aqueous liquid-vapor equilibrium (HLVE) to the lower temperature and higher pressure which forces the oil and gas system to be in hydrate free region. The examples of this are mostly alcohols and slats such as NaCl, methanol and ethylene glycol. Various THIs can be corrosions and toxic and harmful for the humans and environment hence LDHIs has been invented which consists of antiagglomerants (AAs) and kinetic hydrate inhibitors (KHIs) which didn't change the P-T conditions of the formation of hydrate but delayed the nucleation of MGHs and retarded the hydrate growth. Hence these chemicals will avoid the blockage of the pipeline due to hydrate formation for duration more than

the residence time of the free water in the pipeline. The concentration limit of THIs is 50wt% and KHIs is 0.1-1 wt%. The examples of KHIs are polyvinyl lactams and its derivatives such as polyvinylpyrrolidone (PVP), polyvinylcaprolactam (PVCap) and Gaffic VC-713^{7,78,79}. Figure-4 shows the shift in equilibrium conditions of MGHs after the injection of different inhibitors (data taken from⁸⁰).

Effect of Promoters: The MGHs can reserve a huge amount of gas hence it can be a best alternative for the safe transport and storage of natural gas. But there is a problem that the hydrate formation process is slow and the gas uptake will be far away from its maximum quantity. Hence, research is going on for increasing the rate of formation and gas uptake of MGHs. Some chemicals are injected into the water to enhance the formation rate of hydrate. These special chemicals are called as the promoters for MGHs. Promoters are divided into two categories based on their effects such as kinetic and thermodynamic type of promoters. The thermodynamic type of promoters shifted the phase boundaries of MGH to the higher temperature or lower pressure. The kinetic class of promoters enhances the rate of formation and gas intake of MGHs. There are several research studies are available which studied the effect of promoters as a former of hydrate on the formation conditions. The example of the thermodynamic promoter is propanone, 1,4-dioxane on methane MGHs and kinetic promoters are surfactants on ethane MGHs, sodium dodecyl sulfate, hydrotropes, hexadecyltrimethyl-ammonium bromide (CTAB) and 2-(2-nonylphenoxy) ethanol (ENP)^{81,82}. Figure-5 shows the shift in equilibrium conditions of MGH in the presence of different promoters (data taken from^{83,84}).

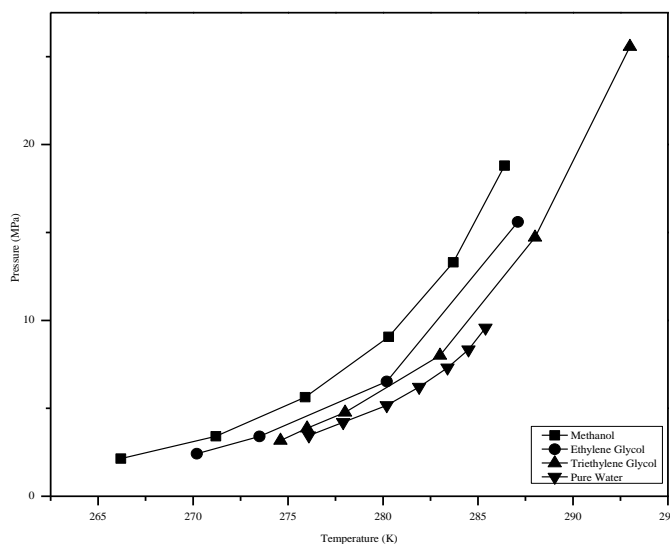


Figure-4: Shift in equilibrium conditions(P-T) of MGHs formed in Pure water afterthe injection of inhibitors.

Effect of Porous materials and Pore Size: The equilibrium condition of methane MGHs is necessary for the observation of the total efficiency of gas hydrate fields. This is also important to locate the bottom stability zone of the methane gas hydrate and to establish the rate of formation and rate of dissociation of MGH. The stability conditions of MGHs are calculated using the bottom simulating reflector (BSR) and changes in equilibrium conditions in sediments as compare with the methane hydrate formed during laboratory works¹¹. The equilibrium condition (P-T) of methane MGHs can be affected by the compositions of gas and concentrations of solute and both can be used for the prediction of the formation condition of MGHs. The pressure for the dissociation of methane MGHs formed in small pores will be greater than those in bulk phase because of the effect of water accommodation in the small pore space⁸⁵. The temperature for the dissociation of the THF hydrates formed in Loam, sand and bentonite decreases as compared with the pure hydrate⁸⁶. The equilibrium conditions (P-T) of MGHs will be affected by the surface and capillary effects in porous media⁸⁷. Miyawaki studied the adsorption of methane in Nanoscale pores. The structure of MGHs in porous media is dissimilar as compared to bulk cubic hydrate due to the smaller pore size as compared to the lattice constant of the

MGHs of structure I type⁸⁸. The dissociation temperature of MGH in confined small pores (100-500Å) has been significant downward shifts in porous glass than bulk hydrate at a known pressure. This shift in dissociation conditions in the presence of small pores is due to the change in the water activity and this change in water activity can be measured by the Gibbs-Thomson effect⁸⁹. Uchida predicted that the temperature of the dissociation of CH₄, CO₂ and C₃H₈ hydrate was shifted to the lower value for bulk hydrate for a given pressure. All shifts in temperature were fitted by the equation of Gibbs-Thomson with the prediction of interfacial energies. They concluded that the effect of pore on the phase equilibrium was because of the change in water activity⁹⁰. The three-phase water-hydrate vapor equilibrium curves were increased to the higher pressure for the pore sizes as compared to bulk MGHs at specific temperatures⁹¹. There are various studies that show that for a temperature range, the dissociation pressures for the MGH in silica gel pores will be greater than those for bulk^{92,93}. The equilibrium curves for the MGHs in porous media have been shifted at the high pressure and low temperature as compare to the equilibrium curves for the bulk MGHs⁹⁴. Figure-6 shows the shift in P-T conditions of MGH in the presence of different porous materials (data taken from ^{89,93,95-100}).

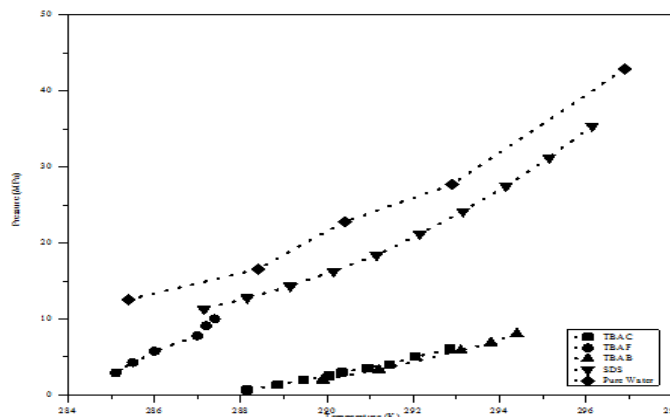


Figure-5: Shift in P-T data of MGH in Pure water and with the promoters.

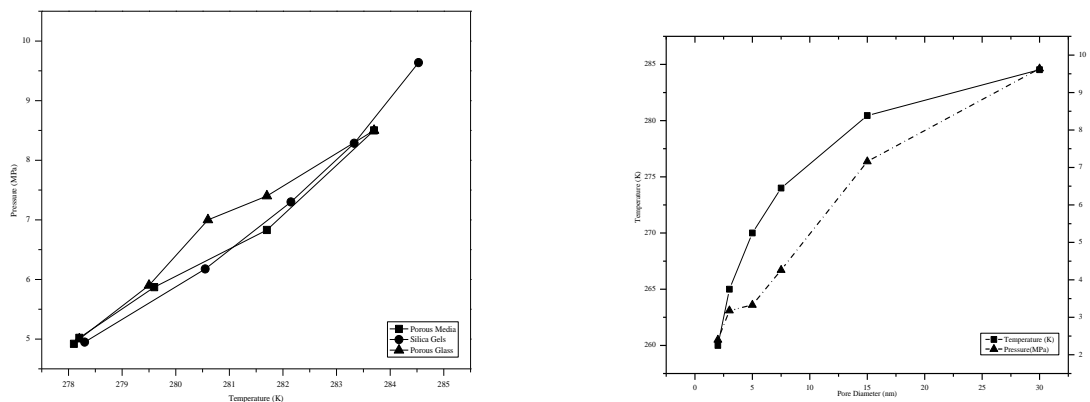


Figure-6: Shift in P-T data for MGH for porous media and pore size.

Conclusion

The stability conditions of MGHs in seawater and pure water will be different because of the existence of ions and salts in seawater. The P-T data for the equilibrium conditions for MGHs are different. MGH will be stable at higher pressure and lower temperature in seawater in comparison with pure water. The stability conditions of MGHs can be disturbed by the simple addition of salts, electrolytes in the host sediments or water of MGHs. All coexisting dissolved ions of seawater depress the dissociation temperature (T) for the stability of methane hydrate ranges between pressures of 2.75-10 MPa. Because of the salinity of 33.5% in seawater, the observed offset in dissociation temperature was 1.1^oC as compared to pure water. Various researchers have done various experiments to find the stability conditions of MGHs at different temperatures and high pressure. The concentration of methane can also affect the stability conditions of methane MGHs. Some researchers conducted the dissociation experiment with the different concentrations of methane and ethane to show the variation of temperature and pressure. The addition of some salts in the host water of MGHs can also disturb the equilibrium conditions of MGHs. The stability condition of MGHs in water and methanol solutions can be different because of the inhibiting strength of salts. The promoters promote the formation of MGHs to some extent. The presence of porous media and the size of pores also affect the stability data of MGH.

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