Dissociation Heat Transfer Characteristics of Methane Hydrates

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Introduction

Knowledge of the interfacial heat transfer phenomenon during the dissociation of gas hydrates is essential in modeling the hydrate dissociation process. Such knowledge has applications in natural gas processing, storage, or transportation (Hammerschmidt, 1934; Parent, 1948); in the drilling and recovery of oil and gas in the presence of gas hydrates (Holder et al., 1976; Collett, 1985; Kamath et al., 1985); in the desalination of sea water (Barduhn, 1967); and in the production of natural gas from hydrate reservoirs (McGuire, 1981; Holder et al., 1982; Bayles et al., 1984; Kamath and Godbole, 1985).

The process of hydrate dissociation is a unique phenomenon in which gas and water are simultaneously produced at the dissociated hydrate surface and play an important role in the mechanism of heat transfer to hydrates. An earlier study of propane hydrate dissociation (Kamath et al.; 1984) showed that hydrate dissociation is a heat-transfer-limited process and somewhat similar to the nucleate boiling of liquids. In the present study, heat transfer limitations for methane hydrate dissociation were studied for two reasons. First, a comparison of the results of this study with propane hydrate was desired. Second, the effect of hydrate structure and gas molecule type on the rate of heat transfer during hydrate dissociation was sought.

Experimental

Methane hydrates were formed under isothermal conditions (274 K) by pressurizing porous cores of very fine ice particles (0.42 to 0.63 voidage) with gaseous methane (initial pressures up to 7.6 MPa) for several days. Hydrate formation was evident from the drop in pressure as methane from the gas phase entered the solid phase. Hydrate formation was stopped when the rate of pressure drop decreased below 2 kPa/h, and these methane hydrate cores were dissociated at a constant pressure by circulating warm water at a constant flow rate over the top surface of the hydrates at a constant temperature. These dissociation experiments lasted for 30 to 60 min, during which time the amount of gas liberated from hydrates, the pressure, the bulk water phase temperature, and the temperature of the dissociating hydrate surface were measured at 1 min intervals. Figure 1 shows the hydrate dissociation process. The detailed mechanistic descriptions of these experiments and hydrate dissociation process are given by Kamath (1984). The accuracy of temperature measurements was ±0.1 K, of the pressure measurements ±0.1%, and of the gas flow measurements ±0.5%.

Results and Discussion

Table 1 summarizes the experimental conditions for the methane hydrate formation and dissociation runs. The raw data and their analysis are described by Kamath (1984). The pressure-temperature (PT) conditions before and after hydrate formation were used to calculate the amount of methane transferred from the gas phase to the hydrate phase. A methane hydrate number (i.e., the number of moles of water per mole methane in the hydrate phase) of 6.15 was used in these calculations. This value was determined from the data for run 15, in which the conversion of ice to hydrates was found to be complete (indicated by no drop in pressure with time). The cumulative amount of methane liberated from the complete dissociation of hydrates was measured and also was used in the calculation of the conversion of ice to methane hydrates. The conversions

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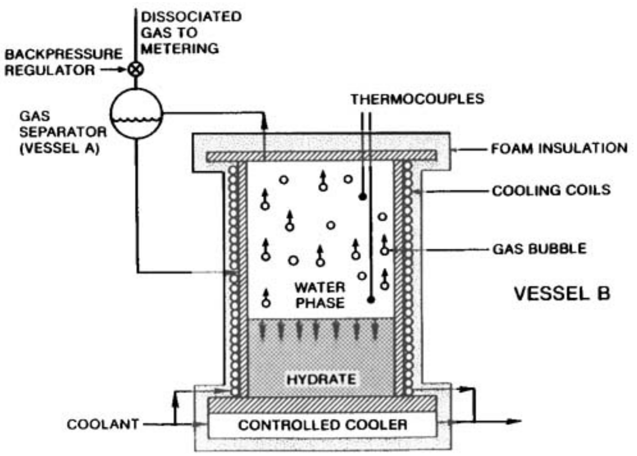

Figure 1. Cylindrical hydrate dissociation vessel.
Heat is transfered across downward-moving hydrate interface; bubble density is higher than illustration indicates.

obtained by both methods were in close agreement (±3.0%) and ranged from 59 to 100% for all the runs.

A typical methane hydrate dissociation run is illustrated in Figure 2, where the dissociation rate is plotted as a function of time. This plot is similar to that for propane hydrate dissociation (Kamath et al., 1984), and such behavior was observed in all the methane hydrate dissociation runs. Ideally, at constant pressure and temperature conditions a uniform core of hydrates should dissociate at a constant rate. In all dissociation runs, usually 1–2 min were required to reach steady state (i.e., thermal equilibrium and constant pressure conditions). In Figure 2, the steady state period is shown. The fluctuations in dissociation rate from the steady state value represent the nonuniformities in the core. All the measured variables were time-averaged over this steady state dissociation period. The measurements of bulk water temperature, pressure, and amount of gas liberated were used in the calculation of hydrate dissociation rates, heat flux, and temperature drop across the hydrate-water interface. The details of these calculations are given by Kamath (1984). The interfacial temperature drop at the hydrate surface (temperature driving force), ΔT, was obtained from the three-phase (VL_1H) equilibrium PT conditions for methane hydrates and is given by the following correlation:

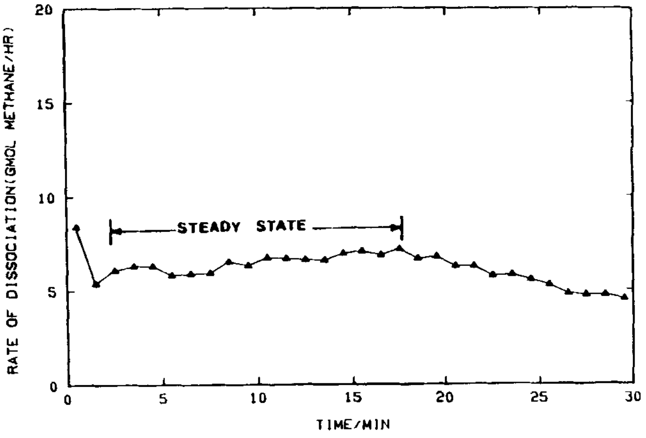

Figure 2. Rate of methane hydrate dissociation as a function of time.

$$\Delta T = T_B - T_I = T_B - \frac{8533.8}{38.98 - \ln(P)} \tag{1}$$

where temperatures ΔT, T_B, and T_I are in K, and P is pressure in kPa. The heat of dissociation of methane hydrates was obtained from the modified Clapeyron equation; the correlation is given by

$$\Delta H_D = 13.521 - 0.00402\,T_I \tag{2}$$

where ΔH_D is in kcal/gmol CH_4, and T_I is in K.

Hydrate dissociation is a heat-transfer-limited process and the water generated from hydrate dissociation continually forms a thin liquid film on the surface of the remaining hydrates, resulting in a resistance to the heat transfer. However, the gas

Table 1. Experimental Conditions for Methane Hydrate Formation and Dissociation Runs

	Methane Hydrate Formation at 274 K						Methane Hydrate Dissociation			
Run No.	Time h	P_o kPa	P_f kPa	x	ϕ_H	ϕ_I	T_B K	ΔT K	P kPa	$\dot{m}_H$ gmol CH_4/h
1	43	—	—	0.593	0.355	0.212	288.2	10.0	4,144	2.15
2	44	5,241	3,041	0.851	0.441	0.068	293.2	15.0	4,135	7.15
3	41	5,690	2,862	0.675	0.364	0.152	287.3	11.0	3,314	1.85
4	44	5,593	3,469	0.901	0.500	0.049	292.6	13.8	4,491	4.88
5	42	6,248	3,324	0.894	0.464	0.049	295.1	15.9	4,648	8.60
6	66	6,626	3,551	0.903	0.499	0.047	301.1	21.9	4,668	13.27
7	26	6,876	3,572	0.848	0.469	0.070	286.3	8.0	4,222	1.34
8	26	6,876	3,572	0.848	0.449	0.070	287.0	8.6	4,230	1.92
9	38	6,338	3,193	0.910	0.487	0.043	306.9	27.8	4,608	22.30
10	65	7,613	3,110	0.913	0.553	0.047	294.9	15.7	4,682	6.41
11	66	6,736	3,123	0.752	0.470	0.135	290.7	13.7	3,581	4.69
12	88	7,074	3,065	0.866	0.554	0.075	290.1	15.2	2,800	3.83
13	89	6,809	3,179	0.900	0.543	0.053	290.8	15.0	3,136	4.03
14	141	6,914	3,040	0.805	0.470	0.089	291.9	15.1	3,514	5.18
15	221	6,731	3,041	1.000	0.663	0.000	294.6	15.4	4,650	5.33
16	60	7,353	3,978	0.874	0.386	0.047	291.8	13.4	4,249	3.73

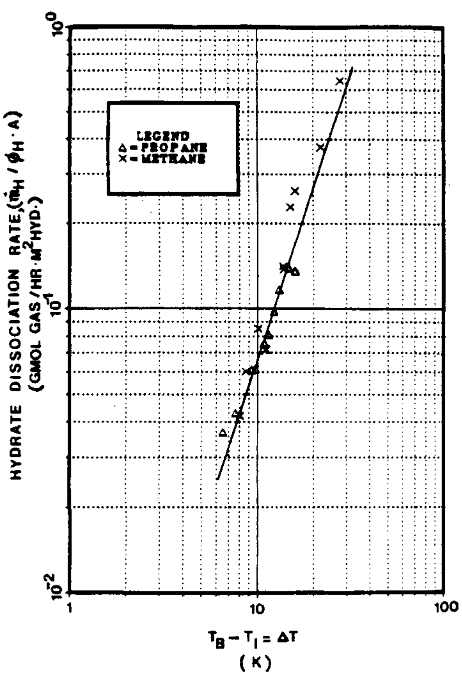

Figure 3. Rate of dissociation as a function of ΔT, interfacial temperature drop.

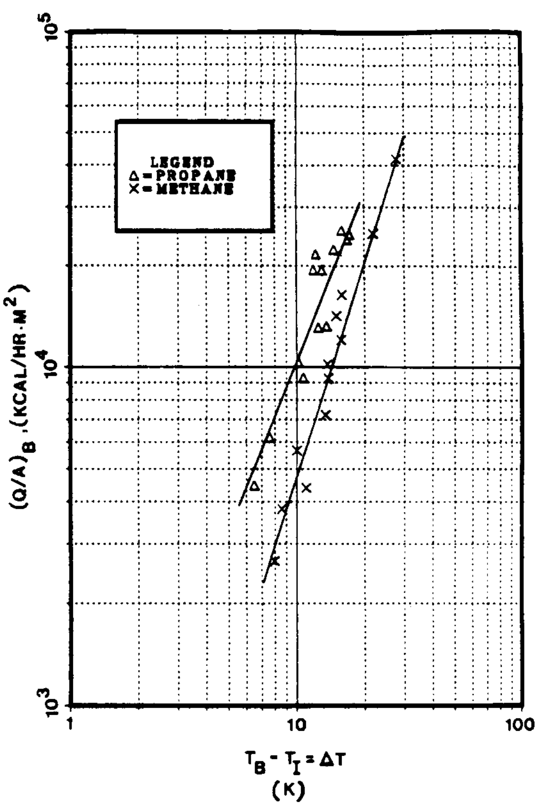

Figure 4. Heat flux to gas hydrates as a function of ΔT.

bubbles generated at the hydrate surface makes this film convective in nature. The degree of convection depends upon the bubble size and the bubble generation frequency. The experimental results indicate that the rate of heat transfer and dissociation are power functions of the temperature drop across the interfacial film. Also, the rate of dissociation is directly proportional to the surface area of hydrates. The normalized dissociation rate (i.e., the rate of dissociation per unit surface area of hydrates) for methane hydrates (this study) and propane hydrates (Kamath et al., 1984) at a fixed ΔT were found to be in good agreement, see Figure 3. A unified correlation for the rate of dissociation as a function of interfacial temperature drop was obtained and is:

$$\frac{\dot{m}_H}{\phi_H A} = 6.464 \times 10^{-4} (\Delta T)^{2.05} \tag{3}$$

where $\dot{m}_H$ is the rate of dissociation in gmol gas/h, $\phi_H A$ is the surface area of hydrates in cm^2, and ΔT is the interfacial temperature drop in K. This correlation is valid for propane and methane hydrates with an average accuracy of ±13.5%. Figure 4 shows the heat flux density vs. interfacial temperature drop for methane and propane hydrates. For ΔT values ranging from 6 to 28 K, hydrate dissociation did not indicate that a critical heat flux (peak in heat flux) had been reached. In boiling, the critical heat flux occurs when the heating surface is no longer wetted by the liquid, as a result of very high vapor bubble generation rate. However, in the case of hydrate dissociation the solid hydrate surface is always wetted by liquid water (generated continuously from dissociation of hydrates). Also, it is clear from this figure that at a fixed ΔT, the heat flux density for propane hydrates is 2 to 2.5 times higher than that for methane hydrates. A unified heat transfer correlation for both methane hydrates and propane hydrates was obtained by plotting bubble Reynolds number Re_b vs. the ratio of Jakob number Ja_b to Prandtl number Pr (Kamath et al., 1984), and is given as:

$$Ja_b = 0.0248\, Re_b^{0.53}\, Pr \tag{4}$$

Note that this correlation is different from Eq. 3 since it includes the heat flux obtained after correcting for forced convection effects (Kamath et al., 1984). The correlation has an accuracy of ±20%.

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Notation

A = cross-sectional area, cm^2
Ja_b = bubble Jakob number
$\dot{m}_H$ = rate of methane hydrate dissociation, gmol CH$_4$/h
P = pressure, kPa
Pr = Prandtl number
$(Q/A)_B$ = heat flux density, kcal/h · m^2 · K
Re_b = bubble Reynolds number
T_B = bulk water phase temperature, K
T_I = interfacial temperature, K
x = fractional conversion of ice to hydrates
ΔT = interfacial temperature drop, K
ΔH_D = heat of methane hydrate dissociation, kcal/gmol CH$_4$
ϕ_H, ϕ_I, ϕ_G = volume fraction of methane hydrates, unconverted ice, and voids in the core, respectively.

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