Estimation of methane hydrates dissociation kinetic coefficients at T < 273 K

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Abstract. To simulate and optimize the processes of low-temperature processing of methane hydrate, it is necessary to obtain appropriate information on the kinetic coefficient of the dissociation process. Excluding self-preservation in the analysis of experimental data, general patterns can be distinguished, including estimating the activation energy of the dissociation process (in the approximation of a shrinking core). The obtained kinetic coefficients were used to reproduce the kinetic curves obtained by different authors. These coefficients are recommended for using in kinetic models of methane dissociation hydrate in the temperature range T < 273 K.

1. Introduction
Gas hydrates are of interest for several reasons. First of all, hydrate formation can be a problem during gas production in the cold regions and its transportation over long distances [1, 2]. Secondly, natural gas hydrates are a potential source of hydrocarbons: current estimates show that natural gas hydrates contain a huge amount of combustible gases, although cost-effective and technically reliable methods for their production have not yet been developed [3]. Thirdly, the storage of gases in hydrated form softens the requirements for thermobaric conditions (compared with the storage of liquefied gases) [4, 5]. Some researchers have proposed technological processes based on the transition of gases to hydrates (moisture removal, air conditioning, etc.) [1, 6]. Finally, there are the issues related to the role of natural hydrates in global processes such as climate changes [2, 7], including the possibility of greenhouse gases burial [8]. However, the industrial use of hydrates is so far limited by attempts to extract natural gas from permafrost and seabed [3], as well as projects for gas hydrate transport and storage [9, 10].

The existing problems of using hydrates are related to an insufficient understanding of the physics of the processes that occur during the formation and destruction of the hydrate phase. This, in turn, is associated with the variety of according phenomena. Usually, theoretical considerations of such processes use simplified approaches: phase transition models, diffusion models, etc. More detailed models take into account the formal kinetics of physicochemical transformations [11], heat and mass transfer [12], filtration of particles in the pores [13] and in rocks containing hydrates [14]. Energy utilization of hydrates requires understanding of hydrates decomposition at high heat fluxes and complex flows [15-18].
An important problem is the selection of reliable kinetic coefficients describing the rate of decomposition of hydrate particles. At present, the scope of works on the experimental measurement of the rate constants of hydrate dissociation is very limited. This is due to a number of problems arising from such measurements: interactions of heat and mass transfer processes, the need to maintain isothermal conditions, self-preservation, etc. The results of Bishnoi et al. are most widely used [19, 20]. Kinetic coefficients were measured for the conditions of decomposition of particles at temperatures above 273 K (which allows us to avoid self-preservation). For temperatures below ice melting point, these coefficients, however, give a significant error, which may be due to differences between the mechanism of "low temperature" (T < 273 K) and "high temperature" (T > 273 K) dissociation.

In this paper, an attempt is made to clarify the kinetic coefficients for the region of negative temperatures (in Celsius scale), as well as to generalize the known experimental data on this topic.

2. Low-temperature kinetic model of methane hydrate dissociation

The mathematical model of decomposition of gas hydrate is based on the model of a shrinking-core and irreversible kinetics of dissociation in the Bishnoi form [19, 20]. It is supposed that the particle is isothermal (deviations from isothermal will be discussed below). In this case, one can write:

\[
\frac{dX}{dt} = -k_d^0 e^{E_a/RT} \left( P^{eq} - P \right) \frac{S_r}{B m_0}
\]

Here \(X\) is the degree of decomposition of the particle (the ratio of the gas contained in the hydrated form to its initial amount); \(k_d\) is the preexponential factor of the kinetic coefficient, kg/Pa/m²/s; \(E_a\) is the activation energy of the dissociation process, J/mol; \(P\) is the gas pressure in the pores of the particle; \(P^{eq}\) is equilibrium gas pressure above the hydrate; \(S_r\) is the surface area of the dissociation front, m²; \(S_0\) is the surface of the particle; \(B\) is the mass fraction of gas in hydrate; \(m_0\) is the initial mass of the particle. As it is shown in [21], this model fits carbon dioxide hydrate decomposition as well (with different kinetic coefficients).

For a spherical particle, we can write:

\[
\frac{dX}{dt} = -k_d^0 e^{E_a/RT} \pi d_0^2 \left( P^{eq} - P \right) \frac{1 - X}{3} = -6k_d^0 e^{E_a/RT} \pi d_0^2 \left( P^{eq} - P \right) (1 - X) \frac{1}{6}
\]

For isothermal conditions, the entire coefficient written before \((1-X)^{2/3}\) can be considered constant. Thus, the conversion rate increases with decreasing particle size, which is consistent with empirical observations. In experiments one can measure following value:

\[
K = \frac{6k_d^0 e^{E_a/RT} \left( P^{eq} - P \right)}{B_0 d_0}
\]

To compare the data obtained at different temperatures, it is necessary to take into account the temperature dependence of the reaction rate both for the kinetic coefficient (by means of activation energy) and the equilibrium pressure. The superposition of the temperature functions in the kinetic coefficient and the equilibrium pressure can lead to a wide range of possible observed dissociation rate dependences on temperature. Therefore, it is necessary to separate these factors with sufficient accuracy. The equilibrium pressure of methane over hydrate is usually expressed by an exponential function of temperature:

\[
\log \left( P^{eq} - \Delta P^0 \right) = A_1 - \frac{A_2}{T}
\]
Coefficients $A_1$ and $A_2$ can be determined from experimental data or from theoretical considerations [22]. In this paper, the following numbers are accepted: $A_1 = 4.77047; A_2 = 920.701; \Delta P^0 = 0.5$. These coefficients give main features for the dissociation of methane hydrate: equilibrium temperature of -80 °C for 1 atm and equilibrium pressure of 25 atm for 0°C. It should be noted that kinetic analysis results are very sensitive to equilibrium curve equation.

The kinetic coefficients can be determined in two ways: by the differential method (by measuring the rate of the process and comparing it with kinetic models) and by the integral method (by measuring the characteristic transformation time intervals). We will use both for different data, depending on the convenience.

2.1. Differential method:

$$K = -\frac{(1-X)^3}{\Delta X / \Delta t}$$

The numerator is the value of the function for the selected value of $X$, and in the denominator is the average rate for a given moment, calculated in the difference approximation. For a constant heating rate $\beta$, one can obtain:

$$K = -\frac{\Delta T (1-X)^3}{\beta \Delta X}$$

2.2. Integral Method:

Knowing the characteristic time, for example, the time of complete decomposition or half-life (which can be determined more precisely), we can write:

$$K = \frac{3(1 - \sqrt[3]{X})}{\tau_X}$$

After the coefficient $K$ is found by any method, it is possible to find its components that correspond directly to dissociation kinetics:

$$k_d = k_0^0 e^{-\frac{E_a^0}{RT}} = \frac{B \rho_0 d_0}{6(P^0 - P)} K$$

The pre-exponent and activation energy can be determined by constructing the usual Arrhenius plot in the coordinates $\ln(k_d) \sim 1/T$.

3. Results and discussion

Two main sets of measurements that will be considered here are the data of Stern et al. [23] and Takeya et al. [24]. The work [24] gives curves of the relative intensity of the methane-hydrate bond signal in samples of hydrated powder of different fractions at constant heating rate of 1 K/min. The low rate of temperature change makes it possible to consider the conditions as isothermal between two consecutive measurements; therefore, in this case, we can use the differential method. In [23], measurements of the half-life for methane hydrate samples are made. The authors report possible temperature inhomogeneities, however, in the first approximation, we consider their experiments to be isothermal. The integral method is well suited for these data.

Some experimental points are obviously not suitable for analysis, since base kinetic equation does not take into account self-preservation. According to well-known literature data, this process begins at temperatures of the order of 240 K. That is, in order to isolate the kinetic coefficients without the influence of transfer processes, we need to sacrifice the temperature range from 240 K and higher.
Nevertheless, there are still enough experimental points: 10 points from the experiments [23] and about 20 from [24]. The processed results are shown in figure 1.

![Figure 1. Arrhenius plot for experiments from [23, 24]. Bold solid line is linear approximation, thin solid line is kinetic coefficient for T > 273 K [19, 20].](image)

The average mass content of gas in hydrate is assumed to be 12%. The density of the hydrate is 910 kg/m$^3$. The average particle size for the data [24] is taken equal to the average of the boundary values of these ranges. In [23], samples were prepared by pressing a hydrated powder (average size of 200-300 µm) into cylinders with an average porosity of 0.29. However, in this case, the hydrate particles do not form homogeneous solid mass, and the porosity and average pore size (which, obviously, is of the order of the initial particle size) provide an effective outflow of the evolved gas. It is assumed that the characteristic granule size is an order of magnitude larger than the particle size of the original powder.

It can be seen from figure 1 that, despite significant differences in the experimental methods, the obtained kinetic coefficients quite well fall into general dependence. The effective parameters of the Arrhenius form of the kinetic coefficient are equal to: $k^0 = 3.25 \times 10^{-3}$ kg/Pa/m$^2$/s; $E_a = 34$ kJ/mol. These values differ significantly from the kinetic coefficients from [19, 20]. This difference can be explained by different dissociation mechanisms. Above the ice melting point, dissociation is accompanied by the formation of a stable liquid phase, and therefore requires greater energy consumption. The energy barrier of such one-stage decomposition will be higher as compared to dissociation resulting in the formation of porous ice.

The estimation of kinetic coefficients from the measurement results is a typical inverse problem, the solution of which is not always unambiguous and stable. In this paper, the solution is found by the least squares method (minimization of the non-negative residual function $\Phi$):

$$\min \Phi = \sum_j \omega \left( Y_j^{\text{exp}} - Y_j^{\text{calc}} \right)^2$$

Since the direct problem is non-linear (especially in the non-isothermal case), and the set of the experimental data includes experiments carried out under different conditions, it is necessary to carefully select the weight coefficients for the residuals obtained by approximating the kinetic coefficients for different options (heating rates, particle sizes, etc.).

The residual function includes the discrepancies that arise when comparing the experimental and calculated data for four experimental sets: integral data [23]; isothermal kinetic curves [23]; non-
isothermal kinetic curves with constant heating rate [24]; non-isothermal kinetic curves with varying heating rate [13]. In total, the residual function $\Phi$ includes about fifty terms.

![Figure 2. Dependence of residual function $\Phi$ on Arrhenius coefficients for selected kinetic data sets.](image)

![Figure 3. Comparison of experimental and calculated kinetic curves of methane hydrate dissociation at constant heating rate (1 K/min [24]).](image)

The results of optimizing the residual function in the space of coefficients $k_0$ and $E_a$ are shown in figure 2: there is a significant range of parameters in which the pre-exponent and activation energy, varying over a fairly wide range, give approximately the same summary residual (the so-called compensation effect is observed). Therefore, for certainty of the calculations, the activation energy is taken to be 34 kJ/mol, as the generalized Arrhenius plot gives (figure 1). Pre-exponential factor under these conditions is $0.019$ kg/Pa/m$^2$/s. For these conditions, kinetic calculations were carried out according to data [24], the results of which are shown in figure 3. The calculated curves are in very good agreement with the experiment for small fractions (up to about 200 $\mu$m). With a further increase in size under experimental conditions, the effects of transport processes most likely begin to affect (for
example, the resistance of the ice crust increases, which is one of the mechanisms of self-preservation [13]). Therefore, the decomposition of particles after reaching a degree of conversion of 50% is slower than expected from the kinetic model.

Conclusion

The dissociation kinetics of gas hydrate in the form of powders and pressed granules with different diameters has been investigated. The activation energy value of 34 kJ/mol for methane hydrate has been obtained for dissociation at negative temperatures (outside the self-preservation region), which satisfactorily generalizes the experimental data of various works. The resulting $E_a$ is substantially less than value obtained at $T > 273$ K (81 kJ/mol). As a result, at negative temperatures the dissociation rate is significantly higher than extrapolated from positive temperatures range.

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