
Introduction: A substance’s saturation vapor pressure is the pressure at which the gas phase is in thermodynamic equilibrium with a solid or liquid phase; condensation and sublimation (or evaporation) rates are equal under these conditions. Knowledge of vapor pressures as a function of temperature is crucial for modeling processes such as seasonal migration of planetary volatiles [1][2], loss of volatiles from planetesimals [3], cometary gas production, and compositional evolution of gas and solids in protoplanetary nebulae [4].

Vapor pressures are relatively simple to measure in the continuum flow regime where gas density is high enough to be fully collisional, which equalizes the pressure throughout the gas. But at the low pressures and densities relevant to numerous solar system environments, the mean free path for collisions between gas molecules becomes comparable to or larger than the dimensions of any practical laboratory apparatus. In such Knudsen or free molecular flow regimes, gas pressure can vary with location within an apparatus; a gauge can measure pressure at its location, but that may differ from the pressure of interest at the solid-gas equilibrium interface. Ionization gauges used to measure low pressures also have different sensitivities to different species, owing to their different ionization efficiencies. A quartz crystal microbalance (QCM) offers a way of handling these experimental challenges to measuring vapor pressures in this regime.

Apparatus: At the Astrophysical Materials Laboratory at Northern Arizona University, a system built for measuring infrared optical constants of volatile ices is also suitable for measuring vapor pressures in the free molecular flow regime. A QCM in a copper housing is attached to the cold tip of an Advanced Research Systems DE-204PB closed cycle helium cryocooler. These are enclosed within a ultra-high vacuum chamber pumped by a Varian Agilent Twist-Torr 305 FT turbomolecular pump backed by a rotary vane roughing pump. An Inficon BPG400 Bayard-Alpert Pirani combination gauge monitors the gas pressure in the chamber and a Stanford Research Systems RGA 200 quadrupole mass spectrometer monitors its composition. A Lake Shore model 335 temperature controller regulates temperature over the range from just below 10 K to room temperature. An Agilent model 951-5106 variable leak valve is used to admit gas to the chamber for condensation onto the QCM.

During deposition, we orient the QCM away from the leak valve so that molecules arrive at the QCM from random directions and at speeds consistent with a room temperature Maxwell-Boltzmann distribution.

Methods: The vibration frequency of a piezoelectric quartz crystal drops as mass adheres to it. This property provides a sensitive way to measure the mass balance of ice condensation or sublimation, with the change in areal mass Q (mass per unit area) being derived from the frequency change. An ice film on the QCM can be warmed to a desired temperature and the sublimation mass flux measured at that temperature. The sublimation mass flux according to the Hertz-Knudsen-Langmuir equation [5] is

\[
\frac{dQ}{dt} = -P_\text{vap}(T_{\text{QCM}}) \frac{M}{2 \pi R T_{\text{QCM}}} \] (1)

where \( T_{\text{QCM}} \) is the temperature of the QCM and its ice film, \( P_\text{vap}(T_{\text{QCM}}) \) is the vapor pressure at \( T_{\text{QCM}} \), M is the molecular mass, and R is the gas constant. This equation can be inverted to obtain \( P_\text{vap} \), and is all that would be needed for sublimation into a perfect vacuum.

But at the same time as molecules are sublimating from the surface of the ice film, gas molecules in the apparatus are also arriving at and sticking to the ice, according to the analogous equation

\[
\frac{dQ}{dt} = S_c P_{\text{QCM}} \frac{M}{2 \pi R T_{\text{room}}} \] (2)

where \( P_{\text{QCM}} \) is the gas pressure impinging on the QCM, \( T_{\text{room}} \) is the temperature of the chamber walls (room temperature), and \( S_c \) is a sticking coefficient assumed to be unity for molecules arriving at a solid composed of like molecules at low temperature [5]. In the non-collisional, free molecular flow regime, gas fluxes onto and off of the ice are independent of one another and the mass flux measured by the QCM is simply the net of the two terms (Eqs. 1 and 2). This can be written as

\[
\frac{dQ}{dt} = \left[ P_{\text{QCM}} T_{\text{room}}^{-1/2} - P_\text{vap}(T_{\text{QCM}}) T_{\text{QCM}}^{1/2} \right] \frac{M}{2 \pi R T_{\text{QCM}}} \] (3)

which can be rearranged to solve for \( P_\text{vap}(T_{\text{QCM}}) \):

\[
P_\text{vap}(T_{\text{QCM}}) = P_{\text{QCM}} \left( \frac{T_{\text{QCM}}}{T_{\text{room}}} - \frac{dQ}{dt} \right) \sqrt{\frac{2 \pi R T_{\text{QCM}}}{M}}. \] (4)

Pressure Correction. \( P_{\text{QCM}} \) can’t simply be measured with a pressure gauge mounted in the chamber, but the QCM does provide a convenient way of quantifying differences between \( P_\text{vap} \), the pressure measured with a gauge and \( P_{\text{QCM}} \) via Eq. 2. At temperatures low
enough that sublimation is negligible, we can record \( P_{\text{gauge}} \) at the same time as we record the condensation mass flux onto the QCM. From these we can compute a correction factor \( \Phi \) relating \( P_{\text{QCM}} = \Phi P_{\text{gauge}} \). This \( \Phi \) factor accommodates discrepancies due to ionization efficiency effects as well as geometric effects. We find \( \Phi \) does not depend on temperature, at least not over the range of temperatures where we can measure \( \Phi \) via condensation onto the QCM without sublimation interfering with its measurement. But it does depend on pressure, exhibiting a functional form that can be modeled as a linear dependence on log(\( P \)) modified at low pressures by the presence of non-condensible background gases at a constant partial pressure (~5×10^{-9} torr in our system).

\[
\Phi = \frac{P_{\text{QCM}}}{P_{\text{gauge}}}
\]

**Temperature Calibration.** Vapor pressure is a sensitive function of temperature, so it is crucial to measure and control the temperature of the QCM as accurately as possible. We have no way of measuring the crystal temperature directly, only that of the adjacent copper housing. We performed two calibration tests. First we used FTIR spectra of CH\(_4\) ice across the solid-solid phase transition between CH\(_4\) I and CH\(_4\) II at 20.4 K. This test indicated an offset with \( T_{\text{QCM}} \) being about 1 K warmer than the temperature recorded by the diodes. Our second test involved the melting of C\(_2\)H\(_8\) at 85.5 K. At this warmer temperature, we found a negative offset of ~0.1 K. We applied a linear fit between these two points to correct our measured temperatures to \( T_{\text{QCM}} \).

**Results:** Measured vapor pressures for N\(_2\), CO, and CH\(_4\) are shown in Fig. 2. At these temperatures and pressures, the Fray & Schmitt [6] polynomial approximations appear to be quite accurate for CH\(_4\), but less so for N\(_2\) and CO. The vapor pressure contrast between N\(_2\) and CO is larger than previously thought, by about a factor of five. The greater \( P_{\text{vap}} \) contrast means that N\(_2\) and CO can be more readily separated by sublimation and condensation cycles on icy dwarf planes like Pluto, Triton, Eris, and Makemake. Our temperature calibration uncertainty makes it hard to be sure how much of the greater contrast is due to CO having a lower \( P_{\text{vap}} \) than previously thought, but to the extent that it does, it implies slower loss of CO from small TNOs and distant comets. Also, it pushes the nebular CO snow line inward, implying a greater extent of nebular environments where CO freezes onto dust grains where it can participate in surface chemistry such as hydrogen addition to form compounds like H\(_2\)CO and CH\(_3\)OH [7].

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**References:**