Measurements of enthalpy of sublimation of Ne, N$_2$, O$_2$, Ar, CO$_2$, Kr, Xe, and H$_2$O using a double paddle oscillator

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ABSTRACT

We report precise experimental values of the enthalpy of sublimation (ΔH_s) of quenched condensed films of neon (Ne), nitrogen (N$_2$), oxygen (O$_2$), argon (Ar), carbon dioxide (CO$_2$), krypton (Kr), xenon (Xe), and water (H$_2$O) vapour using a single consistent measurement platform. The experiments are performed well below the triple point temperature of each gas and fall in the temperature range where existing experimental data is very limited. A 6 cm^2 and 400 μm thick double paddle oscillator (DPO) with high quality factor (Q $\approx 4 \times 10^5$ at 298 K) and high frequency stability (33 parts per 10^{-9}) is utilized for the measurements. The enthalpies of sublimation are derived by measuring the rate of mass loss during temperature programmed desorption. The mass change is detected due to change in the resonance frequency of the self-tracking oscillator. Our measurements typically remain within 10% of the available literature, theory, and National Institute of Standards and Technology (NIST) *Web Thermo Tables* (*WTT*) values, but are performed using an internally consistent method across different gases.

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1. Introduction

The intermolecular interaction of the condensed solid phase is a critical thermodynamic property and measured as the enthalpy of sublimation (ΔH_s). A variety of techniques has been developed experimentally to determine the sublimation energies. They are broadly categorized as either direct or indirect [4–6]. Direct techniques, utilizing appropriate calorimeters, involve the measurement of heat during the sublimation process [9,10]. Indirect methods measure the vapour pressure at different temperatures and assume that the sublimation enthalpies remain constant in the experimental temperature range [8,11–13]. The sublimation vapour pressure measurements are typically carried out by either using standard manometers or non-traditional resonant base micro-sensors. Resonant micro-sensors such as quartz crystal microbalances (QCMs) [15–17] and silicon micro-machined double paddle oscillators (DPOs) [7,18–20] are two methods utilized to measure the sublimation vapour pressures and enthalpies of different atmospheric gases. The change in mass of the deposited solid film is measured as a change in the resonance frequency of the

micro-sensor. Subsequently, the evaluation of sublimation enthalpy is carried out during a temperature programmed desorption (TPD) of the film. Compared to DPO measurements, QCM measurements have the advantage of being able to operate in air and liquid environments. However, DPOs can provide better mass sensitivity ($\approx$0.027 ng/cm^2) and frequency stability (33 parts per billion) [18,22] under ultra-high vacuum and at cryogenic temperature conditions. QCMs have been able to measure vapour pressures between 10^{-1} Pa and 10^{-7} Pa for H$_2$O, N$_2$O and CO$_2$ films [16] while DPOs have been able to reach vapour pressures down to 4.8×10^{-11} Pa for quenched condensed films of neon [20].

Despite a large number of experiments performed over the last century to experimentally evaluate enthalpies of sublimation of common atmospheric gases, we found limited experimental data for enthalpy values well below the triple point temperatures. For example, in the National Institute of Standards and Technology (NIST) Web Thermo Tables (*WTT*) [1], no data are included for sublimation experiments of neon below 10 K, nitrogen below 35 K, and oxygen below 36 K. Consequently, the sublimation energies reported on the WTT [1] at these temperatures for each film are extrapolated from their respective triple point values and therefore have both large absolute and relative uncertainties. According to the WTT [1], the enthalpy of sublimation of neon at 10 K is (2.16

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± 0.22) kJ·mol^{-1}, nitrogen at 36 K is (6.9 ± 4.6) kJ·mol^{-1} and oxygen at 36 K is (8.7 ± 3.7) kJ·mol^{-1}. Experiments have shown that nitrogen, CO_2, and water films exist in different solid phases [8,28] below their triple points and thus can have different activation energies. Therefore, a thorough experimental study is required to benchmark the enthalpies of different atmospheric gases well below their triple point temperatures.

To address this need, we employed a single 400 μm thick DPO (for all the experiments presented) which was excited in the 2nd anti-symmetric (AS2) torsional mode with a resonant frequency around 7.2 kHz. The AS2 mode of the DPO shows extremely high intrinsic quality factors both at room temperature ($Q \approx 4 \times 10^5$) and 5 K ($Q \approx 8 \times 10^7$). In general, the mass sensitivity of an oscillator is proportional to its mechanical quality factor. Therefore, a DPO excited in the AS2 mode provides an ideal measurement platform to study the evaporative mass loss during the sublimation process. In this study, we determined the enthalpy of sublimation for eight different atmospheric gases including Ne, N_2, O_2, Ar, CO_2, Kr, Xe, and H_2O with the 400 μm thick DPO. During the course of the current study, the same sensor was used for all measurements and was never removed from the chamber. The method presented here provides a single consistent measurement platform which reduces any systematic uncertainties that could be introduced during loading and unloading of the sensor. In the subsequent sections, we explain the theoretical background, apparatus, detailed example experiment using nitrogen, sources of uncertainties, and compile all results.

2. Theoretical background

2.1. DPO mechanics

The basic equation for the resonance frequency of the DPO in the torsional mode is given by

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{I}} \tag{1}$$

where k is the torsional spring (elastic) constant and I is the moment of inertia of the paddle. Mass loading on the surface of the DPO will change both the elastic constant and the moment of inertia in Eq. (1). The resulting change in the resonance frequency upon mass loading is the primary mechanism used to quantitatively derive different properties (thickness, elastic modulus, porosity, internal friction and heat of sublimation [7,19,20,30–34]) of the deposited material. The frequency shift for the AS2 mode for a film laden DPO relative to a bare DPO is mathematically approximated by Eq. (2) [20].

$$\left.\frac{\Delta f}{f}\right|_{total} = \left.\frac{\Delta f}{f}\right|_{elastic} + \left.\frac{\Delta f}{f}\right|_{mass} = \frac{3G_{film}h_{film}}{2G_{DPO}h_{DPO}} - \frac{\rho_{film}h_{film}}{2\rho_{DPO}h_{DPO}} \tag{2}$$

where subscript "DPO" stands for the bare paddle with metal electrodes, "film" refers to the film of the gas molecules adsorbed onto the DPO, Δf is the resulting frequency shift, G are the shear moduli, h is the thickness, and ρ are the densities. The total change in the resonance frequency of the paddle can be attributed to the change in the shear modulus (first term) and mass loading (second term) of the deposited film. Analysis of the contribution from each mechanism is discussed below.

2.2. Fundamental sublimation mechanism

Determination of the enthalpy of sublimation is based on the principle of mass conservation and involves three main steps. This three step process is pictorially depicted in Fig. 1 and explained in detail below.

2.2.1. Mass loading

The gas atoms/molecules arriving at the surface of the DPO (kept below the triple-point temperature of the target gas) resulted in a highly disordered solid film. The random distribution of the adsorbed gas molecules initially results in a highly porous film with a very small shear modulus [37]. In order to estimate the thickness of the deposited material, typically bulk values of shear modulus and density of the film are used in Eq. (2). For example, for bulk neon $G_{film}/G_{DPO} \cong 0.01$ [20] and $\rho_{film}/\rho_{DPO} \cong 0.65$ [2]. Therefore, the contribution of the elastic term in Eq. (2) is small compared to the mass term. The following linear frequency-mass relationship, relative to the base resonance frequency of the paddle, is typically used to estimate the thickness of the deposited film [20,38].

$$\left.\frac{\Delta f}{f}\right|_{total} \approx \left.\frac{\Delta f}{f}\right|_{mass} = -\frac{\rho_{film}h_{film}}{2\rho_{DPO}h_{DPO}} \tag{3}$$

The thickness of a film is computed using the bulk density values in Eq. (3). The negative sign in Eq. (3) signifies that during mass loading the resonance frequency of the paddle decreases. The estimation of the film thickness is only used as a control parameter during different experimental runs performed for the same target gas and not used for the enthalpy measurements.

2.2.2. Relaxation

The as-deposited ice films are initially highly disordered and porous [37]. Once the temperature of the DPO is increased, the atoms/molecules start to rearrange themselves into a more ordered form. This rearrangement leads to atomic relaxations and increases both the stiffness (G_{film}) and the density (ρ_{film}) of the film. The rise in the resonance frequency is due to the stiffening of the film ($G_{film}h_{film}$ increases) and a small amount of evaporative mass loss ($\rho_{film}h_{film}$ decreases) as the temperature rises. Earlier studies carried out on neon and argon solid films have shown [20] that these two mechanisms can be separated (to some extent) by controlling the DPO temperature. The rise in resonance frequency is mainly due to the increasing film stiffness at temperatures above the deposition temperature but where the vapour pressure is still low. In order to reduce the effect of the changing elastic term during the sublimation experiment, each film is annealed at temperatures where evaporative mass loss is small for 35 min–50 min.

2.2.3. Desorption

The time reversal process of adsorption is desorption (sublimation) and studied here. The enthalpies of sublimation are derived from the apparent vapour pressures (P_a) of each gas during desorption and measured in narrow temperature ranges where the sublimation enthalpies can be treated as constants [20]. In principle, all the thermally activated molecules should escape. However experimentally, a constant of proportionality (condensation coefficient) is used to account for difference between absolute and apparent vapour pressures. We are not able to independently determine the condensation coefficient. Therefore, we report the measured "apparent" vapour pressures in this work. We also see uncontrolled variations in the absolute value of the apparent vapour pressures from different experimental runs. We assume the differences are due to a change in condensation coefficient resulting from some surface changes. However, the temperature dependence of the apparent vapour pressure from run to run change little resulting in consistent heat of sublimation values. Therefore, the data supports the conclusion that the condensation coefficient is a temperature independent constant within the range of our data sets. The sublimation of gas molecules by sequentially heating the DPO is determined by monitoring the mass loss. In our study, the