

LABORATORY MEASUREMENT OF VOLATILE ICE VAPOR PRESSURES USING A QUARTZ CRYSTAL MICROBALANCE. W.M. Grundy^{1,2}, S.C. Tegler², J.K. Steckloff³, A.V. Jasko⁴, K.J. Koga², M.J. Loeffler², S.M. Raposa², A.E. Engle², C.L. Thieberger², J. Hanley^{1,2}, G.E. Lindberg², S. Tan³, M.D. Gomez², and A.O. Madden-Watson²; ¹Lowell Observatory, ²Northern Arizona University, ³Planetary Science Institute, ⁴Case Western Reserve University.

Introduction: The vapor pressure of a substance 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 for solar system ices is crucial for modeling processes such as seasonal migration of planetary volatiles [1], loss of volatiles from planetesimals [2], cometary gas production, and compositional evolution of gas and solids in protoplanetary nebulae [3].

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. The procedure is to measure the pressure and temperature in a vessel that contains both gas and solid phases in equilibrium.

But at the low pressures and densities relevant to numerous solar system bodies, 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 is not necessarily uniform. It can vary with location within an apparatus. A pressure gauge can measure the pressure where it is situated, but that pressure may differ from the pressure of interest at the solid-gas equilibrium interface. Additionally, ionization gauges used to measure low pressures have different sensitivities to different species, owing to their different ionization efficiencies. Different methods are thus needed. A quartz crystal microbalance (QCM) offers a way of overcoming these experimental challenges to measuring vapor pressures in this regime.

Apparatus: At the Astrophysical Materials Laboratory at Northern Arizona University, we have built a new system for measuring infrared optical constants of volatile ices that is also suitable for measuring vapor pressures in the free molecular flow regime. The heart of the system is a QCM controlled by an Inficon IC6 controller, attached to the cold tip of an Advanced Research Systems DE-204PB closed cycle helium cryocooler. These are enclosed within an ultra-high vacuum chamber pumped by a Varian Agilent Twis-Torr 305 FT turbomolecular pump backed by a rotary vane roughing pump. An Inficon BPG400 Bayard-Alpert Pirani combination gauge monitors the pressure in the chamber. A LakeShore 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. A Stanford Research Systems RGA 200 quadrupole mass spectrometer (QMS) monitors the composition of gas in the chamber.

Methodology: The natural 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. The time rate of change in areal mass Q (mass m per unit area A) on the QCM can be computed from the frequencies f_1 and f_2 measured at two times t_1 and t_2 according to the equation

$$\frac{1}{A} \frac{dm}{dt} = \frac{dQ}{dt} = \frac{c(f_1 - f_2)}{f_1 f_2 (t_2 - t_1)} \quad (1)$$

where the constant c is 4.417×10^5 Hz g cm⁻² [4][5]. After an ice film has been condensed on the QCM, it 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 [6] is

$$\frac{dQ}{dt} = -P_{\text{vap}}(T_{\text{QCM}}) \sqrt{\frac{M}{2\pi RT_{\text{QCM}}}} \quad (2)$$

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

But of course, no vacuum is perfect, especially not in a laboratory! 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 a comparable equation

$$\frac{dQ}{dt} = S_c P_{\text{QCM}} \sqrt{\frac{M}{2\pi RT_{\text{room}}}} \quad (3)$$

where P_{QCM} is the gas pressure impinging on the QCM, T_{room} is the temperature of the chamber walls (room temperature), and S_c is a sticking coefficient which can generally be assumed to be unity for molecules arriving at a solid composed of like molecules at low temp-

erature [6]. In the free molecular flow regime where the gas is non-collisional, 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 sublimation and condensation terms (eqs. 2 and 3).

For reasons described earlier, P_{QCM} can't simply be measured with a pressure gauge mounted in the chamber. The QCM provides a convenient way of quantifying differences between P_{gauge} and P_{QCM} via eq. 3. At temperatures low enough that sublimation is negligible, we can record P_{gauge} at the same time as we record the condensation mass flux onto the QCM. From these we can compute a correction factor Φ to relate $P_{\text{QCM}} = \Phi P_{\text{gauge}}$, compensating for ionization efficiency effects as well as geometric effects. We find Φ to be a weak function of pressure, but it does not appear to depend on temperature, at least not over the range of temperatures where we can measure Φ via condensation onto the QCM while remaining in the free molecular flow regime.

Combining condensation and sublimation terms, we have

$$\frac{dQ}{dt} = (\Phi P_{\text{gauge}} T_{\text{room}}^{-1/2} - P_{\text{vap}}(T_{\text{QCM}}) T_{\text{QCM}}^{-1/2}) \sqrt{\frac{M}{2\pi R}}, \quad (4)$$

which can be rearranged to solve for $P_{\text{vap}}(T_{\text{QCM}})$ as a function of measured and known quantities:

$$P_{\text{vap}}(T_{\text{QCM}}) = \Phi P_{\text{gauge}} \sqrt{\frac{T_{\text{QCM}}}{T_{\text{room}}}} - \frac{dQ}{dt} \sqrt{\frac{2\pi R T_{\text{QCM}}}{M}}. \quad (5)$$

Results: Preliminary P_{vap} measurements for volatile species N_2 , Ar, CH_4 , C_2H_6 , and CO_2 are shown in Fig. 1. Our points are slightly to the right of the published curves of Fray & Schmitt 2009 [7]. A tempe-

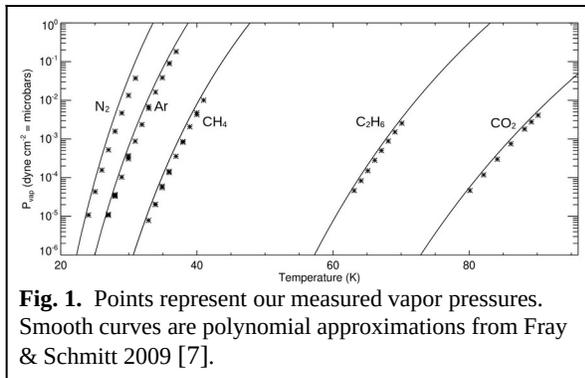


Fig. 1. Points represent our measured vapor pressures. Smooth curves are polynomial approximations from Fray & Schmitt 2009 [7].

perature shift of ~ 0.6 K would bring our measurements into better alignment with those curves. More work is needed to assess whether the apparent discrepancy can be attributed to temperature calibration.

From these tests it appears that our system can measure vapor pressures in the range between 10^{-5} and 10^{-1} μbar . The low pressure limit results from the low rate of sublimation at low temperatures and the finite

precision of QCM frequency measurement, while the high pressure limit is caused by rapid sublimation and loss of the ice sample before the temperature can stabilize after a temperature change. For each species, this pressure range corresponds to a relatively narrow temperature range. It is possible to extrapolate beyond this range, so long as the solid phase remains the same, since the temperature dependence of the vapor pressure provides the specific latent heat of sublimation L for the solid via the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{PL}{T^2 R}. \quad (7)$$

We plan to measure additional pure species including at least CO , O_2 , H_2O , CH_3OH , NH_3 , C_2H_4 , and C_3H_8 .

Sublimation of ice mixtures. There is considerable interest in sublimation from mixtures of ices, since they occur in many solar system settings (e.g., [8][9]) and can have distinct thermodynamic properties from their constituents as pure species. The logical next step beyond measuring sublimation and vapor pressures of pure species is to investigate sublimation of mixtures. This will require monitoring the partial pressures of the component species in the chamber using the RGA 200 mass spectrometer. An important feature of mixtures is that their sublimation is not a purely equilibrium phenomenon, since molecular diffusion within the ice mixture enables the composition at its surface to evolve as a function of time.

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References:

- [1] Trafton et al. (1998) In *Solar System Ices*, Kluwer 773-812.
- [2] Lisse et al. (2021) *Icarus* 356, 114072.
- [3] Oberg et al. (2011) *ApJ* 743, L16.
- [4] Lu & Lewis (1972) *J. Appl. Physics* 43, 4385.
- [5] Vashist & Vashist (2011) *J. Sensors* 2011, 571405.
- [6] Langmuir (1913) *Phys. Rev.* 2, 329.
- [7] Fray & Schmitt (2009) *Planet. Space Sci.* 57, 2053.
- [8] Trafton (2015) *Icarus* 246, 197.
- [9] Tan & Kargel (2018) *MNRAS* 474, 4254.