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

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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
JWST Observatory
Introduction (2 of 3)

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
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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

$$p_v(T) = p_{ref} \exp\left(\frac{-l}{RT}\right) = \exp\left(C - \frac{Θ}{T}\right)$$
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)

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

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

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

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

\[
p_{2, \text{diatomic}}(T) \approx \exp \left\{ \ln \left( \frac{I_{\text{rot}} k^{7/2}}{\hbar^5} \left( \frac{m}{2\pi} \right)^{3/2} \right) + \frac{7}{2} \ln(T) - \frac{(\eta + \hbar \omega/2)}{kT} - \int_0^T \frac{dT}{kT^{1/2}} \int_0^{T'} c(T'')dT'' \right\}
\]

- 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

![Graph showing model comparison with data points and fits for Sack-Baragiola and Bryson, et al.](image)

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

- Found very little $p_v, \text{H}_2\text{O}$ data below 150 K, none below 131 K
- Description of Sack-Baragiola apparatus mentioned sensitivity level of $5.0e^{-4}$ molecular monolayers/s
  - May translate to a QCM sensitivity exceeding 10 Hz/hr
- Test times typically limited to < 15 min
  - 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
  - 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)

- \((d, L) \approx (36'', 46'')\)
- LN\textsubscript{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/cm\textsuperscript{2}/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 $\sim 10$ 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)**

**Axes:**
- **PRESSURE [Pa]**
- **TEMPERATURE [K]**
Murphy-Koop Comparison

- 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

Pressure vs. Temperature graph with various data sets and fits.
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.