Thermodynamics and Kinetics of Silicate Vaporization

Nathan S. Jacobson
Gustavo C. C. Costa
NASA Glenn Research Center

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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 \( (\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4 \) 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

- 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

\[ I_{\text{Au}} = 552 \pm 12 \text{cps} \]
\[ S_{\text{Au}} = 2.94 \pm 0.07 \times 10^{13} \text{cps-K/atm} \]
\[ P_{\text{Au}} = 2.56 \times 10^{-8} \text{ atm at triple point} \]

\[ P_M = \frac{SIT}{\sigma} \]
Standard Calibration Material: Au
Heat of Vaporization Checks Temperature Calibration and Instrument Response

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

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

\( \ln P_M \) vs \( 1/T \) is a van't Hoff plot with slope \( \frac{-\Delta_v H}{R} \)

Mass Spectrometer

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

\( P_M \) = partial pressure of \( M \);
\( k \) = instrument constant; \( I \) = ion intensity;
\( T \) = Absolute temperature;
\( \sigma \) = ionization cross section

\[ \Delta_v H^0 = -R^*(-41.162) = 342.20 \text{ kJ/mol} \]

Tables = 342 kJ/mol
Proceed to Oxide Solutions

- Partial pressures ↔ activities

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

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

- 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!
Olivine: FeO$_{1-\alpha}$(MgO)$_{1-\beta}$(SiO$_2$)$_{1-\gamma}$

Same Phase; Variable Stoichiometry

Pure Compound:

FeO(s) = Fe(g) + 1/2 O$_2$(g)

$$K_p = \frac{P_Fe^o [P_{O_2}^o]^{1/2}}{a_{FeO}} = \frac{P_Fe^o [P_{O_2}^o]^{1/2}}{1}$$

Solution:

FeO(solution, a < 1) = Fe(g) + 1/2 O$_2$(g)

$$K_p = \frac{P_Fe [P_{O_2}^o]^{1/2}}{a_{FeO}}$$

$$a_{FeO} = \frac{P_Fe [P_{O_2}^o]^{1/2}}{P_Fe^o [P_{O_2}^o]^{1/2}}$$

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

- Mg$_2$SiO$_4$ (Forsterite)-Fe$_2$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, \( \text{Fo}_{93}\text{Fa}_{7} \) - \((\text{Fe}_{0.07}\text{Mg}_{0.93})_{2}\text{SiO}_{4}\)

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>

*Uncertainties of the analyses are given in parentheses.

XRD pattern and Rietveld refinement of the as received olivine samples.

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.
Temperature dependence of ion intensity ratios of Mg\textsuperscript{+}, Fe\textsuperscript{+}, SiO\textsuperscript{+}, O\textsuperscript{+} and O\textsubscript{2}\textsuperscript{+} 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)_2SiO_4 Regular Solution Lo = 9000

- Decterov et al.: Sublattice

- Fabrichnaya (1998): (Mg,Fe)_2SiO_4 β and γ spinel; subregular solution with temperature dependent mixing parameters
Thermodynamic Activities in Olivine – \((\text{Fe}_2\text{SiO}_4)_{0.07}(\text{Mg}_2\text{SiO}_4)_{0.93} + \text{MgO}\)

<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 – \((\text{Fe}_2\text{SiO}_4)_{0.07}(\text{Mg}_2\text{SiO}_4)_{0.93}\)

<table>
<thead>
<tr>
<th>Component</th>
<th>x</th>
<th>(a) (1900K)</th>
<th>Compare to ideality</th>
<th>(\Delta\overline{H}_i(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>SiO(_2)</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)

![Graph of Olivine + 0.01 MgO](Image)

![Graph of Olivine + 0.01 SiO2](Image)
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 SiO₂ scale
  - Slow growing, good in pure oxygen
  - BUT… Attacked by basic molten salts; volatilized by water

SiC/SiC CMC HPBR Paralinear
(1100 °-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
  - $\text{SiC} + \frac{3}{2} \text{O}_2(g) = \text{SiO}_2 + \text{CO}(g)$
  - $\text{SiO}_2 + 2 \text{H}_2\text{O}(g) = \text{Si(OH)}_4(g)$
  - $P[\text{Si(OH)}_4] = K_a(\text{SiO}_2) \ [P(\text{H}_2\text{O})]^2$

$\text{H}_2\text{O}(g) \xrightarrow{\cdot \cdot} \text{Si(OH)}_4(g) \downarrow, \text{MOH(g) \downarrow}$

SiO₂, MO

(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 $a$(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 $a$(SiO$_2$) > ~0.02
    - Mo(s) + 3SiO$_2$(soln) = 3SiO(g) + MoO$_3$(g)
  - For $a$(SiO$_2$) < ~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:
1. Au (reference)
2. 3Mo + Y_2O_3 · 2SiO_2 + Y_2O_3 · SiO_2
3. Mo + SiO_2

Mo as powder and cell material

Mo(s) + 3SiO_2(soln) = 3SiO(g) + MoO_3(g)

- Compare cells 1 and 2

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

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

Cell 2: pure SiO_2

\[ Mo + 3SiO_2 = 3SiO + MoO_3 \]

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

Cell 3: SiO_2 in silicate

\[ Mo + 3SiO_2 = 3SiO + MoO_3 \]

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

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

<table>
<thead>
<tr>
<th>Two Phase Mixture</th>
<th>a(SiO_2), 1650K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y_2O_3\cdot(SiO_2) + Y_2O_3\cdot2(SiO_2))</td>
<td>0.281</td>
</tr>
<tr>
<td>(Y_2O_3\cdot(SiO_2) + Y_2O_3\cdot2(SiO_2))</td>
<td>0.194</td>
</tr>
</tbody>
</table>
XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

Yttrium monosilicate + disilicate + Mo

Phase
Y_2O_3(SiO_2)
Y_2O_3.2(SiO_2)
Mo

Ytterbium monosilicate + disilicate + Mo

Phase
Yb_2O_3(SiO_2) 56
Yb_2O_3.2(SiO_2) 36
Mo 8
Monosilicate + RE$_2$O$_3$

Y$_2$O$_3$-SiO$_2$  

Yb$_2$O$_3$-SiO$_2$
Monosilicate + RE$_2$O$_3$

Two cells:
- Au
- $3\text{Ta} \; + \; \text{Y}_2\text{O}_3 \; + \; \text{Y}_2\text{O}_3 \cdot \text{SiO}_2$
  - Ta as powder and cell material—cell is part of system

$2\text{Ta}(s) + 3\text{SiO}_2(s) = 3\text{SiO}(g) + \text{TaO}(g) + \text{TaO}_2(g)$

- Using $P_{eq}(\text{SiO})$ and FactSage (free energy minimization)
- Correction for non-equilibrium vaporization
XRD after KEMS Measurements of RE Monosilicates + RE$_2$O$_3$ + Ta:

Yttrium monosilicate + Y$_2$O$_3$ + Ta

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$.(SiO$_2$)</td>
<td>41</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>49</td>
</tr>
<tr>
<td>Ta</td>
<td>4</td>
</tr>
<tr>
<td>Ta$_3$Si</td>
<td>4</td>
</tr>
</tbody>
</table>

Ytterbium monosilicate + Yb$_2$O$_3$ + Ta

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb$_2$O$_3$.(SiO$_2$)</td>
<td>24</td>
</tr>
<tr>
<td>Yb$_2$O$_3$</td>
<td>66</td>
</tr>
<tr>
<td>Ta</td>
<td>2</td>
</tr>
<tr>
<td>Ta$_2$Si</td>
<td>2</td>
</tr>
</tbody>
</table>
\[
\Delta H_{(SiO_2, 1600 \text{ K})} = (5200.26) \cdot R \cdot 2.303 = 99.57 \text{ kJ/mol}
\]

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

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

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) 
$\text{SiO}_2 \; \alpha \; \text{(from total flux)} = (4.5 \pm 1.4) \times 10^{-3}$
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
Acknowledgements

• Helpful discussions with E. Opila (Formerly NASA Glenn now Univ of Virginia); B. Fegley (WUSTL)

• Multiple cell and sampling system improvements to mass spectrometer: E. Copland (formerly NASA Glenn; now CSIRO, Melbourne, Australia)

• XRD: R. Rogers (NASA Glenn)