Thermodynamics and Kinetics of Silicate Vaporization

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Phase Stability, Diffusion Kinetics, and their Applications
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Outline of Presentation

• Silicates are truly the ‘ubiquitous material’—found everywhere!
  – Natural systems: found in many minerals and rocks
  – Technology—coatings, structural ceramics

• Apply Knudsen Effusion Mass Spectrometry (KEMS) to study thermochemistry of silicates
  – KEMS allows measurement of equilibrium vapor pressures above condensed phase
  – Unique challenges
    • Complex vaporization behavior
    • Kinetic barriers to vaporization

• Examples
  – Geology: Thermochemistry of Olivine
  – Technology: Thermochemistry $Y_2O_3$-$SiO_2$ and $Yb_2O_3$-$SiO_2$ coating systems

• Vaporization kinetics of silicates
Over 90% of the Earth’s crust consists of silicate minerals
- Olivine (Fe\textsubscript{x}Mg\textsubscript{1-x})\textsubscript{2}SiO\textsubscript{4} primary constituent of earth’s mantle

- Moon, Mars, Asteroids, Comets, Interplanetary dust particles and...

..Hot, rocky exoplanets (maybe!)


Silicates in Materials Science

- High-Temperature Materials: Silicate Coatings

- Silicon-based ceramics: combustion chambers, static parts in hot stage

- Protective coating against water vapor, condensed phase deposits
  - Rare earth (RE) silicates \((\text{RE}_2\text{O}_3)\cdot n(\text{SiO}_2)\)
Knudsen Effusion Mass Spectrometry (KEMS)

Knudsen Cell: Condensed Phase/Gas Equilibrium

Direct Molecular Beam from Effusate Into Mass Spectrometer

- Knudsen Cell: 1909
- Couple to mass Spectrometer: 1950s (Ingrahm et al.)
- Continuing valuable applications of these methods!
Standard Calibration Material: Au

- Temperature Measurement: very critical
- Use pyrometer (non-contact)
- At triple point: determine calibration constant

\[ P_M = \frac{SIT}{\sigma} \]

\[ I_{Au} = 552 \pm 12 \text{cps} \]
\[ S_{Au} = 2.94 \pm 0.07 \times 10^{13} \text{ cps-K/atm} \]
\[ P_{Au} = 2.56 \times 10^{-8} \text{ atm at triple point} \]
Standard Calibration Material: Au
Heat of Vaporization Checks Temperature Calibration and Instrument Response

\[ \Delta_v G = \Delta_v H - T \Delta_v S = -RT \ln K_p = -RT \ln (P_M) \]

\[ \ln P_M = -\frac{\Delta_v H}{R} \left( \frac{1}{T} \right) + \frac{\Delta_v S}{R} \]

\[ \ln P_M \text{ vs } 1/T \text{ is a van't Hoff plot with slope } = \frac{-\Delta_v H}{R} \]

Mass Spectrometer \[ P_M = \frac{kIT}{\sigma} \]

\[ P_M = \text{partial pressure of } M; \]
\[ k = \text{instrument constant; } I = \text{ion intensity; } \]
\[ T = \text{Absolute temperature; } \]
\[ \sigma = \text{ionization cross section} \]

\[ \Delta_v H^o = -R^*(-41.162) = 342.20 \text{ kJ/mol} \]

Tables = 342 kJ/mol

Black numbers = order data taken on 2-16-10
Green numbers = order data taken on 2-17-10
Proceed to Oxide Solutions

- Partial pressures ↔ activities

- Complex vaporization and ionization behavior
  - \( \text{SiO}_2(s) = \text{SiO}_2(g) \)
  - \( \text{SiO}_2(g) + e^- \rightarrow \text{SiO}_2^+ + 2e^- \)
  - \( \rightarrow \text{SiO}^+ + \text{O} + 2e^- \)

  - \( \text{SiO}_2(s) = \text{SiO} (g) + \frac{1}{2} \text{O}_2(g) \)
  - \( \text{SiO}(g) + e^- \rightarrow \text{SiO}^+ + 2e^- \)
  - \( \rightarrow \text{Si}^+ + \text{O} + 2e^- \)

- Calculation of cross sections for molecules

- Vaporization may be kinetically limited

- Container Issues
  - Need inert container or container with known interactions: Mo, W, Pt, Ir
  - Silicates are very reactive!
Solutions: Measure Partial Thermodynamic Quantities

Olivine: $\text{FeO}_{1-\alpha}(\text{MgO})_{1-\beta}(\text{SiO}_2)_{1-\gamma}$
Same Phase; Variable Stoichiometry

Pure Compound:
$\text{FeO}(s) = \text{Fe}(g) + \frac{1}{2} \text{O}_2(g)$

$$K_p = \frac{P^o_{Fe}[P^o_{O_2}]^{1/2}}{a_{FeO}} = \frac{P^o_{Fe}[P^o_{O_2}]^{1/2}}{1}$$

Solution:
$\text{FeO}(\text{solution, a < 1}) = \text{Fe}(g) + \frac{1}{2} \text{O}_2(g)$

$$K_p = \frac{P^o_{Fe}[P^o_{O_2}]^{1/2}}{a_{FeO}}$$

$$a_{FeO} = \frac{P^o_{Fe}[P^o_{O_2}]^{1/2}}{P^o_{Fe}[P^o_{O_2}]^{1/2}}$$

$\ln(a_{FeO}) \text{ vs } 1/T$ — partial molar enthalpy
Procedure

- Ion intensity measurements of relevant species for:
  1. Pure compound
  2. Solution
- Best to have *in-situ* pure compound and solution

- BUT, for the highest temperature (>2000K), need to use one cell and change specimens. Assume constant calibration factor.
Example I—Natural Systems: Olivine

- $\text{Mg}_2\text{SiO}_4$ (Forsterite)-$\text{Fe}_2\text{SiO}_4$ (Fayalite)
- Primary Constituent of Earth’s Mantle
- Sources:
  - Pure form found on Hawaii Green Sand Beaches: Volcanic pipeline to Mantle
  - Mining debris
- Important in volcanism, meteorites, likely constituent of other planetary bodies
- Very reactive, particularly above melting. Use Ir cell.
Olivine – Starting Material and Characterization

93% forsterite and 7% fayalite, Fo$_{93}$Fa$_7$ - (Fe$_{0.07}$Mg$_{0.93}$)$_2$SiO$_4$

ICP-OES analysis of the as received olivine samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>*Wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.0120(6)</td>
</tr>
<tr>
<td>Ca</td>
<td>0.035(2)</td>
</tr>
<tr>
<td>Co</td>
<td>0.0120(6)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.052(3)</td>
</tr>
<tr>
<td>Fe</td>
<td>5.01(3)</td>
</tr>
<tr>
<td>Mg</td>
<td>30(2)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.075(4)</td>
</tr>
<tr>
<td>Na</td>
<td>0.0080(4)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.27(1)</td>
</tr>
<tr>
<td>Sc</td>
<td>0.0040(2)</td>
</tr>
<tr>
<td>Si</td>
<td>20(1)</td>
</tr>
</tbody>
</table>

*X*Uncertainties of the analyses are given in parentheses.

Phase content

- Forsterite – 87.7 ± 0.3%
- Enstatite – 7.1 ± 0.2%
- Silica – 0.84 ± 0.6%
- Sapphirine – 0.5 ± 0.1%
- Clinochlore – 3.9 ± 0.2%

Heating to > 1060°C removes impurities.

XRD pattern and Rietveld refinement of the as received olivine samples.
Temperature dependence of ion intensity ratios of Mg\(^+\), Fe\(^+\), SiO\(^+\), O\(^+\) and O\(_2\)\(^+\) in the olivine sample.

Measurements show good agreement with the phase diagram calculated by Bowen and Shairer.


Fegley and Osborne, *Practical Chemical Thermodynamics For Geoscientists*, Elsevier 2013, Fig. 12-11.
Olivine—Solution of $\text{Mg}_2\text{SiO}_4$ (Fosterite)-$\text{Fe}_2\text{SiO}_4$ (Fayalite)

- Composition of Interest: $\text{Fo}_{0.93}\text{Fa}_{0.07}$
- Activity gradient across olivine
- Work in two phase regions
  - Excess $\text{SiO}_2$: Olivine + Pyroxene
  - Excess $\text{MgO}$: Olivine + Magnesiowustite
Previous Data and Models of Olivine

- Thermodynamic measurements
  - Nafziger & Muan (1967); Kitayama & Katsura (1968)—from P(O$_2$) and stable phases
  - Sakawa et al. (1976): Equilibration method for a(FeO)
  - Plante et al. (1992): KEMS measurements of a(FeO)
  - Wood & Kleppa, Kojitani & Akaogi: Calorimetry
  - General agreement: a(FeO): Positive deviation from ideality

- Saxena et al. (1993): (Mg,Fe)$_2$SiO$_4$ Regular Solution Lo = 9000

- Decterov et al.: Sublattice

- Fabrichnaya (1998): (Mg,Fe)$_2$SiO$_4$ β and γ spinel; subregular solution with temperature dependent mixing parameters
Thermodynamic Activities in Olivine – \((\text{Fe}_2\text{SiO}_4)_{0.07}(\text{Mg}_2\text{SiO}_4)_{0.93}+\text{MgO}\)

![Graph showing thermodynamic activities in Olivine](image)

<table>
<thead>
<tr>
<th>Component</th>
<th>x</th>
<th>(a) (1800K)</th>
<th>Compare to Ideality</th>
<th>(\Delta H_i) (1700 – 1950)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>0.62</td>
<td>0.353</td>
<td>(-)ve deviations</td>
<td>30.2 kJ/mol</td>
</tr>
<tr>
<td>“FeO”</td>
<td>0.047</td>
<td>0.081</td>
<td>(+)ve deviations</td>
<td>212.5 kJ/mol</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>0.33</td>
<td>0.046</td>
<td>(-)ve deviations</td>
<td>220.2 kJ/mol</td>
</tr>
</tbody>
</table>
# Thermodynamic Activities in Olivine – \((Fe_2SiO_4)_{0.07}(Mg_2SiO_4)_{0.93}\)

![Graph showing thermodynamic activities](graph.png)

<table>
<thead>
<tr>
<th>Component</th>
<th>x</th>
<th>a (1900K)</th>
<th>Compare to ideality</th>
<th>(\Delta H_f(1700 – 1950))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>0.62</td>
<td>0.165</td>
<td>(-)ve deviation</td>
<td>-222.0 kJ/mol</td>
</tr>
<tr>
<td>“FeO”</td>
<td>0.047</td>
<td>0.053</td>
<td>(+)ve deviation</td>
<td>-55.2 kJ/mol</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.333</td>
<td>0.341</td>
<td>(+)ve deviation</td>
<td>116.2 kJ/mol</td>
</tr>
</tbody>
</table>
Comparison to Models (FactSage)

![Graphs showing comparison to models for Olivine + 0.01 MgO and Olivine + 0.01 SiO2](image_url)
Thermodynamics of Olivine: Lots to Do!

- Understand changes in activities on melting
- Compare partial molar enthalpies to total excess free energy
- Refine current models: our data suggests some components far from ideality
Example 2: Rare Earth Silicates
SiC and SiC based Composites for Heat Engines

- Strength retained to higher temperatures than metals
- Lighter weight
- Fiber Reinforced composites give some fracture toughness
- Protected by SiO$_2$ scale
  - Slow growing, good in pure oxygen
  - BUT…Attacked by basic molten salts; volatilized by water

![Graph showing wt. change vs. exposure time for different conditions]

**SiC/SiC CMC HPBR Paralinear**
(1100 °C-1300°C, 6 atm; Robinson/Smialek 1998)
Si(OH)$_4$ volatility (Opila et al., 1998-2006)
Combine *Desirable Mechanical Properties of SiC with Chemical Inertness of Refractory Oxide*

- Lower activity of silica ⇒ less reaction
- Molten salt reaction
  - \( \text{Na}_2\text{O}(s) + \text{SiO}_2(s) = \text{Na}_2\text{O} \cdot x\text{SiO}_2 \)
- Water vapor enhanced volatilization
  - \( \text{SiC} + \frac{3}{2} \text{O}_2(g) = \text{SiO}_2 + \text{CO}(g) \)
  - \( \text{SiO}_2 + 2 \text{H}_2\text{O}(g) = \text{Si(OH)}_4(g) \)
  - \( P[\text{Si(OH)}_4] = K a(\text{SiO}_2) [P(\text{H}_2\text{O})]^2 \)

\[
\text{H}_2\text{O}(g) \quad \overset{\text{SiO}_2, \text{MO}}{\longrightarrow} \quad \text{Si(OH)}_4(g) \downarrow, \text{MOH}(g) \downarrow
\]

(Underline indicates in solution)

Rare Earth Silicates: Good CTE Match to SiC
Calculated $Y_2O_3$-$SiO_2$ Phase Diagram

Indirect evidence suggests that the $SiO_2$ thermodynamic activity is lower in the $Y_2O_3$-$Y_2SiO_5$ and $Y_2SiO_5$-$Y_2Si_2O_7$ regions.
But there are no direct measurements!

Fabrichnaya-Seifert Database
Issues with Measuring $a(\text{SiO}_2)$ in RE Silicates

- Vapor pressure of SiO$_2$ too low to measure in temperature range of interest

- Need measurable signal for SiO$_2$—use reducing agent to make excess SiO(g). Tried several, selected Mo or Ta
  - For $a(\text{SiO}_2) > \sim 0.02$
    - Mo(s) + 3SiO$_2$(soln) = 3SiO(g) + MoO$_3$(g)
  - For $a(\text{SiO}_2) < \sim 0.02$
    - 2Ta(s) + 2SiO$_2$(soln) = 2SiO(g) + TaO(g) + TaO$_2$(g)
- Note reducing agent must not change solid phase composition
- Monosilicates + disilicates +Ta – leads to tantalates

- Need to account for non-equilibrium vaporization

- SiO overlaps with CO$_2$ (m/e = 44)
  - Use LN$_2$ cold finger for improved pumping
  - Shutter to distinguish vapor from cell and background
  - High resolution instrument (in our dreams…)
  - Gettering pump for CO$_2$
Monosilicate + Disilicate

\[ \text{Y}_2\text{O}_3-\text{SiO}_2 + \text{Y}_2\text{O}_3-2\text{SiO}_2 \]

\[ \text{Yb}_2\text{O}_3-\text{SiO}_2 + \text{Yb}_2\text{O}_3-2\text{SiO}_2 \]

THERMO-CALC (2010.08.10:09.24):
DATABASE: USER
AC(O)=1, N=1, P=1.01325E5;
Work in Two Phase Region: Monosilicate + Disilicate

Three cells:

- **Au (reference)**
- **3Mo + Y₂O₃ · 2SiO₂ + Y₂O₃ · SiO₂**
- **3Mo + SiO₂**

Mo as powder and cell material

\[
\text{Mo(s)} + 3\text{SiO}_2(\text{soln}) = 3\text{SiO(g)} + \text{MoO}_3(\text{g})
\]

- Compare cells 1 and 2

Note that cell is part of the thermodynamic system: Best way to overcome container issue!

\[
K = \frac{[P(SiO)]^3 P(MoO_3)}{[a(SiO_2)]^3}
\]

\[
Mo + 3\text{SiO}_2 = 3\text{SiO} + \text{MoO}_3
\]

Cell 2: pure SiO₂

\[
a(SiO_2) = 1 = \left\{ \left[ \frac{P^o(SiO)}{P^o(MoO_3)} \right]^3 \right\}^{0.33}
\]

Cell 3: SiO₂ in silicate

\[
a(SiO_2) = \left\{ \left[ \frac{P(SiO)}{P(MoO_3)} \right]^3 \right\}^{0.33}
\]

\[
a(SiO_2) = \left\{ \left[ \frac{I(SiO)}{I(MoO_3)} \right]^3 \right\}^{0.33}
\]
\[ \text{Two Phase Mixture} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(a(\text{SiO}_2), 1650\text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Y}_2\text{O}_3\cdot(\text{SiO}_2) + \text{Y}_2\text{O}_3\cdot2(\text{SiO}_2) )</td>
<td>0.281</td>
</tr>
<tr>
<td>( \text{Y}_2\text{O}_3\cdot(\text{SiO}_2) + \text{Y}_2\text{O}_3\cdot2(\text{SiO}_2) )</td>
<td>0.194</td>
</tr>
</tbody>
</table>
XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

Yttrium monosilicate + disilicate + Mo

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y\textsubscript{2}O\textsubscript{3}.(SiO\textsubscript{2})</td>
<td></td>
</tr>
<tr>
<td>Y\textsubscript{2}O\textsubscript{3}.2(SiO\textsubscript{2})</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td></td>
</tr>
</tbody>
</table>

Ytterbium monosilicate + disilicate + Mo

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb\textsubscript{2}O\textsubscript{3}.(SiO\textsubscript{2})</td>
<td>56</td>
</tr>
<tr>
<td>Yb\textsubscript{2}O\textsubscript{3}.2(SiO\textsubscript{2})</td>
<td>36</td>
</tr>
<tr>
<td>Mo</td>
<td>8</td>
</tr>
</tbody>
</table>
Monosilicate + RE$_2$O$_3$

$Y_2$O$_3$-SiO$_2$  \hspace{2cm} Yb$_2$O$_3$-SiO$_2$

THERMO-CALC (2010.08.10:09.24) :
DATABASE:USER
AC(O)=1, N=1, P=1.01325E5;
Monosilicate + RE$_2$O$_3$

Two cells:
- Au
- 3Ta + Y$_2$O$_3$ + Y$_2$O$_3$ · SiO$_2$
  - Ta as powder and cell material—cell is part of system

2Ta(s) + 3SiO$_2$(soln) = 3SiO(g) + TaO(g) + TaO$_2$(g)

- Using $P_{\text{eq}}$(SiO) and FactSage (free energy minimization)
- Correction for non-equilibrium vaporization

![Graph showing the relationship between log(a(SiO$_2$)) and log P(SiO).]
XRD after KEMS Measurements of RE Monosilicates + RE₂O₃ + Ta:

Yttrium monosilicate + Y₂O₃ + Ta

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃.(SiO₂)</td>
<td>41</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>49</td>
</tr>
<tr>
<td>Ta</td>
<td>4</td>
</tr>
<tr>
<td>Ta₃Si</td>
<td>4</td>
</tr>
</tbody>
</table>

Ytterbium monosilicate + Yb₂O₃ + Ta

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb₂O₃.(SiO₂)</td>
<td>24</td>
</tr>
<tr>
<td>Yb₂O₃</td>
<td>66</td>
</tr>
<tr>
<td>Ta</td>
<td>2</td>
</tr>
<tr>
<td>Ta₂Si</td>
<td>2</td>
</tr>
</tbody>
</table>
\[ \Delta H_{(SiO_2, 1600 \text{ K})} = (5200.26) \cdot R \cdot 2.303 = 99.57 \text{ kJ/mol} \]

\[
\begin{align*}
\text{KEMS 1-2012} & \quad \text{KEMS 4-2013} \\
\text{Fabrichnaya-Seifert Optimization} & \quad \text{ } \\
\end{align*}
\]

\[ y = -5200.26(\frac{1}{T}) + 0.0567 \]

\[ y = -2864.9(\frac{1}{T}) - 2.0853 \]

\[ \Delta H_{(SiO_2, 1600 \text{ K})} = (1412.60) \cdot R \cdot 2.303 = 27.05 \text{ kJ/mol} \]

\[
\begin{align*}
\text{RE}_2\text{O}_3(\text{s, 1600 K}) + \text{SiO}_2(\text{s, 1600 K}) & \rightarrow \text{RE}_2\text{SiO}_5(\text{s, 1600 K}) \\
\text{RE}_2\text{SiO}_5(\text{s, 1600 K}) & \rightarrow \text{RE}_2\text{SiO}_5(\text{s, 298 K}) \\
\text{RE}_2\text{O}_3(\text{s, 298 K}) & \rightarrow \text{RE}_2\text{O}_3(\text{s, 1600 K}) \\
\text{SiO}_2(\text{s, 298 K}) & \rightarrow \text{SiO}_2(\text{s, 1600 K}) \\
2 \text{RE}_2(\text{s, 298 K}) + \frac{3}{2} \text{O}_2(\text{g, 298 K}) & \rightarrow \text{RE}_2\text{O}_3(\text{s, 298 K}) \\
\text{Si}(\text{s, 298 K}) + \text{O}_2(\text{g, 298 K}) & \rightarrow \text{SiO}_2(\text{s, 298 K}) \\
2 \text{RE}_2(\text{s, 298 K}) + \frac{5}{2} \text{O}_2(\text{g, 298 K}) & \rightarrow \text{RE}_2\text{SiO}_5(\text{s, 298 K}) \\
\end{align*}
\]

\[ \Delta H_1 = \text{measured in this work} \]

\[ \Delta H_2 = H_{1600 \text{ K}} - H_{298 \text{ K}} \]

\[ \Delta H_3 \]

\[ \Delta H_4 \]

\[ \Delta H_5 \]

\[ \Delta H_6 \]

\[ \Delta H_7 = \Delta H_f, \text{RE}_2\text{SiO}_5, 298 \text{ K} \]

\[ \Delta H_f, \text{RE silicate, 298 K} \text{ (kJ/mol)} \]

KEMS \quad \text{Calorimetry}^* 

Y_2\text{O}_3\cdot(\text{SiO}_2) \quad -2907 \pm 16 \quad -2868.54 \pm 5.34 

Yb_2\text{O}_3\cdot(\text{SiO}_2) \quad -2744 \pm 11 \quad -2774.75 \pm 16.48 

a(\text{SiO}_2), 1650 \text{ K} 

0.000804 

0.00298

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 \( \alpha \): Vaporization Coefficient

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

  – Metals: Generally unity; Oxides 10^{-1} to 10^{-5}!

• 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
  – \( \text{SiO}_2(s) = \text{SiO}_2(g) \)
  – \( \text{SiO}_2(s) = \text{SiO}(g) + \frac{1}{2} \text{O}_2(g) \)
  – \( \text{SiO}_2(s) = \text{SiO}(g) + \text{O}(g) \)

• Complex process
  – Break apart \( \text{SiO}_4^{2-} \)
  – Adsorbed \( \text{SiO}_2(a), \text{SiO}(a), \text{O}_2(a), \text{O}(a) \)
  – Desorption to \( \text{SiO}_2(g), \text{SiO}(g), \text{O}_2(g), \text{O}(g) \)
  – Break O-O, Si-O bonds; make O=O double bond

• Expect a kinetic barrier \( \Rightarrow \) flux reduced from equilibrium
Measure 1798-1948K (1525-1675°C)
$\text{SiO}_2 \alpha$ (from total flux) = $(4.5 \pm 1.4) \times 10^{-3}$
Importance of Vaporization Coefficient

• Calculate vapor pressures above a condensed phase oxide:
  – Modify by vaporization coefficient

• Thermodynamic measurements
  – Implicitly assume that $\alpha(A(g), \text{solution}) = \alpha(A(g), \text{pure component})$
  – $A(g)$—particular species

• Measurements of these until 1970s, then relatively little work

• Important parameter has major effect on vapor pressures
Summary

- **Knudsen Effusion Mass Spectrometry**
  - Powerful tool for thermodynamic measurements
  - In use for many years; but still very useful particularly for solutions
  - Procedures are system specific

- **Example: Olivine**
  - Challenge to find ‘inert’ cell material. Iridium probably the best
  - Treat as solid solution of ‘FeO’, MgO, SiO₂
  - The melting point of the olivine sample was determined by the ion intensity discontinuity to be 1805 °C
  - Compare to standards and derive thermodynamic activities in solid phase. Appears to be significant partial molar heats, deviations from ideality

- **Example: Rare-earth silicates**
  - The reduced SiO₂ activity in Rare-earth silicates should limit their reactivity with water vapor
  - Solid State rare earth oxides—activity of SiO₂
    - Need reducing agent to obtain a measurable signal for SiO(g), which in turn relates to activity of SiO₂. Reducing agent must not change solid phase composition.
    - Method and choice of reducing agent depends on particular silicate

- **Vaporization Kinetics**: Described by vaporization coefficient
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