



Vaporization Coefficients of Oxides

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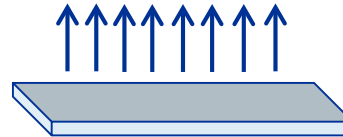
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Vaporization Coefficients

- Vapor Flux (mole/unit area-unit time) leaving a free surface into a vacuum:
Described by Hertz-Knudsen-Langmuir (HKL) equation

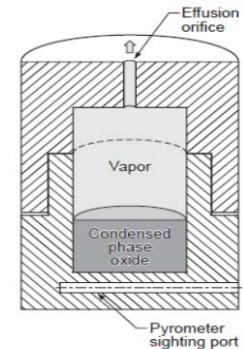
$$J(\text{max}) = \frac{P_{eq}}{\sqrt{2\pi MRT}}$$



- Measured flux--Modified by a factor α : Vaporization Coefficient

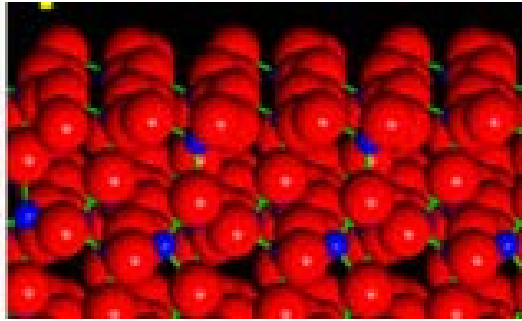
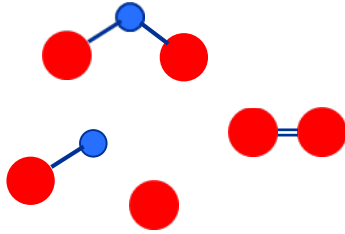
$$J(\text{measured}) = \frac{\alpha P_{eq}}{\sqrt{2\pi MRT}}$$

- Metals: Generally unity; Oxides 10^{-1} to 10^{-5} !
- Vaporization coefficient α_v ; Condensation coefficient α_c **Equal at equilibrium**
- Free surface vaporization = Langmuir vaporization
- Important parameter—relatively little expt'l or theoretical work since 1970s
 - True vapor flux in a deposition processes
 - High temperature material vaporization limit
 - True vapor flux in a geochemical/cosmochemical processes





What Leads to non-unity Vaporization Coefficients?



- Vaporization of silica
 - $\text{SiO}_2(\text{s}) = \text{SiO}_2(\text{g})$
 - $\text{SiO}_2(\text{s}) = \text{SiO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$
 - $\text{SiO}_2(\text{s}) = \text{SiO}(\text{g}) + \text{O}(\text{g})$

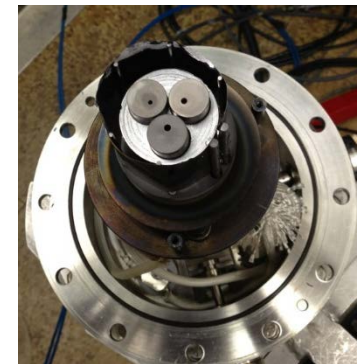
- Complex process
 - Break apart SiO_4^{-2}
 - Adsorbed $\text{SiO}_2(\text{a})$, $\text{SiO}(\text{a})$, $\text{O}_2(\text{a})$, $\text{O}(\text{a})$
 - Desorption to $\text{SiO}_2(\text{g})$, $\text{SiO}(\text{g})$, $\text{O}_2(\text{g})$, $\text{O}(\text{g})$
 - Break O-O, Si-O bonds; make O=O double bond

- Expect a kinetic barrier \Rightarrow flux reduced from equilibrium



Experimental Measurement of Vaporization Coefficients: Two Methods

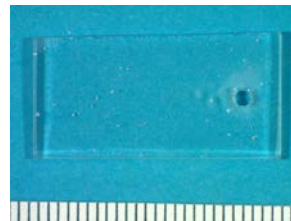
- Compare vaporization flux from a free surface (Langmuir vaporization) to that calculated from equilibrium
 - Advantages: Rapid measurements, minimal container issues, requires only a good vacuum microbalance
 - Disadvantages: Overall vaporization coefficient for many vapor species, would expect a different vaporization coefficient for each species; need good thermodynamic data
- Knudsen Cells of different orifice geometries (Chatillon, modification of Whitman-Motzfeld method)
 - Use several cells with difference orifice geometries \Rightarrow different transmission factors
 - Differences in measured fluxes due to transmission factors and *vaporization coefficient*
 - Extract *vaporization coefficient*





Langmuir Vaporization of Silica (Nolan & Continuing work)

- Starting material:
 - Fused silica plates (QSI, Fairport Harbor, OH) from Corning 7980 high purity silica
 - Cut to 2 x 1 x 0.16 cm squares
 - Grit blast hangwire hole
 - Use Ir hangwire (inert to silica)



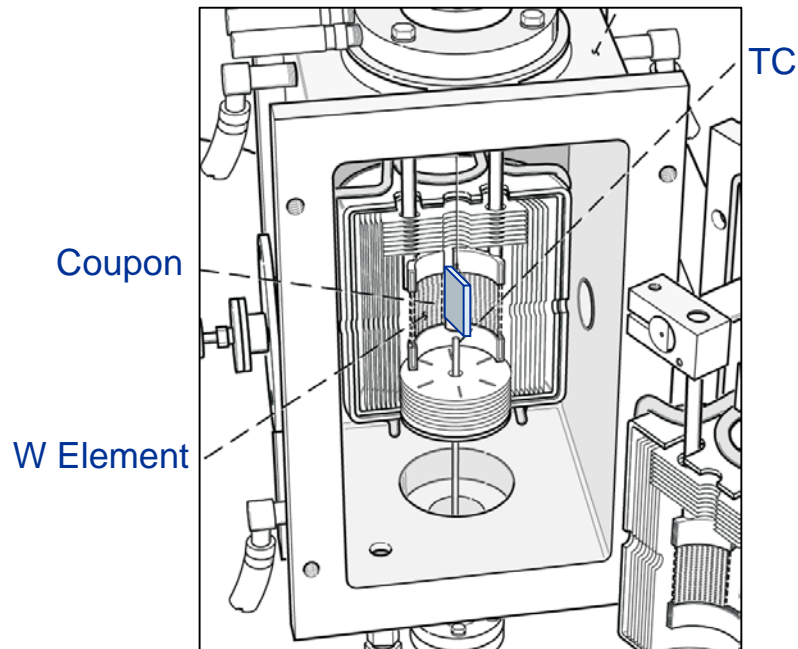
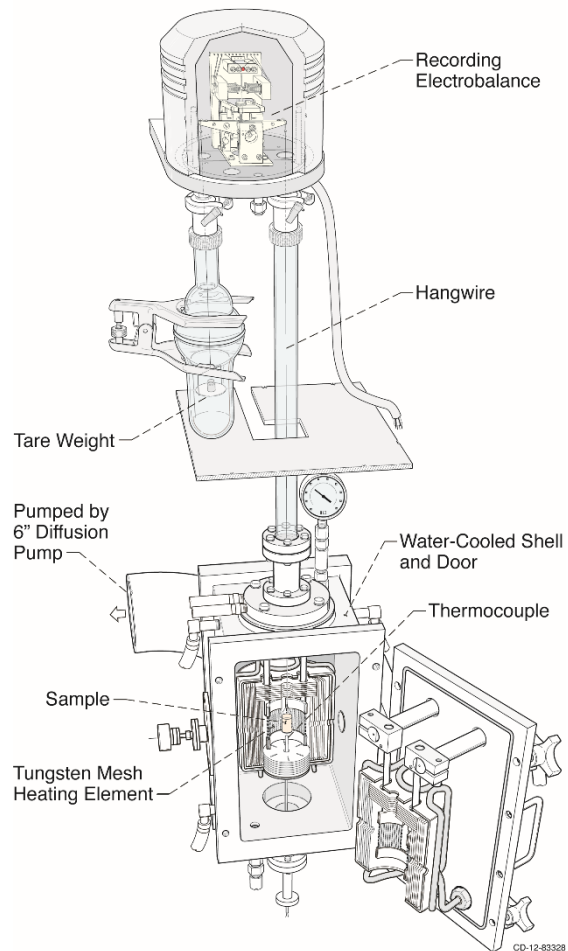
- Measure flux from weight loss
- Compare to calculated total flux
 - $\text{SiO}_2(\text{s}) = \text{SiO}(\text{g}) + \frac{1}{2} \text{O}_2$
 - $\text{SiO}_2(\text{s}) = \text{SiO}_2(\text{g})$
 - $\text{SiO}_2(\text{s}) = \text{Si}(\text{g}) + \text{O}(\text{g}) + \frac{1}{2} \text{O}_2$

$$J_{calc} = \sum J_i = \sum \frac{P_i}{\sqrt{2\pi M_i RT}} = \frac{P_{SiO}}{\sqrt{2\pi M_{SiO} RT}} + \frac{P_{O_2}}{\sqrt{2\pi M_{O_2} RT}} + \frac{P_O}{\sqrt{2\pi M_O RT}} + \frac{P_{SiO_2}}{\sqrt{2\pi M_{SiO_2} RT}}$$

- Thermodynamic data in FactSage free energy minimization code was used to compute the fluxes at temperatures that were experimentally tested. Codes allow easy calculation of **total flux**.

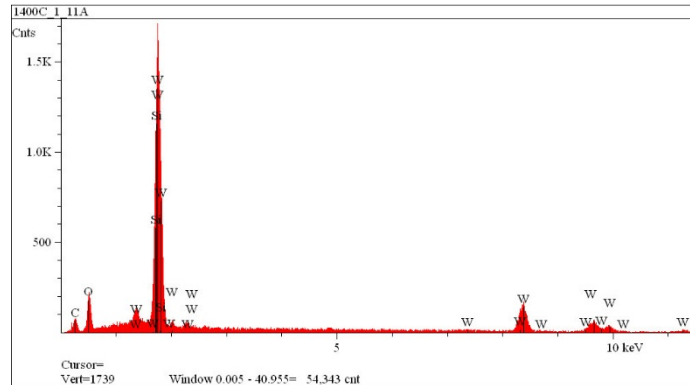
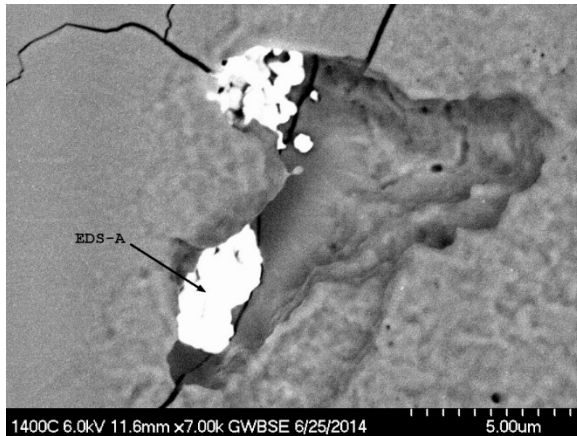
Experimental Method

Vacuum Microbalance

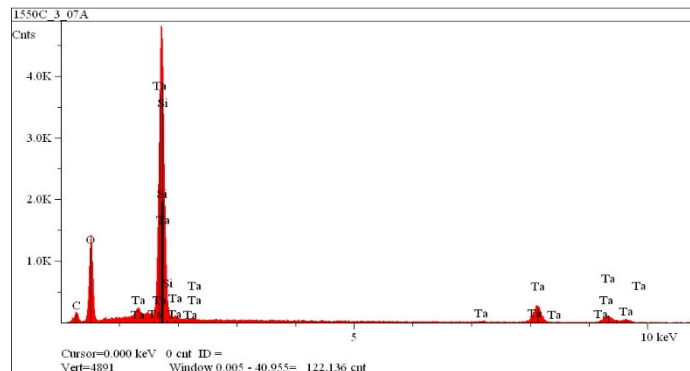
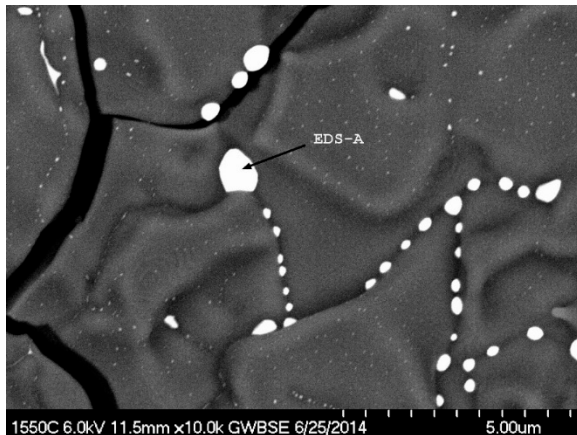


Axial thermocouple—very important!

Experimental Issues: W, Ta deposits on Samples



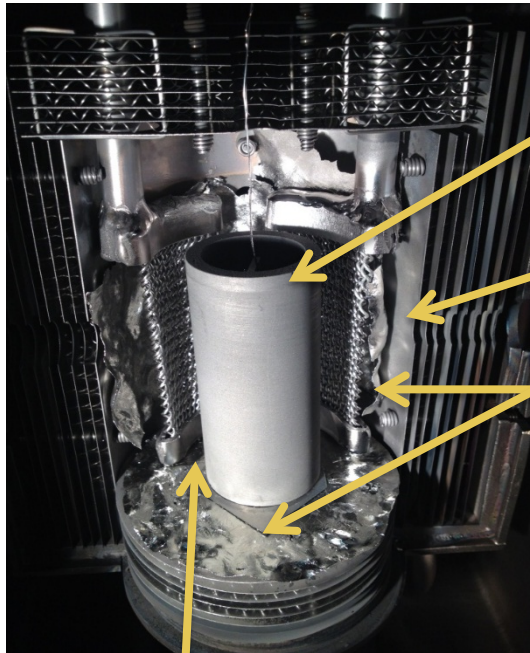
W deposits at
1673K (1400°C)



Ta deposits at
1873K (1550°C)



Use Graphite Shroud and Zr Getter to avoid W, Ta Deposition on Sample 1948K (1675°C)

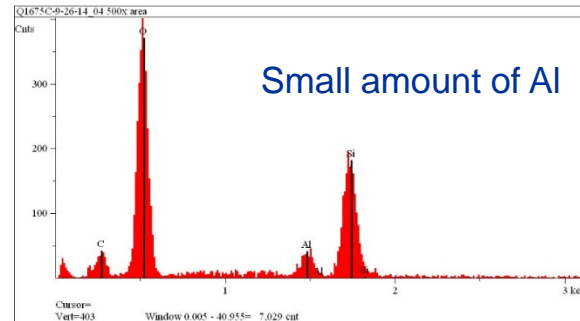
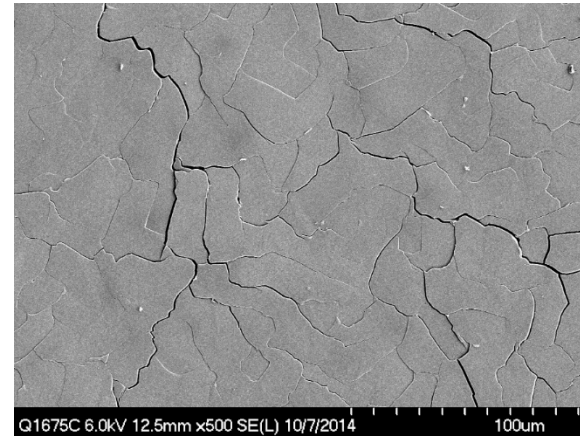


Tungsten

Tantalum

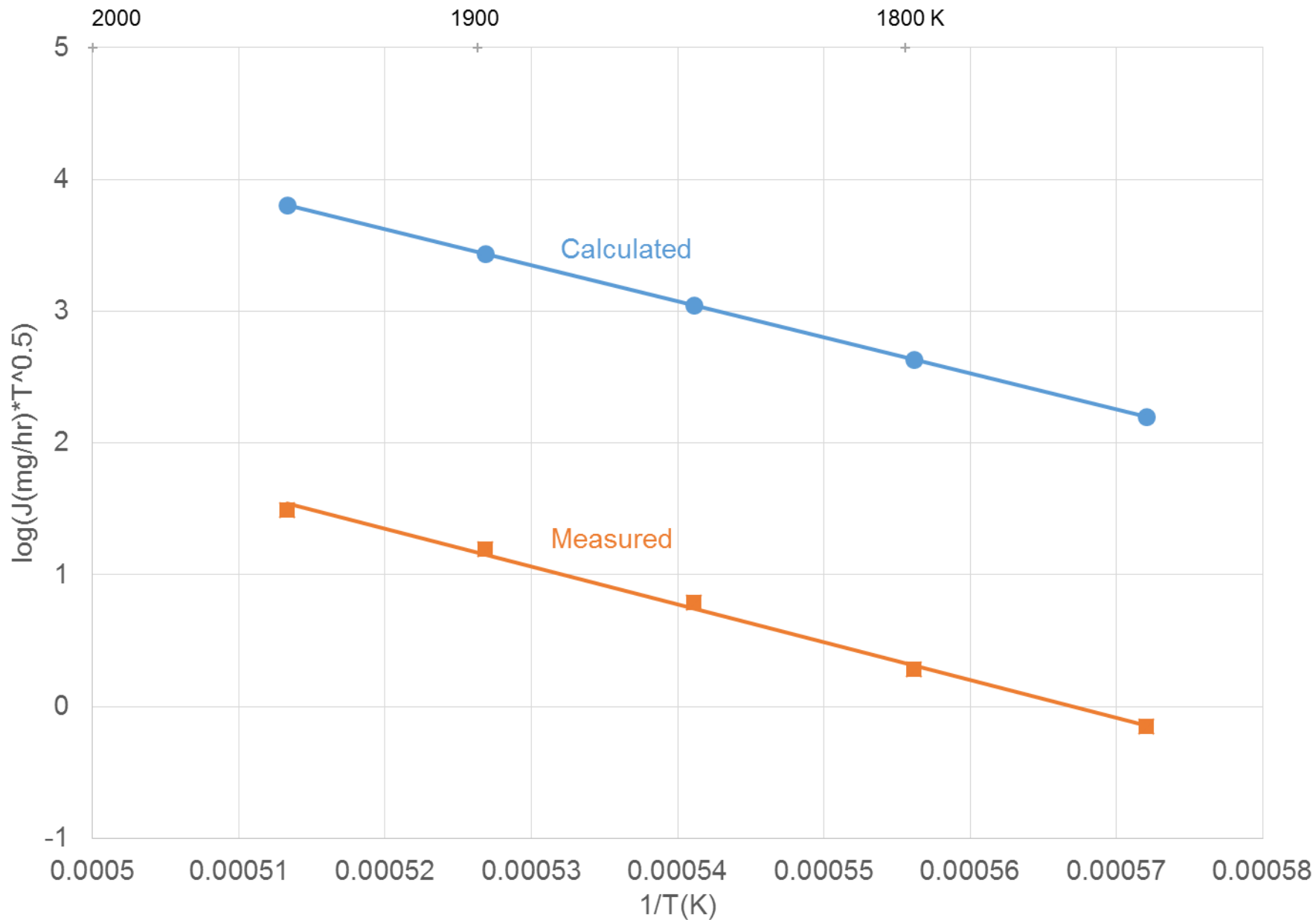
Zirconium

Graphite (no condensable oxides!)



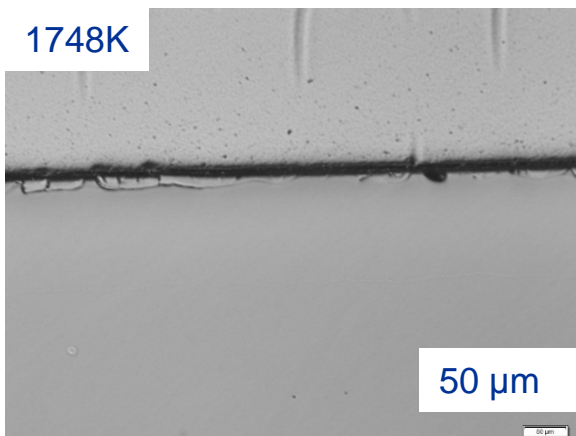


Measured Langmuir Flux Compared to Calculated Flux

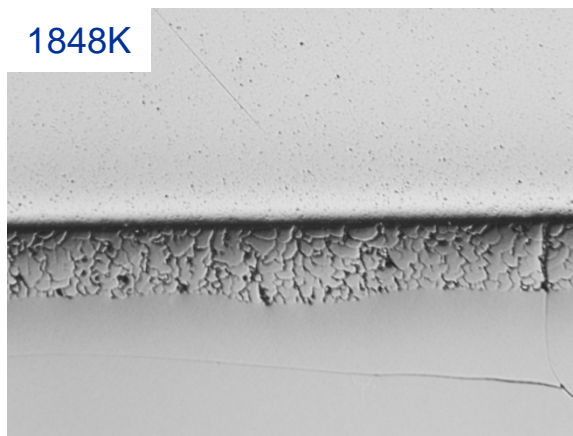


Crystallization of Fused Silica Outer Surface: 8 hrs at Temperature

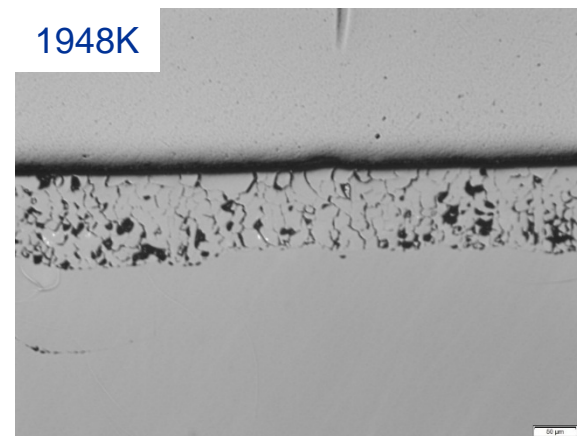
1748K



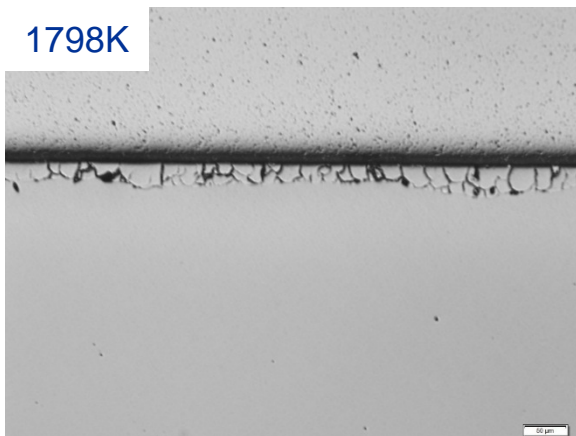
1848K



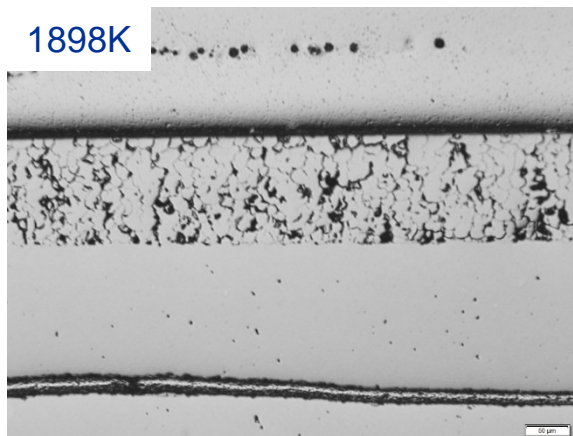
1948K



1798K



1898K



- Vaporizing Surface is effectively crystalline silica above 1798K
- XRD: cristobalite

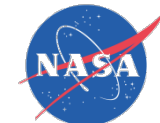


Vaporization Coefficient of Silica from Langmuir Evaporation

T(K)	J(Calc-- SiO+O+O ₂ +SiO ₂) mg/cm ² -hr	J(meas) mg/cm ² -hr	α Total
1798	10.091	0.045	4.47E-03
1848	25.665	0.142	5.54E-03
1898	62.075	0.361	5.81E-03
1948	312.25	0.709	2.27E-03

- Omit 1748K (1475°C)—may not be fully crystalline
- Measure 1798-1948K (1525-1675°C) α (from total flux) = $(4.5 \pm 1.4) \times 10^{-3}$
- Temperature dependence
 - Appears temperature independent below 1900K (1627°C)
 - May decrease near melting? Need more data here!
 - Searcy “Kinetics of Evaporation and Condensation Reactions” Wiley, 1970.
 - Transition state theory
 - Relationship of ΔH^* (Langmuir) to ΔH° (Thermodynamic);
 ΔS^* (Langmuir) to ΔS° (Thermodynamic)
 - Inferences about nature of transition state $\Delta H^* \approx \Delta H^\circ$, $\Delta S^* > \Delta S^\circ$
 - Similar to vapor; excited state?





Comparison to other Measurements

Solid	Vapor Species	T Range (K)	Vaporization Coefficient	Method	Reference
SiO ₂ + Mo	SiO(g)	1692-1739	$(3.2 \pm 0.9) \times 10^{-2}$	Knudsen cell with varying orifice size	Nagai et al.
SiO ₂	SiO(g)	1800-1950	$(2.2 \pm 0.8) \times 10^{-2}$	Free surface compared equilibrium	Firsova & Nesmeyanov
SiO ₂ + Mo	SiO(g)	1700-1950	$(2.2 \pm 0.3) \times 10^{-2}$	Knudsen cell with varying orifice size	Shornikov et al.
SiO ₂	SiO(g) (primarily)	1833-1958	$(1.1 - 1.5) \times 10^{-2}$	Free surface compared equilibrium	Hashimoto
SiO ₂	SiO(g) (primarily)	1800-1950	$(4.5 \pm 1.4) \times 10^{-3}$	Free surface compared equilibrium	This study

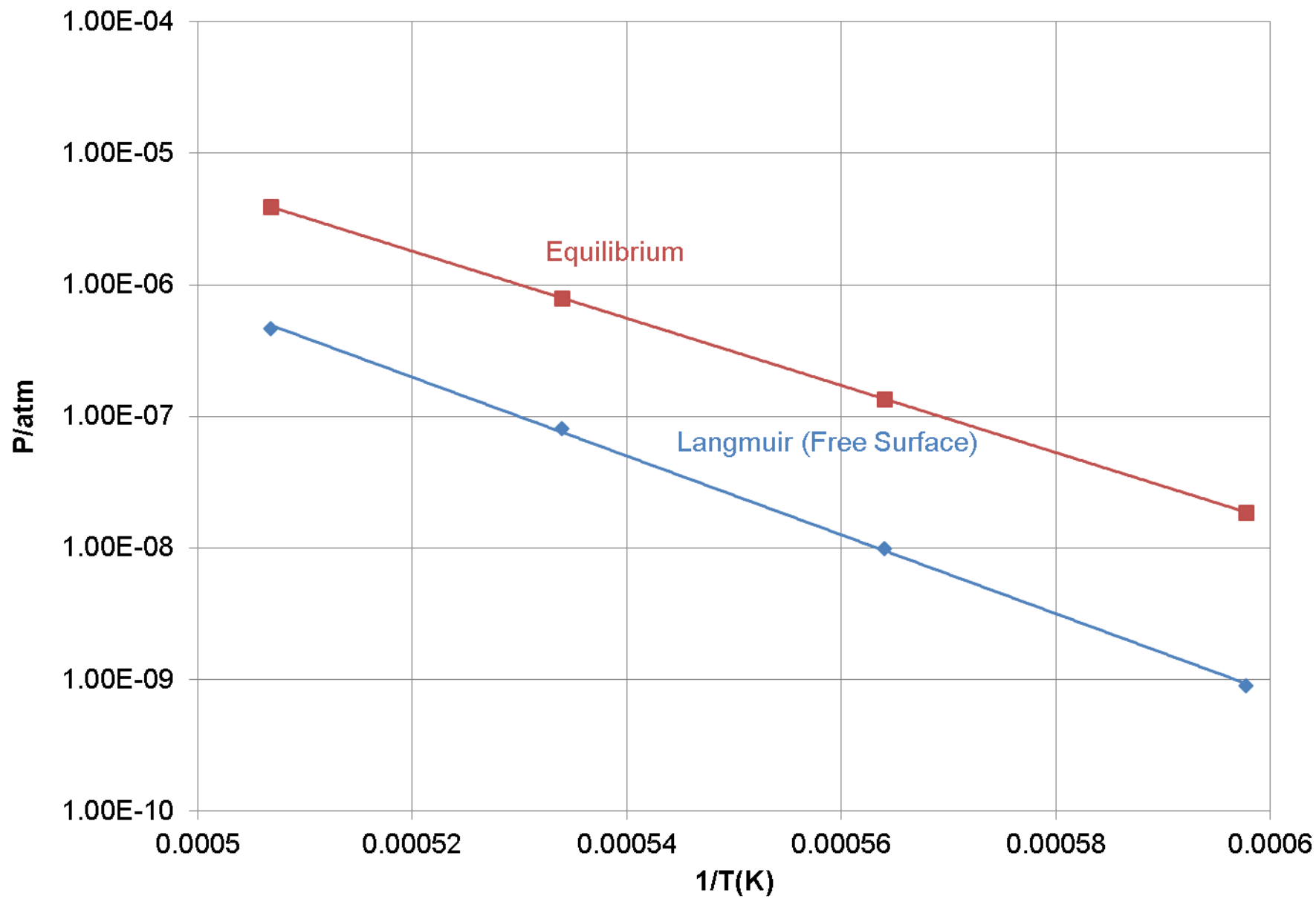
- S. Nagai, K. Niwa, M. Shinmei, and T. Yokokawa, J. Chem. Soc., Faraday Trans. I, 69 [9], 1973, pp. 1628-1634.
- L. P. Firsova and An. N. Nesmeyanov, Russian J. Phys. Chem. 34 [12], 1960, pp. 1279-1281,
- S.I. Shornikov, I. Yu. Archakov, and M. M. Shul'ts. Russian J. Gen. Chem. 69 [2], 1999, pp. 187-196
- A. Hashimoto, Nature. 347. 1990. pp. 53-55.

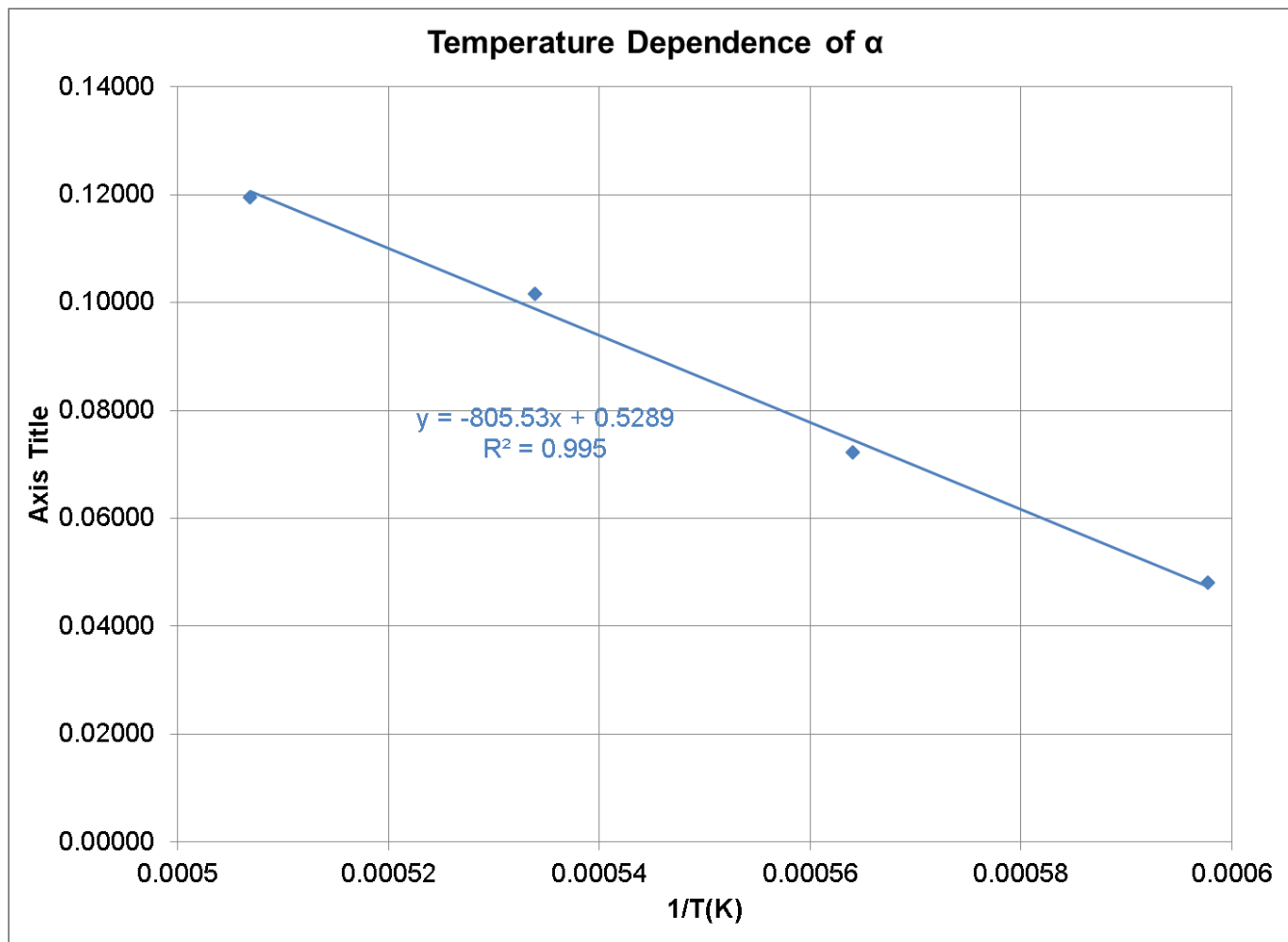
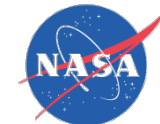
Lower values in this study:

- Selection of thermodynamic data used for calculation
- Considered all vapor components (SiO(g), O(g), O₂(g), SiO₂(g))
- Knudsen cell studies—a different reaction $\text{Mo} + 3\text{SiO}_2 = 3\text{SiO(g)} + \text{MoO}_3(\text{g})$



Experimental vs. Calculated Equilibrium Pressures over MgO





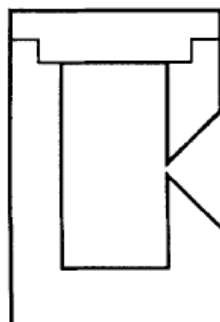
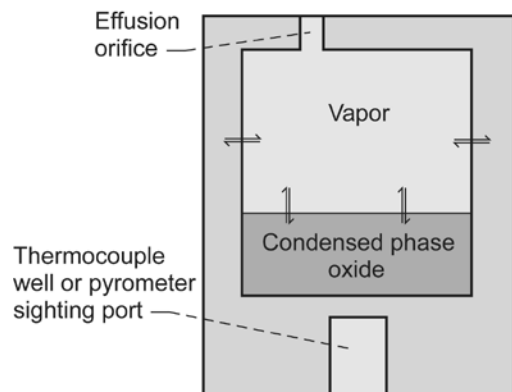
Contrast with SiO_2 , where α is independent of temperature
For MgO —suggests $\Delta H^* > \Delta H^0$ Transition state more complex



Knudsen Cell-Based Method of Determining Vaporization Coefficients

NASA Glenn Center Innovation Fund 2015
Awarded partly on Basis of EPSCoR Studies!

Knudsen Cell Method



- Classic method from high temperature chemistry for studying condensed phase vapor equilibria
- Typically 1 cm diameter x 1 cm high with a 1 mm orifice
- Near equilibrium established in cell, use effusing molecular beam to analyze vapor
- Low pressure method (mean free path) $\geq 10 \times$ (orifice diameter); molecule-wall collisions dominate
- Key parameters:
 - Orifice area,
 - Orifice transmission factor, $W = (\# \text{ escapes})/(\text{total } \#)$ e.g. $L/R = 4$, $W = 0.35$



Knudsen Cell Method of Measuring Vaporization Coefficient

- Start with Whitman-Motzfeld extrapolation to zero-orifice
 - Equation developed independently in 1960s by two different groups
 - Balance up/down pressures in a Knudsen Cell

$$\alpha_L P_{eq} = \alpha_c d_1 + f u_2 \quad \text{Vaporization} = \text{condensation} + \text{escape through orifice}$$

$$u_1 = \alpha_c P_{eq} = \alpha_L P_{eq} + (\alpha_{dr} + \alpha_{sr}) d_1 \quad \text{Upward pressure} = \text{vaporization} - \text{rebounding of molecules from top}$$

$$d_2 = (1 - f) u_2 \quad \text{Downward pressure near top} = \text{reflection from top} - \text{escape through orifice}$$

$$u_2 = W_A u_1 + (1 - W_A) d_2 \quad \text{Upward pressure near top} = \text{fraction molecules moving upward} - \text{fraction rebounding}$$

$$P_m = P_{eq} - P_m f \left(\frac{1}{\alpha} + \frac{1}{W_A} - 2 \right)$$

P_m = Measured pressure

P_{eq} = *Equilibrium* pressure

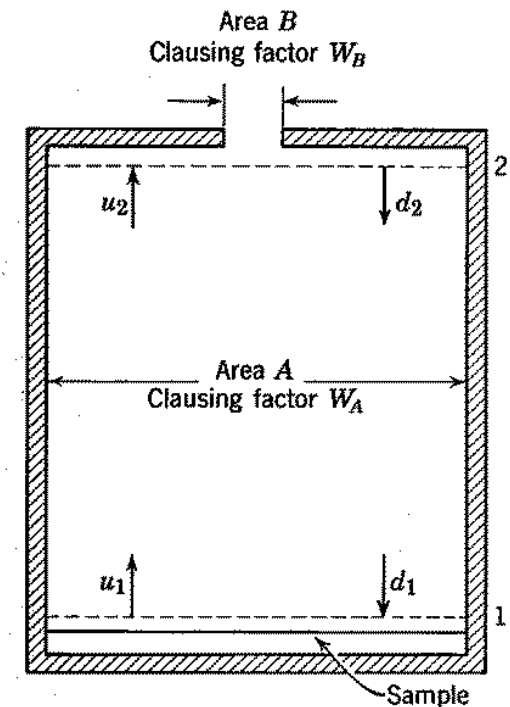
$f = W_B B/A$

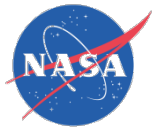
α_L = vaporization coefficient; α_c = condensation coefficient

Assume equal

- Pick several cells with different orifice geometries

- Plot P_m vs $P_m f \Rightarrow$ Slope is $-\left(\frac{1}{\alpha} + \frac{1}{W_A} - 2 \right)$





Adapt to a Mass Spectrometer

- Heyrman and Chatillon, J. Chem. Phys. Solids. 66 (2005), 494-497.
 - Couple a Knudsen effusion mass spectrometer (KEMS) to multiple cells with different transmission factors.
 - Note that $P = kIT/\sigma$, where k = instrument constant, I = ion intensity, T = absolute temperature, σ = ionization cross section
 - Pressure ratios = Ion intensity ratios

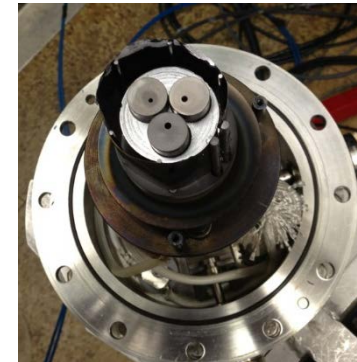
$$P_m \left[1 + f \left(\frac{1}{\alpha_c} + \frac{1}{W_a} - 2 \right) \right] = P_{eq}$$

$$\frac{P_{m2} - P_{m1}}{P_{m2}f_2 - P_{m1}f_1} = m$$

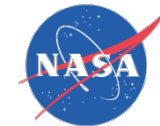
$$\frac{I_{m2} - I_{m1}}{I_{m2}f_2 - I_{m1}f_1} = m$$

$$\frac{1 - \frac{I_{m1}}{I_{m2}}}{f_2 - \frac{I_{m1}f_1}{I_{m2}}} = - \left(\frac{1}{\alpha_c} - 0.51 \right)$$

Use pairs of cells with different orifice geometries

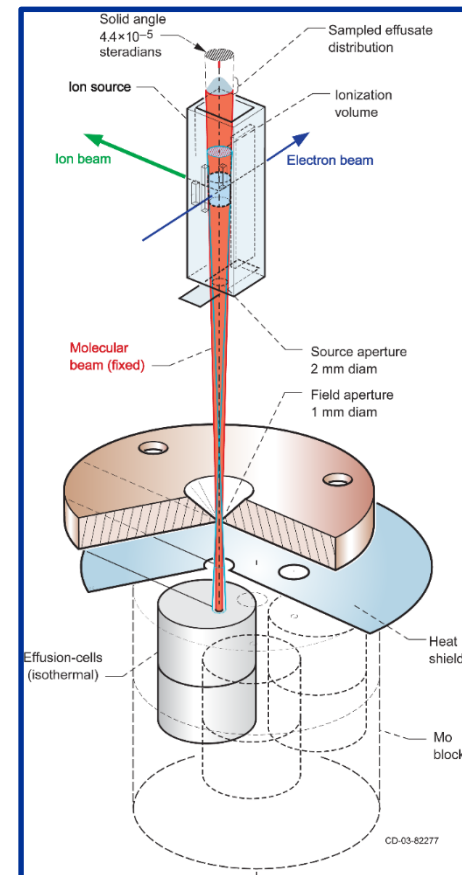
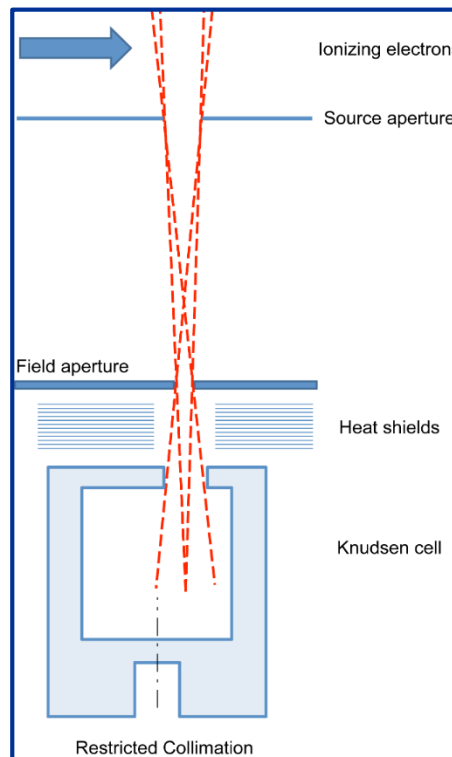


Use Multi-Knudsen Cell Mass Spectrometer with Restricted Collimation (cf. Chatillon)

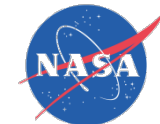


Ionizer effectively 'sees' only inside cell

- Cell diameter always > field aperture
- Differences in ion intensity relate to vaporization coefficient
- Whitman-Motzfeld equation for each pair of cells

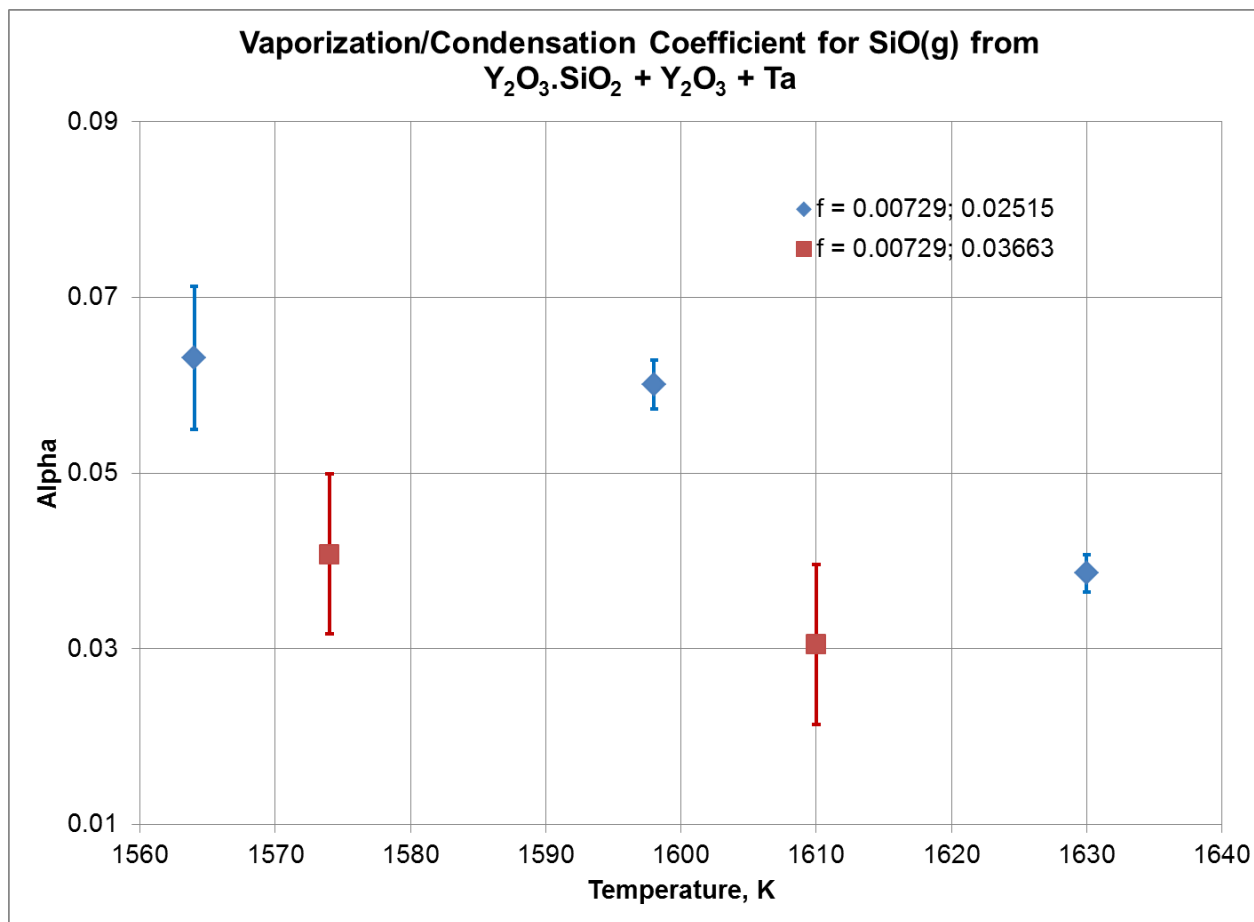


Copland, 2002



Vaporization Coefficients from Knudsen Cell

SiO(g) vaporizing from a mix of $Y_2SiO_5 + Y_2O_3 + 3Ta$





Conclusions: Vaporization Coefficient of Oxides

- Important parameter for vaporization of compounds
 - Kinetic barrier to vaporization
 - Vapor flux from a free surface $\sim (10^{-1}-10^{-5})$ *flux predicted from equilibrium vapor pressures
- Two methods of measurement
 - Comparison of free surface vaporization to equilibrium
 - No container interactions. But gives overall vaporization coefficient for many vapor species. Need consistent thermodynamic data.
 - Knudsen cells with different transmission factors
 - Vaporization for each vapor species. Independent of thermodynamic data. Container issues.
- SiO₂ and MgO studies
 - SiO₂: $(4.5 \pm 1.4) \times 10^{-3}$ (1798-1948K)
 - Somewhat lower than other published values: choice of thermodynamic data
 - MgO: 0.05-0.12 (1700-2000K) Linear temperature dependence
- Developing/adapting method based on Knudsen cells



Conclusions: Vaporization Coefficient of Silica

- Lots to do!
 - Extend to other simple and complex oxides
 - Experimental: methods, data!
 - Theoretical
 - Molecular dynamics modeling?
 - Description of vaporization process
- Important area which has not really been addressed since the 1970s!
- **Acknowledgements**
 - **NASA Glenn Center Innovation Fund ‘Measuring Vaporization Coefficients’**
 - **NASA EPSCoR Grant with Missouri Universities ‘Atmospheres of Hot, Rocky Exoplanets’**
 - **Evan Copland, now with CSIRO Australia, for adding restricted collimation and multi-cell sampling to our system**
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