Upper Limits on the Rates of Dissociation of Clathrate Hydrates to Ice and Free Gas

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The Hertz-Knudsen-Langmuir equation is used to calculate the maximum possible rate at which clathrate hydrates can dissociate. Since hydrate decomposition is endothermic, heat must be added to keep the sample temperature constant. The prediction of the Hertz-Knudsen-Langmuir equation for the rate of dissociation is used to determine the heat flux necessary to keep the sample temperature constant, and thereby maintain this maximum rate of production of gas from the hydrate. Such considerations may be relevant both to the study of the rate of hydrate decomposition and to the eventual efficient production of natural gas from hydrate deposits. In addition, experimental results available in the literature on hydrate decomposition rates and the kinetics of hydrate decomposition are discussed in light of the work done by Langmuir and others on endothermic decomposition reactions. These earlier studies suggest that dissociation experiments in which the sample is exposed to vacuum could help to explore the kinetics involved in hydrate decomposition.

Introduction

Gas hydrates are a set of clathrates formed from the combination of water and certain gases under conditions of high pressure and low temperature. The hydrate structure is stabilized when gas molecules occupy "cages" formed by hydrogen-bonded water molecules. The most common of these compounds is methane hydrate ($CH_4 \cdot nH_2O$; $n \geq 5.75$). Interest in these compounds has risen in recent years due to the discovery of large deposits below the ocean floor and in permafrost regions.[1,2] These deposits are estimated to contain vast amounts of natural gas that could be used as clean fuels if they could be recovered efficiently.

While numerous studies have been performed on the formation and stability of gas hydrates, there are many issues that remain unresolved relative to their decomposition and the subsequent recovery of the sequestered gas. For example, a number of researchers have reported anomalous behavior of such hydrates during the decomposition of various types of samples. These researchers[3−10] report incomplete or delayed dissociation of the hydrates under conditions such that the involved hydrate should be unstable and would therefore be expected to dissociate rapidly.

The purpose of this work is to discuss hydrate decomposition rates and the kinetics of hydrate decomposition in light of the work done by Langmuir[11−13] and others[14−16] on endothermic decomposition reactions. These earlier studies suggest a set of experiments that could help to explore the kinetics involved in hydrate decomposition. In addition, the Hertz-Knudsen-Langmuir equation is used to calculate the maximum possible rate at which a hydrate can dissociate. This in turn is used to determine the necessary heat flux to allow the maintenance of this maximum rate of production of gas from the hydrate. Such

considerations may be relevant both to the study of hydrate decomposition and to the eventual efficient production of natural gas from hydrate deposits.

Problems of Solid Dissociation Reactions. Unlike most chemical processes, vaporization reactions resulting in dissociation to a gas and a solid have maximum possible rates that can be predicted using equilibrium pressure data and the kinetic theory of gases.[11,17,18] The validity of these predictions has been established for many substances[14] by examination of the decomposition rate when the sample is exposed to vacuum. This result was originally predicted by Langmuir[11] as part of the first explicit formulation of what became known as the principle of microscopic reversibility. One notable application of these results is that reported by Beruto and Searcy[15] who examined its application to kinetic studies of calcite ($CaCO_3$) decomposition. Beruto and Searcy based their study on the Hertz-Knudsen-Langmuir equation, which gives the rate of unretarded decomposition in a vacuum in moles per unit time per unit area for a substance that has only one major vapor species. In the case of (solid) calcite decomposing to (solid) calcium oxide and (gaseous) carbon dioxide, various researchers had reported different apparent orders for the decomposition reaction (see ref 15 and refs 28, 31−40 therein). While some of this variation could be attributed to different reaction geometries,[15] the range of the observed reaction order suggested that factors other than the chemical step may have controlled the rate of the process. For example, Hills suggested[19,20] that for "large" samples the observed rate was controlled not by a chemical step at the interface, but by the transfer of heat to the reaction boundary, and by the transfer of CO_2 away from it. For granular samples, it has been suggested[15] that the transport of the generated gas to the outer surface might be inhibited such that a higher pressure could be maintained in the interior (pore-space) of the sample, in effect allowing for the establishment of a local region of near-equilibrium in the interior. Within such interior pore-spaces, diffusion would be slow because gas-phase diffusion is proportional to the partial pressure gradient. In such regions (where the gas pressure could be close to the equilibrium pressure) the

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overall decomposition rate would be roughly proportional to the equilibrium pressure.[15] Near the outer portion of the sample, more efficient escape of the gas into the surrounding system would result in a lower partial pressure, and the rate of dissociation might be controlled by a solid state or surface reaction.[15] Since many of the studies prior to that of Beruto and Searcy involved granular samples and/or were carried out in the presence of either protective atmospheres or incomplete vacuum conditions, these factors affected the observed decompositions, leading to different estimates of the reaction order. After careful study, Beruto and Searcy concluded that the Langmuir experimental method for the determination of vaporization rates from single crystals into vacuum yielded less ambiguous data on the chemical step of the process.[15]

The work that has been done on the kinetics of hydrate decomposition (see Chapter 3 of ref 2 and references therein) shows characteristics similar to the work done on calcite prior to that of Beruto and Searcy, in that the conditions under which the studies have been carried out do not allow for unambiguous conclusions concerning the decomposition kinetics. In particular, none of the studies have been carried out with the sample exposed to vacuum, and some of the studies have involved granular or poly-crystalline samples[10,21,22] under controlled pressure conditions. Since, similar to calcite, hydrates decompose by an endothermic dissociation reaction, the experimental conditions most commonly used by researchers interested in studying hydrate decomposition might lead to difficulties similar to those in the calcite example discussed above. This could explain seemingly inconsistent results in the literature concerning hydrate decomposition kinetics. For example, Kono et al.[21] report different apparent reaction orders for methane hydrate decomposition in consolidated samples involving different custom-designed sediments. All of the estimated reaction orders[21] were different from those reported by Kim et al.,[22] where the order was obtained for decomposition of spherical granules in a semibatch stirred-tank reactor. The order of the reactions reported in these works[21,22] were in the range 0 to 1, similar to those reported in the literature for calcite decomposition[15] (which ranged from 0.2 to 1) when the experimental conditions involved various types of samples and/or atmospheres. In light of the results obtained in other systems involving decomposition of solid compounds to a different solid and a gas,[15] it seems that the maximum amount of information might be gained about the kinetics of hydrate decomposition by examining the decomposition rate in a vacuum. In addition, comparison of dissociation rates into vacuum with those predicted by the Hertz-Knudsen-Langmuir equation might give information about the kinetics of the "chemical step" of the dissociation. Beruto and Searcy[15] suggest that the ratio of the measured decomposition rate to that calculated from the Hertz-Knudsen-Langmuir equation is a useful parameter in correlating and predicting decomposition reaction rates. The analysis of such so-called "unretarded" dissociation provides insights into the nature of diffusion in the self-adsorbed layer.[14] The experiments suggested by Searcy and Beruto[14] for a different endothermic dissociation reaction, if used to study hydrate dissociation, might give insight into the nature of the rate limiting step in the dissociation of gas hydrates. In particular, Searcy and Beruto discuss a set of experiments to determine whether the rate limiting step is the desorption of excited molecules, the catalyzed dissociation of molecules from active sites or particles, or whether it is some surface step of the dissociation process.[14]

In a recent work, Stern et al.[10] report dissociation rates associated with a set of depressurization experiments involving methane hydrate where the polycrystaline samples were exposed to a constant pressure of approximately 1 atm of methane. While the results of Stern et al.[10] are intriguing, the conditions under which the experiments were carried out were such that no definitive conclusions can be reached at this time. For example, Stern et al. report that they observed sample temperatures up to 30 K lower than the external system temperature during rapid dissociation.[10] Such difficulties were also commented on by Beruto and Searcy in the calcite system, where they note that due to the endothermic nature of such reactions, rapid decomposition can result in excessive heat loss, leading to surface cooling. Since the decomposition rate is strongly dependent on temperature, it is important to control the surface temperature by ensuring that the rate at which heat is transferred to the sample is adequate to maintain a constant sample temperature. In the case of calcite decomposition, this was accomplished by heating the surfaces of the sample holder and cell with radiant heat.[15]

As an example of the difficulty in interpreting data where the sample temperature is not kept constant and this is not taken into account, consider Figure 4 of ref 10 which shows the dissociation rate as a function of external temperature. As reported by Stern et al., the sample temperature was considerably different at some external temperatures. For example, the points near 240 K really involve sample temperatures around 210 K due to the 30 K cooling reported by Stern et al.[10] at an external temperature of 240 K. Clearly, due to the important role of temperature in the kinetics of hydrate decomposition, such effects need to be either eliminated or accounted for in any subsequent analysis. The amount of heat that must be added to the sample to maintain a constant temperature can be calculated from the dissociation rate and the enthalpy of dissociation, as discussed below.

Calculating Maximum Possible Dissociation Rates. The maximum rate of an endothermic dissociation is predicted by the Hertz-Knudsen-Langmuir equation:

$$J_{max}(T) = \frac{P_{eq}(T)}{\sqrt{2\pi MRT}} \tag{1}$$

In eq 1, the maximum possible rate at which the gas can be liberated,[11,15] J_{max}, is given in terms of the molecular weight (M) of the gas, the temperature (T), and the equilibrium gas pressure (P_{eq}) at the corresponding temperature.[14−16] Note that the full temperature dependence of the dissociation rate predicted by eq 1 is only known once the explicit temperature dependence of P_{eq} is given. To illustrate the use of this equation, consider the dissociation of spherical particles of hydrate (similar to the grains making up the sample used by Stern et al.[10]) such that

$$J_{max}(T) = \frac{-1}{4\pi r^2(t)} \frac{dS}{dt} \tag{2}$$

Here, $S(t)$ is the number of moles of gas contained in the sample, meaning that $-dS/dt$ is the number of moles of gas generated per second by the dissociation of the sample, and $4\pi r^2(t)$ is the surface area of the shrinking spherical grain of radius $r(t)$. If we assume that the grain has a uniform (constant) composition, then the total amount of gas in the sample is given by $S(t) = \frac{4}{3}\pi r^3(t)\rho_g$, where ρ_g is the number of moles of gas per unit volume in the hydrate, which can be calculated on the basis of the fraction of the cages in the hydrate occupied by gas

molecules.[2] Using this relation for $S(t)$ in eq 2 gives

$$J_{max}(T) = \frac{-1}{4\pi r^2(t)} \frac{dS}{dt} = -\rho_g \frac{dr}{dt} \qquad (3)$$

Since, as shown in eq 1, J_{max} is a function of temperature (T) only, and is independent of time (t), eq 3 can be integrated to give

$$r(t) = r_0 - \frac{J_{max}(T)}{\rho_g} t \qquad (4)$$

where r_0 is the initial grain radius. Using eqs 2 and 4 allows the calculation of the instantaneous rate (in moles per second) at which gas is produced:

$$R_i(T,t) = -\frac{dS}{dt} = 4\pi J_{max}(T)\left(r_0 - \frac{J_{max}(T)}{\rho_g} t\right)^2 \qquad (5)$$

To examine the average dissociation rate over the time during which 50% of the hydrate dissociates (the quantity reported in Stern et al.[10]), we need to compute $\tau_{1/2}$, the time until 50% of the sample is dissociated. Note that $S(t) = \frac{4}{3}\pi r^3(t)\rho_g$. From this it follows that $S(\tau_{1/2}) = \frac{4}{3}\pi r^3(\tau_{1/2})\rho_g$. However, since half of the original amount of hydrate has dissociated, we also know that $S(\tau_{1/2}) = (\frac{1}{2})(\frac{4}{3}\pi r_0^3 \rho_g)$. Equating these and solving for $\tau_{1/2}$ yields

$$\tau_{1/2} = \frac{\rho_g r_0}{J_{max}(T)}\left(1 - \frac{1}{2^{1/3}}\right) \qquad (6)$$

The average dissociation rate over the time period $0 \le t \le \tau_{1/2}$ is given (in moles per second) by

$$R_{ave}(T) = \frac{1}{\tau_{1/2}} \int_0^{\tau_{1/2}} R_i(T, t)\, dt = \frac{2\pi r_0^2 J_{max}(T)}{3(1 - 1/2^{1/3})} \qquad (7)$$

This can be converted to the percent-dissociation rate reported by Stern et al. by dividing by the total number of moles of gas in the original sample ($S(0)$):

$$D_{ave}(T) = \frac{J_{max}(T)}{(2 - 2^{2/3}) r_0 \rho_g} \qquad (8)$$

The small disadvantage of eq 8 as compared to eq 7 is that eq 8 involves ρ_g, computation of which requires the consideration of cage occupancies in the hydrate structure, an added complication not present in eq 7.

For the sample temperature to remain constant, the heat transfer rate from the surroundings to the sample must be equal to the heat necessary for the phase transition. The amount of heat necessary to dissociate the hydrate (per mole) is given by ΔH_{dis} (in Joules per mole of hydrate). Since each mole of hydrate contains one mole of gas, the heat that must be transferred to the sample per second is given by $\Delta H_{dis} R_i$. Therefore, the heat transfer rate necessary to maintain the maximum gas generation rate given by eq 5 is

$$R_Q(T, t) = 4\pi \Delta H_{dis}(T) J_{max}(T)\left(r_0 - \frac{J_{max}(T)}{\rho_g} t\right)^2 \qquad (9)$$

Similar to eq 7, the average heat transfer rate over the time
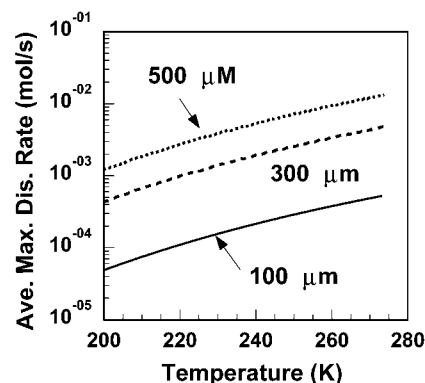

Figure 1. Average maximum dissociation rate over the time interval from $t = 0$ up to the time when 50% of the sample had dissociated as a function of temperature for spherical hydrate particles with initial radii of 100, 300, or 500 μm.

interval $0 \le t \le \tau_{1/2}$ can be calculated as

$$R_{Q,ave}(T) = \frac{1}{\tau_{1/2}} \int_0^{\tau_{1/2}} R_Q(T, t)dt = \frac{2\pi r_0^2 J_{max}(T)\Delta H_{dis}(T)}{3(1 - 1/2^{1/3})} \qquad (10)$$

Equations 5−10 depend on the maximum dissociation rate, J_{max}, predicted by eq 1, which involves the equilibrium gas pressure at temperature T. While hydrate equilibrium pressures can be computed on the basis of a statistical thermodynamic model (see Chapter 4 of ref 2), empirical relations for the equilibrium pressure for hydrates involving a single gas species are available,[2,23] and have been shown to be derivable from the full statistical-thermodynamic model.[24] These simple relations are of the form

$$P_{eq} = e^{a + b/T} \qquad (11)$$

This allows J_{max} to be written in the form

$$J_{max}(T) = \frac{e^{a+b/T}}{\sqrt{2\pi MRT}} \qquad (12)$$

Using eq 12 in eq 7 gives a simple equation for the average maximum rate at which gas is generated over the time interval $0 \le t \le \tau_{1/2}$ during hydrate decomposition:

$$R_{ave}(T) = \frac{2\pi r_0^2 e^{a+b/T}}{3(1 - 1/2^{1/3})\sqrt{2\pi MRT}} \qquad (13)$$

This average dissociation rate, as a function of temperature, has been plotted for methane hydrate in Figure 1 for several values of the initial radius r_0, and in Figure 2 is shown as a function of the initial grain radius for several temperatures. In constructing these figures we have used values of a and b for methane hydrate of 21.6248 and −1886.79, respectively, to obtain P_{eq} in Pa.[23] Note that the use of a log scale in Figure 1 for the average dissociation rate results in a linear displacement of the curves with different initial radii, even though the dependence of the rate on r_0 is quadratic as shown by eq 13.

Based on eq 13, the average, maximum heat transfer rate is given by

$$R_{Q,ave}(T) = \frac{2\pi r_0^2 e^{a+b/T}\Delta H_{dis}(T)}{3(1 - 1/2^{1/3})\sqrt{2\pi MRT}} \qquad (14)$$

The enthalpy of dissociation of methane hydrate at the desired
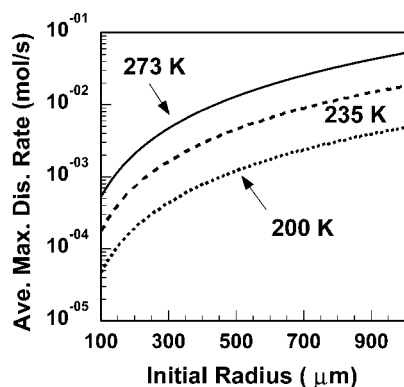
Figure 2. Average maximum dissociation rate over the time interval from $t = 0$ up to the time when 50% of the sample had dissociated as a function of the initial radius of spherical hydrate particles at constant temperatures of 200, 235, or 273 K.
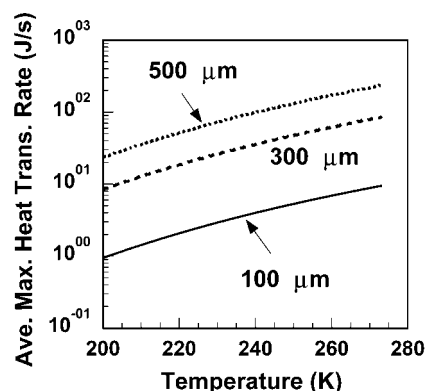

Figure 3. Average maximum heat transfer rate necessary to maintain a constant sample temperature over the time interval from $t = 0$ up to the time when 50% of the sample had dissociated as a function of temperature for spherical hydrate particles with initial radii of 100, 300, or 500 μm.

Figure 4. Average maximum heat transfer rate necessary to maintain a constant sample temperature over the time interval from $t = 0$ up to the time when 50% of the sample had dissociated as a function of the initial radius of spherical hydrate particles at constant temperatures of 200, 235, or 273 K.

Figure 5. Schematic diagram of hydrate dissociation to free gas and ice.

temperature is needed to calculate the average maximum heat transfer rate. This enthalpy can be calculated from $\Delta H_{dis}(T) = \Delta H_{dis}{}^0 + \int_{T_0}^{T} \Delta C_p(T') \, dT'$, where $\Delta H_{dis}{}^0$ is the enthalpy change at 273.15 K, and ΔC_p is the molar heat capacity difference. $\Delta H_{dis}{}^0$ has been experimentally determined by Handa[25] to be 18.13 kJ/mol. Since $\Delta C_p = c_p{}^{hyd} - nC_p{}^{water} - C_p{}^{gas}$, the heat capacity difference can be calculated from the heat capacity of methane hydrate given by Handa[25] and standard values for ice and gaseous methane.[26] Figures 3 and 4 show the results of using the values for the enthalpy difference obtained in this manner (where we have used the value for n of 6.0 reported by Handa.[25]) in eq 14 for several values of the initial radius (Figure 3), and for several temperatures (Figure 4).

Examination of Hydrate Decomposition Kinetics. Searcy and Beruto have developed a kinetic theory for endothermic decomposition reactions. They have studied the kinetics in the limiting case of when the sample is exposed to vacuum,[16] as well as the cases when the solid and/or gaseous product affects the kinetics.[27] The model that they developed assumes (in agreement with experimental observation for most endothermic decomposition reactions) that the solid product forms a porous layer on the reactant.[27] In the case of hydrates this would imply that the ice formed by the decomposition of the hydrate has pores, as shown schematically in Figure 5. If one considers the decomposition of a portion of the hydrate near or on the upper boundary of the hydrate region depicted in Figure 5, then there are two possibilities, depending on the location of the hydrate that is dissociating: (a) if the
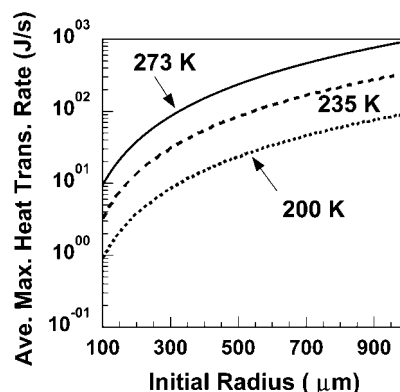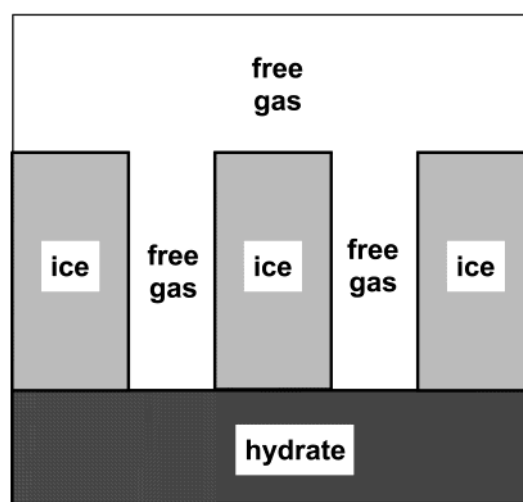
dissociating hydrate is in a region below a pore, then the gas needs to only transfer across the hydrate gas interface, while the ice generated by the dissociation must diffuse on or in the hydrate to reach and then transfer across the hydrate/ice interface; (b) if the dissociating hydrate is below a region containing ice, then it is the gas which must first diffuse on or in the hydrate until it reaches the hydrate/gas interface, and then be transferred across that interface. As a result of their considerations, Searcy and Beruto have identified four steps, any or all of which may be involved in the decomposition. For hydrates these steps are: (1) flux of gas across the hydrate/gas interface into the free gas region; (2) diffusion of gas on or in the hydrate to reach the hydrate/gas interface; (3) transfer of ice across the hydrate/ice interface into the ice region; and (4) the flux formed when the portion of the ice that is at the hydrate/gas interface diffuses on or in the hydrate to reach the ice region. With the model proposed by Seracy and Beruto, one does not need to specify the exact mechanism by which the steps take place.

One of the main conclusions of the work of Searcy and Beruto is that, under the correct conditions, the variation of a decomposition rate with gas pressure can be used to gain information about the rate limiting step of the dissociation. If one of the steps involving the gaseous product is rate limiting, then the net flux of gas from the sample will decrease linearly as the product gas pressure increases toward the equilibrium

value.[27] Conversely, if the slowest step of the dissociation involves the solid product of the dissociation (which in the case of hydrates would be ice), then the decomposition rate will vary inversely with the gas pressure and will be proportional to ($1/P_g - 1/P_{eq}$), where P_g is the free gas pressure.[27]

As mentioned earlier, various researchers have reported incomplete or delayed dissociation of hydrates under conditions such that the hydrate is expected to be unstable and should dissociate rapidly. Most of these observations have been made at 1 atm pressure, and all have been at temperatures below the ice-point of water. A recent publication[10] examined such anomalous behavior for methane hydrates, and found that over a certain external temperature range there was a region where the dissociation rates were over an order of magnitude slower than those for temperatures either above or below this range. Stern et al.[10] have suggested that the hydrate in this region behaved as if it were a different material, or in a different geochemical state. It is well-known that decomposition reactions often yield, as a direct solid product, a metastable crystal modification or an amorphous form of the solid.[28,29] Searcy and Beruto,[27] who studied dissociation reactions in general (not hydrates), found that if such a porous solid were to form, the time dependence of the observed gas flux during its formation could also be used to obtain information about the rate limiting step of the decomposition. In particular, they concluded that if the sample were held at a constant temperature and exposed to vacuum, the observed flux of gas would be proportional to $t^{-1/2}$ if a step involving the gas was rate limiting. If, on the other hand, the rate limiting step involved the solid product (which in the case of hydrates would be ice), then the gas flux would be proportional to $t^{-1/3}$. Unfortunately, there are no tabulated data in Stern et al.,[10] precluding the assessment of which of these behaviors, if either, were evidenced during the decomposition of methane hydrate reported by Stern et al. to potentially involve an intermediate compound.

Summary

The study of hydrate decomposition is essential to the development of efficient methods to recover methane from naturally occurring hydrate deposits. The development of such methods will require information about the nature of the rate limiting step of this dissociation, as well as about the overall rate at which methane can be generated from hydrate samples. Work done by Langmuir and others on the endothermic dissociation of other compounds suggests experiments to obtain the maximum amount of information concerning these aspects of the reaction. In addition, due to the unique nature of vaporization reactions, maximum possible rates can be calculated on the basis of equilibrium pressure data and the kinetic theory of gases. The Hertz-Knudsen-Langmuir equation has been used in this work to calculate these maximum dissociation rates for methane hydrate, as well as the rate at which heat must be added to the sample to maintain this rate without affecting the sample temperature. Such considerations may be relevant to both the study of hydrate decomposition, as well as the

eventual efficient production of natural gases such as methane from hydrate deposits. It is hoped that the considerations presented in this work will help to motivate new experiments involving single-crystal hydrates exposed to vacuum. Such experiments would help to determine the rate limiting step in hydrate dissociation to free gas and ice.

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