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Temperature dependence of the sublimation rate of water ice: Influence of impurities

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A B S T R A C T

The sublimation rate of ice is commonly calculated using the simple Hertz–Knudsen formula. This formula is derived from the kinetic theory of gases and ignores microphysical processes determining the actual sublimation rate. The microphysical processes can be accounted for by including the temperature dependent sublimation coefficient (Kossacki, K.J., et al. [1999]. Planet. Space Sci. 47, 1521–1530; Gundlach, B., Skorov, Y.V., Blum, J. [2011]. Icarus 213, 710–719). Kossacki and Markiewicz (Kossacki, K.J., Markiewicz, W.J. [2013]. Icarus 224, 172–177) discussed to what extent inaccuracy of the simple Hertz–Knudsen equation affects the calculated temperature of Comet 67P/Churyumov-Gerasimenko. Numerical simulations presented in Kossacki and Markiewicz (Kossacki, K.J., Markiewicz, W.J. [2013]. Icarus 224, 172–177) indicate, that derivation of the temperature below the dust mantle from the measured water production rate ignoring temperature dependence of the sublimation coefficient can lead to an underestimate of the temperature by more than 10 K. Thus, it is important to know the dependence on the sublimation coefficient of the composition of the real cometary ice, which can be far from purity.

We intended to check whether a small amount of dissolved minerals can affect the temperature dependence of the sublimation coefficient of ice. According to our experiments the answer is positive.

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1. Introduction

Sublimation processes are significant for many materials of scientific and industrial importance. Typically, the flux of sublimating molecules and the recession rate of a surface due to sublimation are calculated using different forms of the classical Hertz–Knudsen equation (also called Hertz–Knudsen–Langmuir equation). Farther on we call it the HK equation. For the recession rate it is written

$$\frac{dz}{dt}(T) = \frac{\alpha}{\varrho}\left(\frac{\mu}{2\pi R_g T}\right)^{0.5}(p_{sat} - p), \qquad (1)$$

where T is the temperature on the sublimation surface, ϱ is the density of the sublimin material, p is the pressure over the subliming surface, p_{sat} is the equilibrium saturation pressure at temperature T, μ is the molar mass of ice, $R_g = 8.314$ J mol^{-1} K^{-1} is the universal gas constant, and alpha is a coefficient which we investigate experimentally (for sublimation of the water ice) in this work.

The HK equation is derived from the kinetic theory of gases assuming an equilibrium distribution of molecular velocity (Skorov and Rickman, 1995). In its original form the HK equation contains the dimensionless coefficient $\alpha = 1$. This assumption is not sufficient to explain correctly the sublimation-condensation phenomena, even for the pure materials. Moreover, materials encountered in nature are never the pure elements or the pure chemical compounds but they always contain different contaminants. Influence of the volatile impurities and/or the non-subliming (solid) contaminants in the material can be taken into account by replacing $\alpha = 1$ by the temperature dependent sublimation coefficient α_s being also function of the contents and the properties of the impurities. The influence of the collisions and backscatter of molecules can be taken into account by adding an additional multiplicative coefficient. In this case the coefficient is called the return flux coefficient B. Thus, Eq. (1) becomes

$$\frac{dz}{dt}(T) = \frac{B\alpha_s(T)}{\varrho}\left(\frac{\mu}{2\pi R_g T}\right)^{0.5}(p_{sat} - p), \qquad (2)$$

or for the flux of subliming molecules

$$F_s(T) = B\alpha_s\left(\frac{\mu}{2\pi R_g T}\right)^{0.5}(p_{sat} - p). \qquad (3)$$

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The aim of this work is an experimental investigation of the dependence of α_s, on temperature, taking into account presence of dissolved impurities. We intended to check whether a small amount of dissolved minerals, less than 0.1% by mass, may have noticeable influence on the temperature dependence of the sublimation coefficient of ice. The samples were produced of the water ice made of the demineralized water, and of a spring water with dissolved minerals. We performed series of measurements of the sublimation rate at temperature within the range 190–260 K.

2. Sublimation coefficient

Before describing the coefficient α for the water ice we present a short chronological review of representative papers related to determination of α_s for different materials.

2.1. Sublimation of different solids

Hansen et al. (1969) studied sublimation from oriented single-crystals and from powdered lead selenide. Analysis of the data showed that the sublimation coefficient is unity over the experimental range 887–1052 K.

Ishiyama and Fujikawa (2004) studied the evaporation and condensation at an interface of argon vapor and its condensed phase. They investigated the validity of kinetic boundary condition for the Boltzmann equation, which prescribes the velocity distribution function of molecules outgoing from the interface, by the numerical method of molecular dynamics. They found that the condensation coefficient is close to unity below the triple-point temperature and decreases gradually as the temperature rises.

Butman et al. (2008) studied the sublimation of praseodymium tribromide $PrBr_3$ under Knudsen and Langmuir conditions. The high-temperature mass spectrometry over the temperature range 804–957 K were applied. During sublimation from the open surface of a single crystal, the sublimation coefficient of $PrBr_3$ changed abruptly at the polymorphic transition point (UCl_3 – type low-temperature polymorph transforms to $PrBr_3$ – type high-temperature polymorph, $T = 934 \pm 3$ K). The change was reproducible in the heating–cooling cycles.

We note, that comparison of numerical results presented by different authors is rather difficults since it is not clear whether they described the values of α_s, or $B\alpha_s$.

2.2. Water ice

This sublimation of water ice was investigated many times, either with respect to the sublimation, or condensation of ice (Kramers and Stemerding, 1951; Knake and Stranskii, 1959; Davy and Samarjai, 1971; Beckmann and Lacmann, 1982; Kossacki et al., 1999; Gundlach et al., 2011) and other authors. Unfortunately, theoretical calculation of the sublimation coefficient (Knake and Stranskii, 1959) is too computationally intensive to be included into a model describing long term evolution of comet nuclei. Thus, experimental values need to be used.

According to Gadsden (1998) and Winkler et al. (2012) "for the water ice the value $\alpha = 0.83$ is commonly used". Unfortunately, it is not clear, whether the mentioned authors took into account the return flux of subliming molecules. Thus, the values can be either α_s, or $B\alpha_s$. According to the kinetic theory of the non-equilibrium boundary layer, the relative return flux of the water molecules toward such a sublimating surface is 0.25 (Cercignani, 1981; Skorov and Rickman, 1998). Hence, $B = 0.75$.

Kossacki et al. (1999) and Gundlach et al. (2011) investigated temperature dependence of the sublimation coefficient in wide ranges of the temperature. Kossacki et al. (1999) considered the pure ice samples, while Gundlach et al. (2011) investigated the ice samples covered by different layers of dust.

According to Kossacki et al. (1999) the temperature dependence of the sublimation coefficient can be described by

$$\alpha_s = \left(1 - \frac{1}{a_1}\right) + \frac{1}{a_1} \tanh\left[-a_3 \tan\left(\pi \frac{T - a_2}{273 - a_2} - \frac{\pi}{2}\right)\right], \qquad (4)$$

where $a_1 = 2.342$, $a_2 = 150.5$, and $a_3 = 4.353$.

Gundlach et al. (2011) investigated sublimation of a dust covered ice samples. The main reason was investigation of the diffusion of subliming molecules through the layers of dust of different properties. The authors have found, that the diffusivity of dust is insufficient to describe decrease of the vapor flux when compare to that predicted by HK equation for clean ice. Thus, they proposed the new formula for the sublimation coefficient of ice

$$\alpha_s(T) = \frac{b_1}{1.0 + exp[-b_2(T^{-1} - b_3)]} + b_4, \qquad (5)$$

where $b_1 = 0.854$, $b_2 = 11.58 \times 10^3$, $b_3 = 4.99 \times 10^{-3}$, and $b_4 = 0.146$.

Both formulas predict $\alpha_s = 1$ at temperatures lower than 195 K, and $\alpha_s = 0.15$, at temperatures higher than 230 K. However, at moderate temperatures where the sublimation coefficient features the strongest temperature dependence the formulas predict substantially different values of α_s. The discrepancy between formulae (4) and (5) can be the consequence of limited number of data available when the formula (4) was developed. It should also be noted, that the qualitative temperature dependence of the sublimation coefficient predicted by Kossacki et al. (1999) and Gundlach et al. (2011) is in qualitative agreement with the theoretical predictions for subliming argon (Ishiyama and Fujikawa, 2004).

3. Measurements

3.1. Procedure

Sublimation of ice from a sample can be measured in different ways. Gundlach et al. (2011) determined the flux of water molecules escaping the ice samples, using measurements performed by the mass spectrometer. This method allowed building of automatic measurement system, but produced very large scatter of readings when ice slowly sublimed at low temperatures.

We decided to use another approach, direct non-contact measurements of the position of the sample that recedes due to sublimation. Knowledge of the surface position versus time, when the surface temperature is known makes possible calculation of the sublimation rate versus temperature.

3.2. Experimental set-up

The surface temperature of the investigated samples is recorded in two or three different points using resistance thermometers. The temperatures are measured every minute. For each of the sensors we create the separate profile of the temperature versus time.

We use a cylindrical vacuum chamber of 50 cm diameter and 50 cm height. A cooler in the form of an open cylinder, 20 cm high, is located inside the chamber. Liquid nitrogen is pumped through the cooler. Similar cooled chambers are used by Kossacki et al. (1999). On the flat bottom of the cooler we placed samples within plastic, or metal cylindrical holders up to 10 cm in diameter. Thermal isolation of the samples at the sides is not needed because we do not warm up the samples.