Application of ASTM E-1559 apparatus to study H$_2$O desorption

MICHAEL WORONOWICZ
RADFORD PERRY III
GEORGE MEADOWS
SGT, INC.

2015 CONTAMINATION, COATINGS, MATERIALS, AND PLANETARY PROTECTION WORKSHOP
NASA GODDARD SPACE FLIGHT CENTER
29-31 JULY 2015
Outline

- Introduction
- Objectives
- Math model development
  o Clausius-Clayperon
  o Quantum Statistical Mechanics
- Selected candidate expressions
- ASTM E-1559 apparatus “MOLEKIT”
  o Physical description
  o Outgassing measurement procedure
  o Adaptation to desorption measurements
- Results & Discussion
- Concluding Remarks
JWST Observatory
James Webb Space Telescope (JWST)
- Designed to operate for five years at L2
- Contains four IR instruments operating below 50 K
- Sunshield must reject nearly all solar input
  - Radiative properties extremely sensitive to water vapor deposits

Electronics compartment on shadowed side will outgas more than enough water vapor to ruin sunshield effectiveness
- Design vent to also collect sufficient fraction of water vapor
  - Account for temperature-dependent desorption of condensed material
Noted $p_{v,H_2O}$ models tended to disagree at temperatures in range of interest (120—140 K)
- Typically based on data above 150 K
- None found using data below 131 K
- What model to use?

Researchers cited limits for thermal control stability

Our group has experience with ASTM E-1559 apparatus used to collect volatile outgassing rates down to liquid nitrogen temperatures (~90 K)
- Can measure source rates of picograms/s
- Very stable thermal conditions

Simple matter to adapt to H$_2$O desorption study at cryogenic temperatures
Objectives

- Review formulation of water vapor desorption models
  - Features of high-fidelity physical expressions
  - Selected candidates
- Discuss use of NASA-GSFC outgassing measurement apparatus
  - “MOLEKIT” = “Molecular Kinetics”, ASTM E-1559 system
  - Sketch of operational procedures
  - Adaptation to desorption measurements
Outline

- Introduction
- Objectives
- Math model development
  - Clausius-Clayperon
  - Quantum Statistical Mechanics
- Selected candidate expressions
- ASTM E-1559 apparatus “MOLEKIT”
  - Physical description
  - Outgassing measurement procedure
  - Adaptation to desorption measurements
- Results & Discussion
- Concluding Remarks
• Thermodynamically, equilibrium condition for single species in multiple phases characterized by minimum value for Gibbs free energy $G$
  ○ Obtained when $G$ per mole is equal for each phase
  ○ Consequence of this condition gives $p$ as function of $T$

\[
\frac{dp}{dT} = \frac{\Delta s}{\Delta v} = \frac{l}{T\Delta v} = \frac{pl}{RT^2}
\]

• For constant heat of transformation $l$, obtain Arrhenius-type expression

\[
p_v(T) = p_{ref} \exp\left(-\frac{l}{RT}\right) = \exp\left(C - \frac{\Theta}{T}\right)
\]
Quantum Statistical Mechanics

- On molecular scale, work with chemical potential $\mu$, like Gibbs free energy per molecule
  - Determine chemical potentials for solid and gas are equal
- Molecular ensemble described by number of energy states available to phases, increases with $T$
  - Somewhat convoluted path for solid phase 1, easier to describe gas phase 2 (monatomic)

$$\mu_1(T) = -\eta - T \int_0^T \frac{dT'}{T'^2} \int_0^{T'} c(T'')dT''$$
$$\mu_2 = -kT \ln \left[ \frac{kT}{p_2} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right]$$

$$p_2(T) = \exp \left\{ \ln \left( \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right) + \frac{5}{2} \ln(T) - \frac{\eta}{kT} - \int_0^T \frac{dT'}{kT'} \int_0^{T'} c(T'')dT'' \right\}.$$
Quantum Stat. Mech.—Diatomic Gas

- For a diatomic gas, must incorporate influence of internal degrees of freedom (rotational+vibrational)

\[ \mu_{2,\text{diatomic}} \approx -kT \ln \left[ \frac{kT}{p_2} \left( \frac{2\pi mkT}{\hbar^2} \right)^{\frac{3}{2}} \frac{I_{\text{rot}}kT}{\hbar^2} \exp \left( -\frac{\hbar\omega}{2kT} \right) \right] \]

\[ p_{2,\text{diatomic}}(T) \approx \exp \left\{ \ln \left[ \frac{I_{\text{rot}}k^{\frac{7}{2}}}{\hbar^5} \left( \frac{m}{2\pi} \right)^{\frac{3}{2}} \right] + \frac{7}{2} \ln(T) - \frac{(\eta + \hbar\omega/2)}{kT} - \int_0^T \frac{dT}{kT^{\frac{3}{2}}} \int_0^{T'} c(T'')dT'' \right\} \]

- Notice heat of transformation term becomes modified!

- Water vapor is polyatomic, approximate internal d.f. physical models become increasingly approximate

- Punt—replace terms in exponential with fit parameters, functions of temperature
Sack & Baragiola managed to produce sublimation data down to 135 K

- Very careful to distinguish between different types of solid phase ice
  - Hexagonal crystalline
  - Cubic crystalline
  - Amorphous

Noted that vapor deposited at low temperatures not necessarily in most equilibrium state, will relax with time, temp. dep.
Sack & Baragiola recommended the following formula for “stable crystalline” phase ice based on stat. mech. arguments:

\[ p_{v,S-B} = BT^4 \exp \left( - \frac{E}{kT} \right) = \exp \left[ \ln B + 4 \ln(T) - \frac{E}{kT} \right] \]

- \((B,E) = (29.3 \text{ Pa/K}^4, 10.375 \text{ kcal/mole})\)
- \(E\) identified as heat of sublimation = 0.45 ± 0.03 eV
- Amorphous phase vapor pressure identified as being 100x higher
  - Review of paper indicates this rate should be less than 30x higher
Murphy & Koop discussed review of various authors, devised vapor pressure fit claiming use of Clausius-Clayperon equation, but accounting for temperature dependent behavior:

\[ p_{v, M-K} \text{ [Pa]} = \exp \left[ 9.550426 + 3.53068 \ln(T) - \frac{5723.265}{T} - 0.00728332 T \right] \]

- based on
  - Solid phase ice specific heat data down to 110 K
  - Non-ideal gas behavior
    - Did M-K actually resort to stat. mech. arguments?
  - Not directly based on vapor pressure data
Model Comparison

- Sack-Baragiola Data
- Sack-Baragiola Fit (0.45 eV)
- Bryson, et al. Data
- Murphy-Koop Fit

2015 Contamination, Coatings, Materials, and Planetary Protection Workshop
Outline

- Introduction
- Objectives
- Math model development
  - Clausius-Clayperon
  - Quantum Statistical Mechanics
- Selected candidate expressions
- ASTM E-1559 apparatus “MOLEKIT”
  - Physical description
  - Outgassing measurement procedure
  - Adaptation to desorption measurements
- Results & Discussion
- Concluding Remarks
• Found very little $p_v, H_2O$ data below 150 K, none below 131 K
• Description of Sack-Baragiola apparatus mentioned sensitivity level of $5.0e^{-4}$ molecular monolayers/s
  o May translate to a QCM sensitivity exceeding 10 Hz/hr
• Test times typically limited to < 15 min
  o Certain runs lasted ~ 3 hrs.
• NASA GSFC possesses an ASTM E-1559 apparatus designed to measure outgassing from sample materials for gases condensable as low as LN$_2$ would allow
• Often exhibits measurement stability within 0.1 Hz/hr over days-long periods
  o Could we measure vapor pressure levels two OOM below others?
MOLEKIT Description (Genl.)

- Two vacuum chambers
  - Test chamber
  - Loading chamber
- Sample of test material inserted into Effusion Cell
  - Temperature controlled
  - Sample limited to < 2” cube
- Heated, translated from loading chamber into test chamber
MOLEKIT Description (Test Chamber)

- \((d, L) \approx (36'', 46'')\)
- \(\text{LN}_2\) cooled walls
- Four QCM’s
  - Cryogenically cooled (CQCM’s)
  - Temperatures individually controlled
  - Fixed, known viewfactors to EC
    - Can relate QCM collection rate to source outgassing rate (translate from Hz/hr to g/cm²/s)
- Under equilibrium, \(p_v = \dot{\phi} \sqrt{2\pi RT}\)
General Test Procedure

- QCM’s set to pre-selected temperatures
- Typically begins with thermal stability period (~15-20 hrs.)
  - Empty chamber, collect data on how frequency changes with time
  - Often exhibits variability at or below 0.1 Hz/hr
- Sample weighed, loaded into EC, loading chamber evacuated
- EC travels into test chamber position, warmed to $T_{op}$
- Sample exposed to test conditions over pre-determined period or when QCM buildup rates have dropped below detectable limits
- Sample returned to loading chamber, chamber repressurized, sample removed and weighed
Desorption Test Procedure

- Select test sample that releases $\text{H}_2\text{O}$, not much else
  - From experience, chose G10 fiberglass block, exposed to atmospheric conditions
    - Similar to JWST electronics compartment material
- QCM’s collect vapor at various, steady, cryogenic temps.
  - Chose temperatures between 90—140 K
- After sufficient amount of vapor collected, withdraw sample
  - Arbitrary minimum change in frequency ~ 10 kHz
- Continue operating QCM’s at constant temperature, record desorption rates every minute over next 1-2 days
Sample Test Run Results (125 K)
Observation—Phase Change

- Some results exhibited higher initial slopes that relaxed to lower, steady values over time (on order of one day)
  - Similar to behavior recorded by Sack & Baragiola, but rate enhancements were much lower here, less than 2x
  - Identified as solid phase transition to more stable form
  - S-B test runs lasted less than four hours apiece
    - Typically 15 min
  - S-B noted that prior deposition rate factored into amount of amorphous phase desorption rate
    - Uncontrolled in this study
Results

- Performed two runs, attempted to collect data between 120 – 140 K, along with one QCM operating at coldest possible temperature (~90 K)
- Data collected on 90 K demonstrated massive out-of-family behavior, suggests current arrangement would have trouble obtaining useful data below 120 K
  - Could be interference from desorption of H₂O from test chamber walls at 90 K (big area compared to QCM sensor < 1 cm²)
Model Comparison w/ Test Data

- Sack-Baragiola Data
- Sack-Baragiola Fit (0.45 eV)
- Bryson, et al. Data
- Murphy-Koop Fit
- GSFC Molekit Data
- Sack-Baragiola Fit (0.46 eV)
Murphy-Koop Comparison

![Graph showing Murphy-Koop Comparison](image)

- Marti-Mauersberger Fit (0.53 eV)
- Sack-Baragiola Fit (0.45 eV)
- Murphy-Koop Fit
- CRC Handbook (IAPS-1993)
- Sack-Baragiola Data
- Bryson, et al. Data
- GSFC Molekit Data

2015 Contamination, Coatings, Materials, and Planetary Protection Workshop
Concluding Remarks

- Based on comparisons with other investigators, it appears test runs were long enough to firmly establish hexagonal crystalline water vapor desorption rates down to 120 K.
- Narrow data set appears to confirm accuracy of Murphy-Koop model formulation.
  - Established theoretical basis for form of equation.
- JWST project may request further testing to confirm current data.