

CO₂ HYDRATE FORMATION KINETICS AT MARTIAN CONDITIONS. G.

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Introduction: In the early seventies, the possible existence of CO₂ hydrates on Mars was proposed [e.g. 1]. Recent investigations show that clathrates could exist in a large volume of the Martian regolith at all latitudes, for all the present mean annual surface temperatures [2]. Unfortunately, there is limited information about their physical properties and the physical chemistry of the formation and decomposition kinetics at Martian conditions. This paper comes to shed more light on those processes, presenting our results from the experiments on formation kinetics and micro-structural observations.

Possible importance of CO₂ hydrates:

Polar caps: The Martian polar caps are believed to consist of water ice, solid CO₂, CO₂ clathrate and dust in unknown proportions, probably different for both caps. CO₂ clathrate is the strongest of the three ices possibly affecting the rheologic properties [3-6] as suggested for the polar ice layers on the north [7] and the south polar caps [8]. Moreover, the higher the CO₂ hydrate quantity in the cap, the longer the period needed for establishing a steady-state geothermal gradient in the inner parts of the caps, which would affect the process of their basal melting [4, 5]. This follows from the fact that the hydrates are approximately 5 times better thermal insulators than the ice.

Terra formation: Some authors [e.g. 9-12] suggest a fast CO₂ hydrate decomposition, driven by some catastrophic events (such as meteorite impacts[§] or volcanic eruptions) to be the reason for the formation of the chaotic terrains and outflow channels, pancake-dome structures and northern plain deposits. They usually assume the existence of some layered or mixed underground deposits of ice + CO₂ hydrate.

Climatology: In **Table 1** are represented the values of the specific latent heat [kJ/mol] of different phase transition processes between liquid (L), vapor (V) and solid (S), which can occur on Mars (H for hydrate). It is obvious that sublimation-condensation cycles can transport large amounts of heat involving pure water and CO₂ ice as well as CO₂ hydrate. However, if CO₂ hydrates are present on Mars in large quantities the extended stability regions for CO₂ in condensed form would alter the geographic localities of heat redistribution.

[§] Such an impact can create a local overheating of more than 1600 K [13]

	H ₂ O	CO ₂	Hydrate
V ↔ S	± 51.4	± 28.13	---
L ↔ S	± 6.04	---	---
H↔S+G	---	---	± 24.53 ^{\$\$}
H↔L+G	---	---	± 68.7 ^{\$\$\$}

Results and discussion:

Neutron diffraction: Guided by the relevance of clathrate hydrate formation from water ice for Mars, a series of kinetic *in-situ* neutron diffraction experiments for CO₂ hydrate formation at 263 K, 253 K and 230 K were performed (**Fig. 1**). As a starting material, D₂O ice Ih spherical grains with a specific surface area of 750 cm²/g were used. The large and

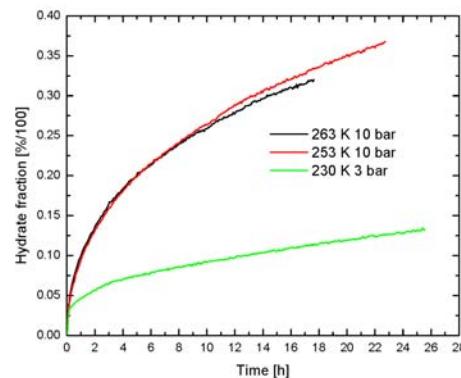


Fig. 1 A comparison between the reaction rates in the three runs. The reaction at 253 K at some stage exceeds the one at 263 K because of the higher excess fugacity in the first case.

well-defined surface turned out to be essential for a quantitative analysis. Moreover, Staykova et al. [20] showed that there was no significant difference between the activation energies for CH₄ hydrate formation from D₂O and H₂O ice. The goal of these three runs was to obtain a first idea about the time scale of the reactions at those conditions. For the analysis we use a multistage model [16, 17] for the hydrate formation to find the activation energy of the process. Using this activation energy and putting it

^{\$\$} Represents the latent heat of hydrate formation / decomposition from / to ice + gas (After [14])

^{\$\$\$} Represents the latent heat of hydrate formation / decomposition from / to liquid + gas (After [15])

into the previously mentioned model, we extrapolate the parameters of the reaction at Martian conditions. The model divides the formation process into three stages: **I stage**: ice surface coverage with a hydrate film; **II stage** – reaction limited: depends on the gas and water redistribution across the phase boundaries and **III stage**: affected or fully controlled by the water and gas mass transport through the hydrate layers, respectively from and to the inner parts of the original ice grains.

Gas consumption: A series of in-house formation kinetic experiments at low temperature were performed to complement the neutron diffraction experiments. The results were obtained via

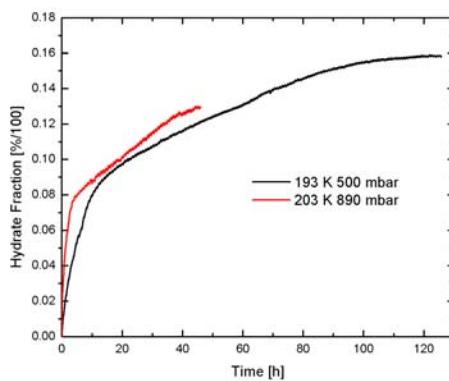


Fig. 2 A comparison between the reaction rates in the runs at 203 K and 193 K.

calculation of the gas consumption during the formation process. Here are presented two runs at 203 K and 193 K (**Fig. 2**).

Results of the kinetic experiments: Applying the model of Salamatin & Kuhs for the second stage of the reaction, values for the rate coefficients for the different reactions were obtained (**Fig. 3**). Initially, we assumed that the activation energy obeyed the Arrhenius equation:

$$k = A \cdot \exp(-E_a/RT)$$

If this assumption was correct, all the points from **Fig. 3** would lay on the same line. A huge bias, of the two points at 272 K and 263 K, from the linear fit is observed. This can be explained with the fact that a quasi-liquid layer (QLL) with a significant thickness appears on the ice surface at temperatures, close to the melting point. The thickness of the layer decreases with the temperature and at -20°C (253 K) becomes negligible [18]. The existence of such a QLL will lead effectively to hydrate formation from “liquid” and gaseous substances. This certainly can change dramatically the energy balance (see **Table 1**) of the reactions occurring in this temperature interval causing the observed bias. The other points, from 193 K to 253 K are perfectly described by a linear

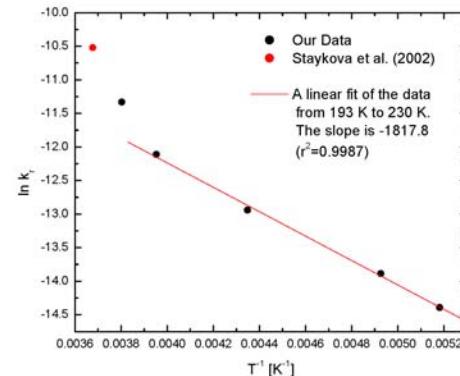


Fig. 3 Plot of the model results for the reaction rate coefficients vs. the temperature, for the second stage of the formation.

function. From the slope of this fit, the value of the activation energy was obtained to be $E_a = 15.1 \text{ kJ/mol}$ (3.8 kcal/mol). A model prediction about the hydrate development at 150 K and 6 mbar pressure, based on this activation energy, was made (**Fig. 4**). The simulation was performed for a period of approximately one month. Two regions can be distinguished: a steep one, corresponding to the first stage of the reaction and a linear one, corresponding

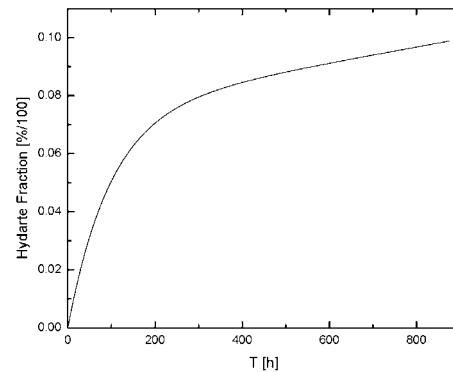


Fig. 4 A model prediction for the reaction development at Mars surface conditions.

to the second stage. The second stage seems to be reached after about 400 hours and at that moment, the hydrate content will be around 8 % of the available ice. At this point one can start to think that the amount of hydrate, if exists at all, will be negligible. But this would be true if we had a steady-state ice polar cap (which is not the common opinion), suddenly exposed to the influence of the CO₂ atmosphere. In fact, water frost is continuously deposited on the cap, which provides new surface for hydrate formation. If the rate of deposition of the ice is comparable to the hydrate formation rate for the first stage of the reaction, then this may lead to the limiting case of a complete transformation of the ice into hydrate. This could have been the case in some periods of the Martian history, which may have

caused the formation of layers, consisting basically of hydrate.

Field Emission Scanning Electron Microscopic (FE-SEM) observations: The microstructure of the hydrates could affect their physical properties. Moreover, some time ago it was reported that gas

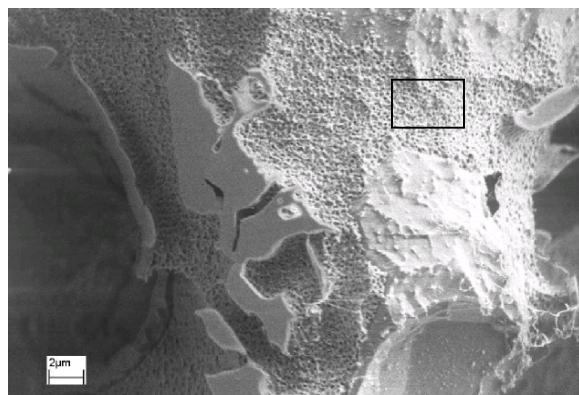


Fig. 5 FE-SEM image of CO_2 hydrate. The black rectangle shows the place, where the pore (bubble) diameters were measured

hydrates formed from ice frequently have a porous sub-micron structure [19]. A large number of FE-SEM pictures of the prepared samples was taken. The porous structure was confirmed and further analyzed. It can be described as solid and partially open foam. An attempt for quantitative description was made (See Fig. 5) and a lognormal distribution of the bubble diameters was obtained (Fig. 6).

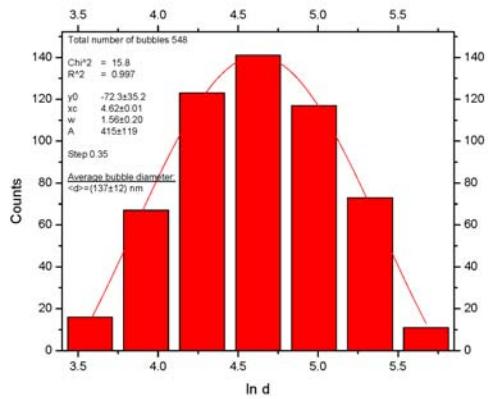


Fig. 6 A distribution of the logarithm of the bubble diameters. It always keeps the lognormal shape but the average diameter usually varies, within large limits even in one sample.

The foam-like structure can add to the large difference between the hydrate and ice thermal conductivities and, furthermore, it can certainly affect the clathrate decomposition kinetics. Staykova et al. [20] confirmed that from ice and gas usually porous

hydrates are formed, while there is some evidence that dense (non-porous) hydrates are formed from a co-condensation of water vapor and gas. The porous nature of CO_2 hydrates will certainly influence the remote detection of clathrates because of the different reflectivity.

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