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 \((\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4\) 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 (RE$_2$O$_3$)$_n$(SiO$_2$)
Knudsen Effusion Mass Spectrometry (KEMS)

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

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

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

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

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

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

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

\[ \text{Tables } = 342 \text{ kJ/mol} \]
Proceed to Oxide Solutions

- Partial pressures ↔ activities

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

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

- 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: 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)

$$K_p = \frac{P_{Fe} [P_{O_2}^{a}]}{a_{FeO}}$$

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

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

- \( \text{Mg}_2\text{SiO}_4 \) (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>

*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.

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 $a(\text{FeO})$
  - Plante et al. (1992): KEMS measurements of $a(\text{FeO})$
  - Wood & Kleppa, Kojitani & Akaogi: Calorimetry
  - General agreement: $a(\text{FeO})$: Positive deviation from ideality

- Saxena et al. (1993): $(\text{Mg,Fe})_2\text{SiO}_4$ Regular Solution $L_0 = 9000$

- Decterov et al.: Sublattice

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

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

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<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>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)
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 weight change over exposure time](image-url)
Combine *Desirable Mechanical Properties of SiC with Chemical Inertness of Refractory Oxide*

- Lower activity of silica $\Rightarrow$ 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
  - $\text{SiC} + \frac{3}{2} \text{O}_2(g) = \text{SiO}_2 + \text{CO}(g)$
  - $\text{SiO}_2 + 2\text{H}_2\text{O}(g) = \text{Si(OH)}_4(g)$
  - $P[\text{Si(OH)}_4] = K_a(\text{SiO}_2)[P(\text{H}_2\text{O})]^2$

\[
\begin{align*}
\text{H}_2\text{O}(g) & \rightarrow \text{Si(OH)}_4(g) \downarrow, \text{MOH}(g) \downarrow \\
\text{SiO}_2, \text{MO} \quad \text{(Underline indicates in solution)}
\end{align*}
\]

Indirect evidence suggests that the $\text{SiO}_2$ thermodynamic activity is lower in the $\text{Y}_2\text{O}_3-\text{Y}_2\text{SiO}_5$ and $\text{Y}_2\text{SiO}_5-\text{Y}_2\text{Si}_2\text{O}_7$ 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) + 3$\text{SiO}_2$(soln) = 3SiO(g) + MoO$_3$(g)
  - For $a(\text{SiO}_2) < \sim 0.02$
    - 2Ta(s) + 2$\text{SiO}_2$(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

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

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

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)
- $3\text{Mo} + Y_2\text{O}_3 \cdot 2\text{SiO}_2 + Y_2\text{O}_3 \cdot \text{SiO}_2$
- $3\text{Mo} + \text{SiO}_2$
- 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!

$$K = \frac{[P(SiO)]^3 P(\text{MoO}_3)}{[a(SiO)]^3}$$

Mo + 3SiO$_2$ = 3SiO + MoO$_3$

Cell 2: pure SiO$_2$

$$a(SiO_2) = 1 = \left[\frac{P^\alpha(SiO)}{K}\right]^{0.33}$$

Mo + 3SiO$_2$ = 3SiO + MoO$_3$

Cell 3: SiO$_2$ in silicate

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

$$a(SiO_2) = \left[\frac{I(SiO)}{I(\text{MoO}_3)}\right]^{0.33}$$
\[ Y_2O_3 \cdot (SiO_2) + Y_2O_3 \cdot 2(SiO_2) \]

\[ Yb_2O_3 \cdot (SiO_2) + Yb_2O_3 \cdot 2(SiO_2) \]

<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 \cdot 2(SiO_2) )</td>
<td>0.281</td>
</tr>
<tr>
<td>( Y_2O_3 \cdot (SiO_2) + Y_2O_3 \cdot 2(SiO_2) )</td>
<td>0.194</td>
</tr>
</tbody>
</table>
XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

Yttrium monosilicate + disilicate + Mo

Ytterbium monosilicate + disilicate + Mo

Y$_2$O$_3$.SiO$_2$

Y$_2$O$_3$.2SiO$_2$

Mo

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb$_2$O$_3$.SiO$_2$</td>
<td>56</td>
</tr>
<tr>
<td>Yb$_2$O$_3$.2SiO$_2$</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$_2$

Yb$_2$O$_3$-SiO$_2$
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

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

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

![Graph showing the relationship between log(a(SiO)) and log(P(SiO))]
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>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$.SiO$_2$</td>
<td>41</td>
<td>Yb$_2$O$_3$.SiO$_2$</td>
<td>24</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>49</td>
<td>Yb$_2$O$_3$</td>
<td>66</td>
</tr>
<tr>
<td>Ta</td>
<td>4</td>
<td>Ta</td>
<td>2</td>
</tr>
<tr>
<td>Ta$_3$Si</td>
<td>4</td>
<td>Ta$_2$Si</td>
<td>2</td>
</tr>
</tbody>
</table>
\[ \Delta H_{(SiO_2, \ 1600 \ K)} = (5200.26) \cdot R \cdot 2.303 = 99.57 \text{ kJ/mol} \]

\[ \Delta H_{f, \text{RE silicate, 298 K}} \]

\[ \begin{align*}
\text{Y}_2\text{O}_3 \cdot (\text{SiO}_2) & \quad \Delta H_1 = \text{measured in this work} \\
\text{Yb}_2\text{O}_3 \cdot (\text{SiO}_2) & \quad \Delta H_2 = H_{1600 \ K} - H_{298 \ K} \\
\end{align*} \]
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) SiO$_2$ $\alpha$ (from total flux) = (4.5 ± 1.4) x 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, SiO$_2$
  • 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 SiO$_2$ activity in Rare-earth silicates should limit their reactivity with water vapor
  • Solid State rare earth oxides—activity of SiO$_2$
    • Need reducing agent to obtain a measurable signal for SiO(g), which in turn relates to activity of SiO$_2$. 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)