Experimental Measurement of Vapor Pressure over a Condensed Phase

Direct vaporization:

        Congruent: $Ni(s) = Ni(g)$

        Incongruent: $Mo_3Te_4(s) = 3\ Mo(s) + 2\ Te_2(g)$

Reactive Vaporization: $SiO_2(s) + 2H_2O(g) = Si(OH)_4(g)$
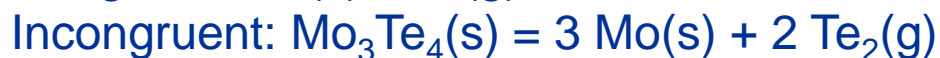
N. Jacobson

August 6, 2013

References

- **Knudsen Effusion**
  - Cater, E. D. (1979) The Effusion Method at Age 69: Current State of the Art. *Characterization of High Temperature Vapors and Gases.* J. W. Hastie, ed. Washington, U. S. Government Printing Office: 3-38.
  - E. H. Copland and N. S. Jacobson, *Measuring Thermodynamic Properties of Metals and Alloys with Knudsen Effusion Mass Spectrometry*, NASA/TP—2010-216795.

- **Transpiration**
  - U. Merten and W. E. Bell (1967), *The Transpiration Method* in The Characterization of High Temperature Vapors, J. L. Margrave, ed., Wiley, New York.
  - N. S. Jacobson, E. J. Opila, D. L. Myers, and E. H. Copland (2005), *Thermodynamics of Gas Phase Species in the Si-O-H System*, J. Chem. Thermodynamics 37, 1130-37.

- **Boundary Layer Limited Vaporization**
  - H. C. Graham and H. H. Davis (1971), *Oxidation/Vaporization Kinetics of Cr_2O_3*, J. Am. Ceram. Soc. 54[2], 89-93.

- **Ambient pressure mass spectrometric sampling**
  - C. A. Stearns, F. J. Kohl, G. C. Fryburg, and R. A. Miller (1977), *A High Pressure Sampling Modulated Molecular Beam Mass Spectrometric Sampling System*, NASA TM 73720.
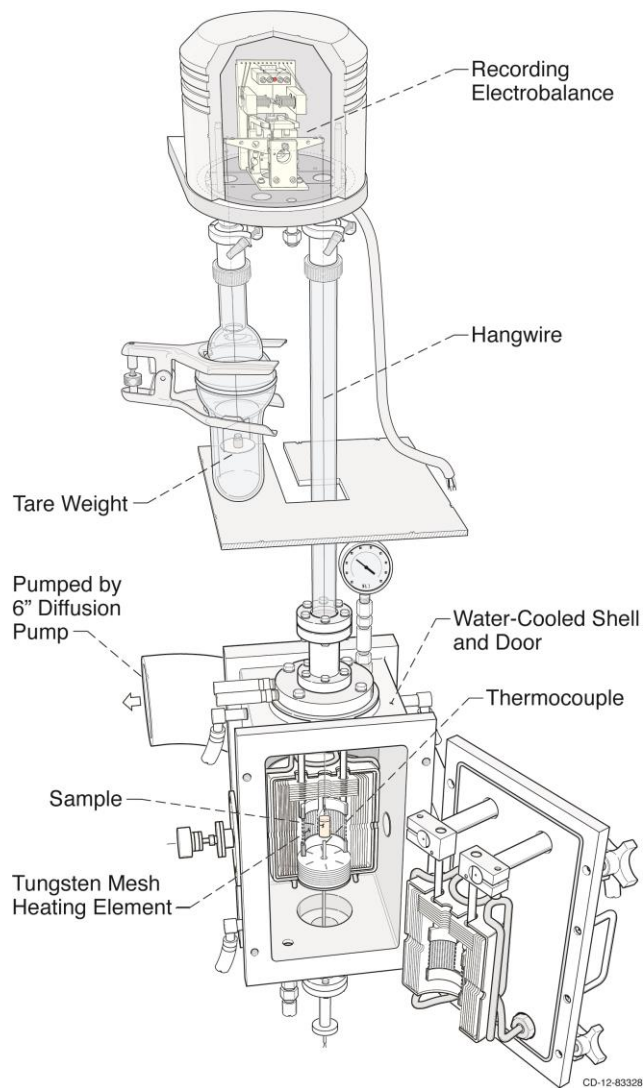
Vapor Pressure/Thermodynamic Parameter Measurements Employed at GRC

- Knudsen cell: Direct Vaporization; some applicability to Reactive Vaporization
  - Vapors flux can be characterized with mass loss, mass spectrometry, target collection, etc.

- Transpiration: Direct Vaporization and Reactive Vaporization

- Boundary Layer Limited Vaporization: Direct Vaporization and Reactive Vaporization

Vacuum Studies are Based on Knudsen Cell
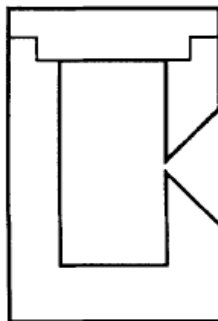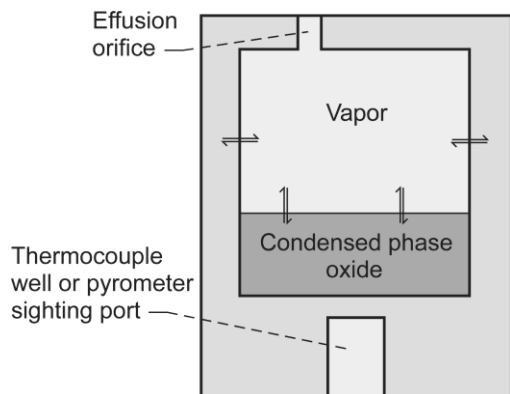
- Typically 1 cm diameter x 1 cm high with a 1 mm orifice

- Cell orifice diameter must be 10X mean free path—only molecule/wall collisions on escape

- Near equilibrium established in cell

- Vapor effusing from orifice leads to a weight loss (measure wt of cell or collect effusate on target) rate which relates to pressure; vapor can also be analyzed with spectrometer

Vacuum Microbalance

- Recording Electrobalance
- Hangwire
- Tare Weight
- Pumped by 6" Diffusion Pump
- Water-Cooled Shell and Door
- Thermocouple
- Sample
- Tungsten Mesh Heating Element

CD-12-83328

Flux (mg/cm^2-sec) to Pressure

$$J = \frac{P}{\sqrt{2\pi MRT}}$$

Range: to 1800C +, 100 gr, $\pm$ 0.1 mg

Temperature Measurement

- Critical parameter for thermodynamic measurements

- High temperature processes are very sensitive to temperature
  $\sim \exp(-E/RT)$

- Accurate methods to measure temperature
  - Thermocouple tightly coupled to sample
  - Pyrometer sighting in black body hole with appropriate corrections

- Frequent calibrations
  - ITS-90: Melting of Au (1337.33K), Ag (1234.93K)

Hertz-Knudsen-Langmuir Equation

M(g)

↑ ↑ ↑ ↑

_____

M
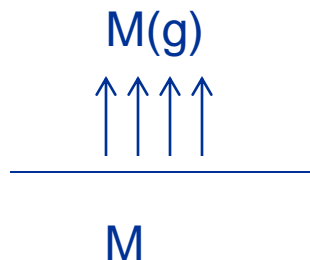
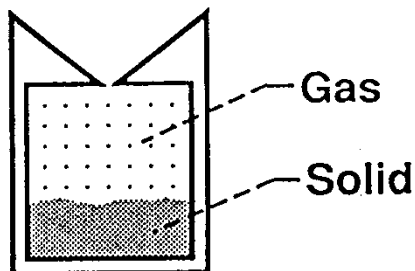- Maximum Flux: Hertz-Knudsen-Langmuir (HKL) Equation

$$J = \frac{P}{\sqrt{2\pi MRT}}$$

- P is in units of force/unit area
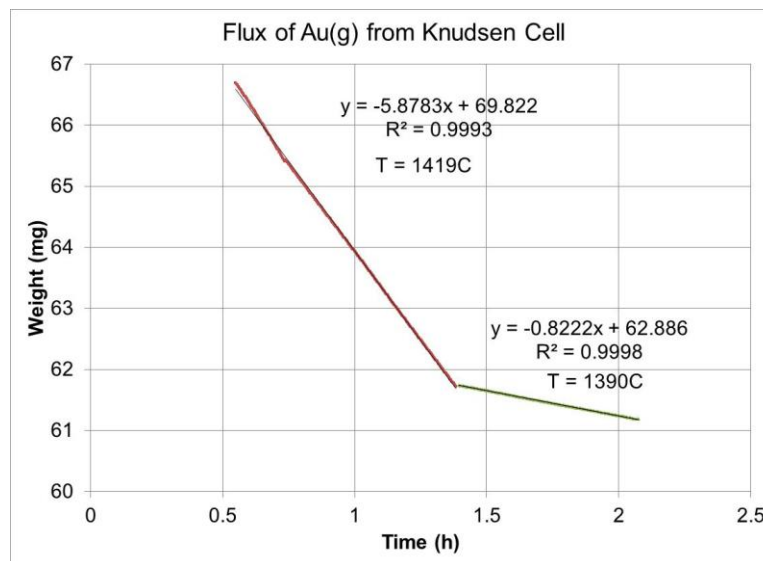
In familiar units:

$$J(\text{mole/cm}^2 - \text{sec}) = \frac{44.32 P(\text{atm})}{\sqrt{M(\text{gm/mole})T(\text{K})}}$$

- Valid only in a vacuum or rapidly moving gas.

Knudsen Cell Method: Sample Vapor in near Equilibrium with Condensed Phase

$$J\,(\text{mole/cm}^2 - \text{sec}) = \frac{44.32\,P(\text{atm})}{\sqrt{M\,(\text{gm/mole})\,T(\text{K})}}$$
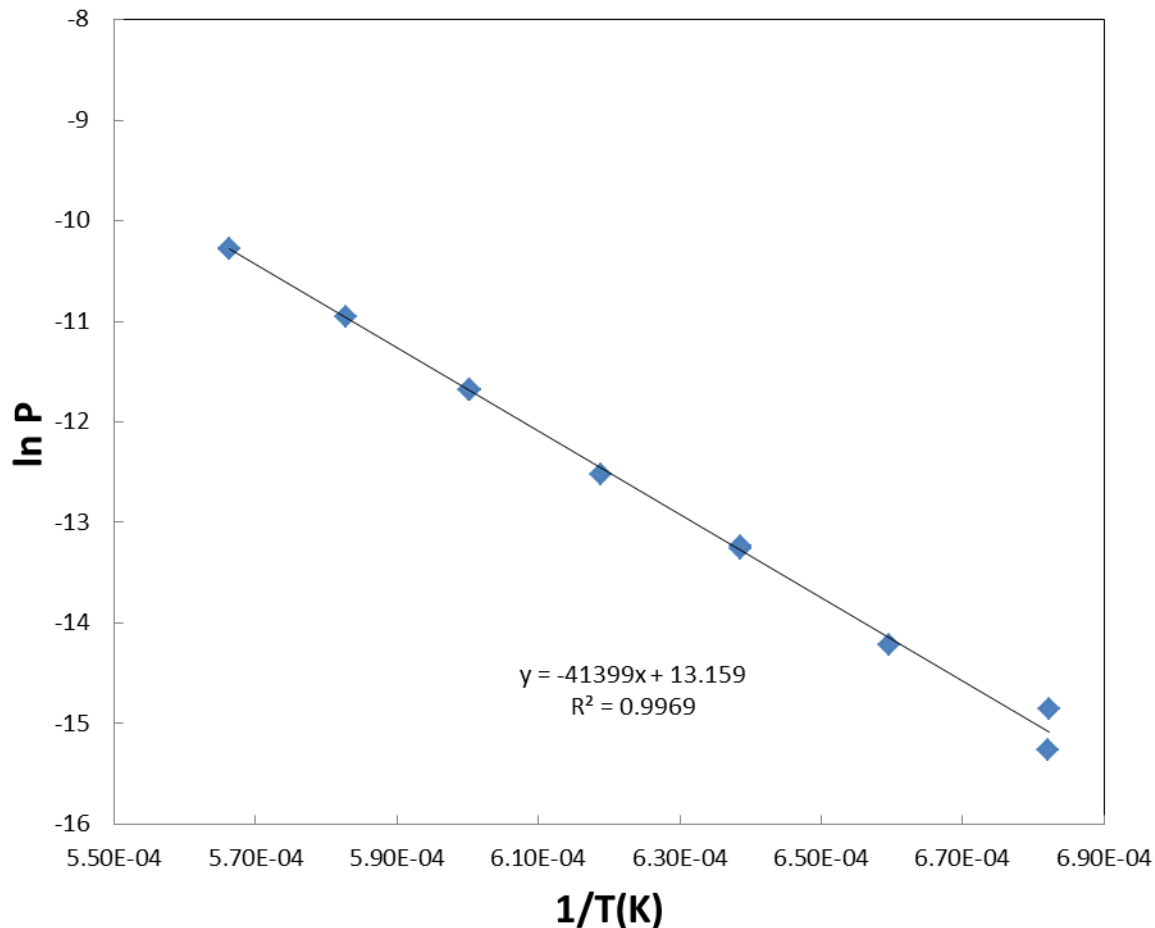
Flux of Au(g) from Knudsen Cell

$y = -5.8783x + 69.822$
$R^2 = 0.9993$
T = 1419C

$y = -0.8222x + 62.886$
$R^2 = 0.9998$
T = 1390C

Take slope and divide by surface area of orifice for Flux

Sample Data from Vacuum Microbalance

Vapor Pressure of Gold vs. 1/T

$$y = -41399x + 13.159$$
$$R^2 = 0.9969$$

$Au(\ell) = Au(g)$

$$\frac{\partial \ln K_p}{\partial\left(\frac{1}{T}\right)} = -\frac{\Delta_V H^o}{R}$$

$\Delta_V H^o$ = -R*(-41.399) =
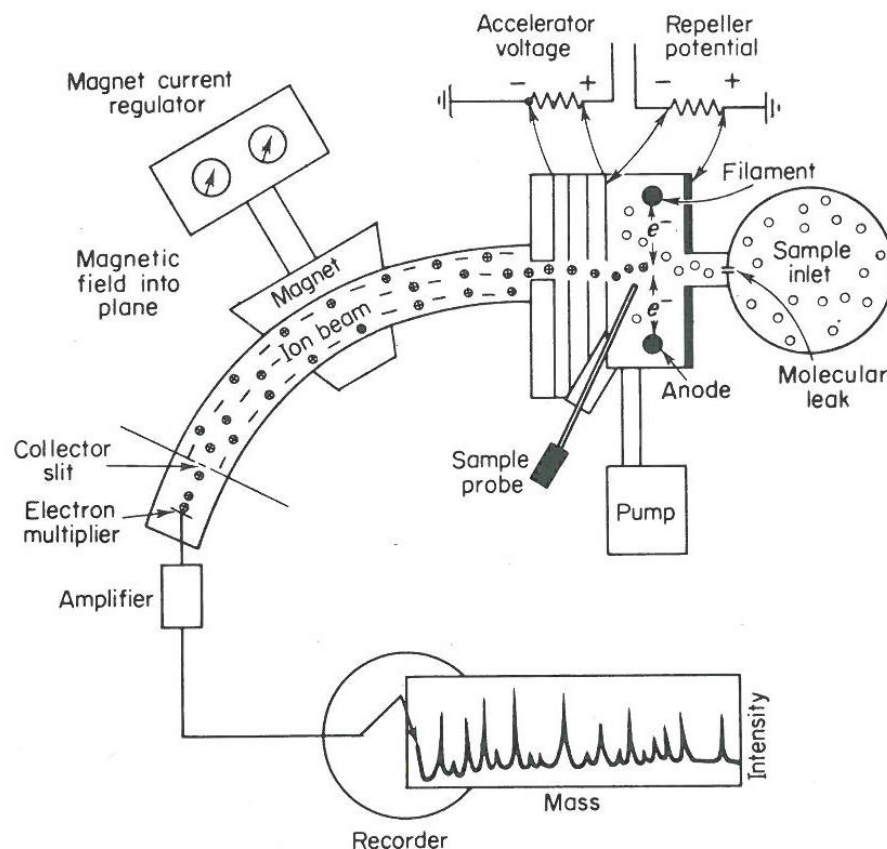
344.19 kJ/mol

Tables = 346.33 kJ/mol

Checks temperature calibration and instrument operation

Glenn Research Center
Knudsen Effusion Mass Spectrometer
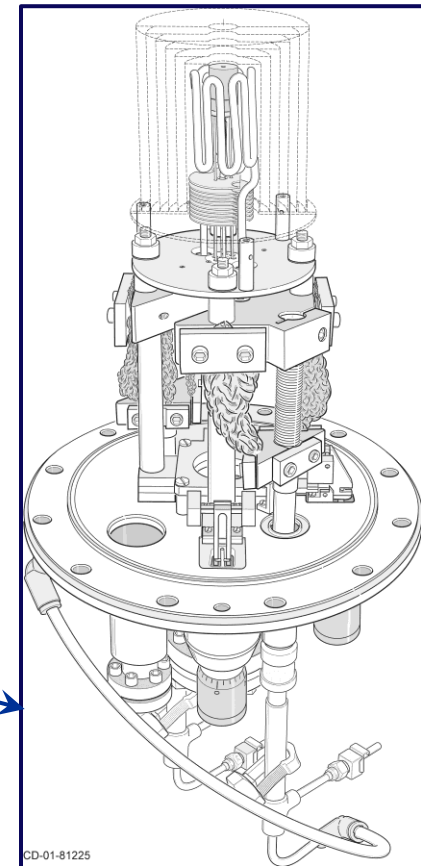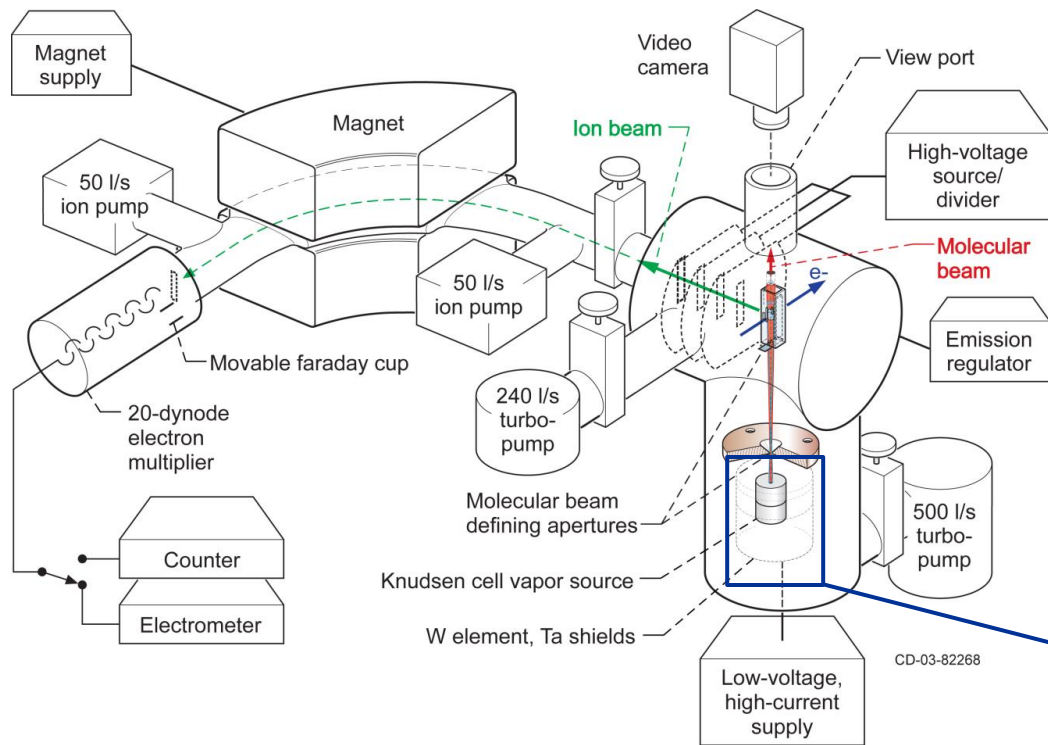
Resistance heated cell; single cell flange for this study
Cross axis electron impact ionizer; 90° magnetic sector; ion counting detector
To 1800C, Pressure to 1 x 10^{-10} bar

Mass Spectrometry: Magnetic Sector

Magnet current regulator

Magnetic field into plane

Magnet

Ion beam

Collector slit

Electron multiplier

Amplifier

Recorder

Accelerator voltage

Repeller potential

Filament

Sample inlet

Molecular leak

Anode

Sample probe

Pump

Mass

Intensity

Positive ions accelerated by Voltage:

$$\tfrac{1}{2} mv^2 = eV$$

Deflected by magnetic field
$$r = mv/eB$$

Relation m/e to B

$$m/e = B^2r^2/2V$$

Advantages:
    Very stable
    High resolution
    No mass discrimination

Disadvantages:
    Large, expensive
    Slow scanning rates

From Pasto and Johnson, Organic Structure Determination

Mass Spectrometry: Quadrupole

Form positive ions—as in Magnetic Sector Instrument

RF voltage and DC voltage applied to four rods

Only one m/e passes through poles at a particular DC voltage: "mass filter"

Advantages:
  Compact
  Less $$ than Magnetic Sector
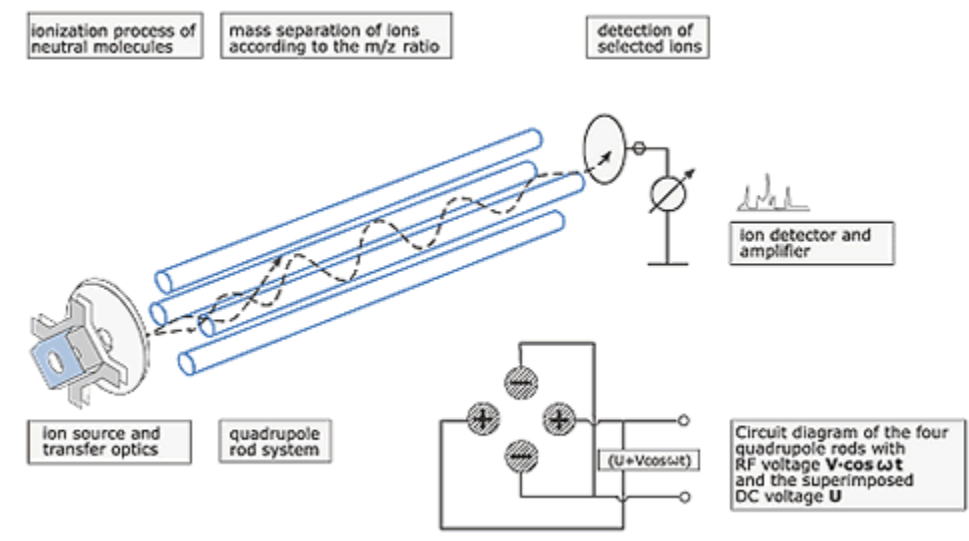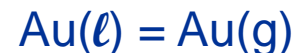 Sensitive
  Rapid Scanning

Disadvantages:
  Lower resolution
  Mass discrimination

| ionization process of neutral molecules | mass separation of ions according to the m/z ratio | | detection of selected ions |

ion detector and amplifier

ion source and transfer optics | quadrupole rod system

Circuit diagram of the four quadrupole rods with RF voltage **V·cos ω t** and the superimposed DC voltage **U**

(U+Vcosωt)

Standard Heat of Vaporization Measurement
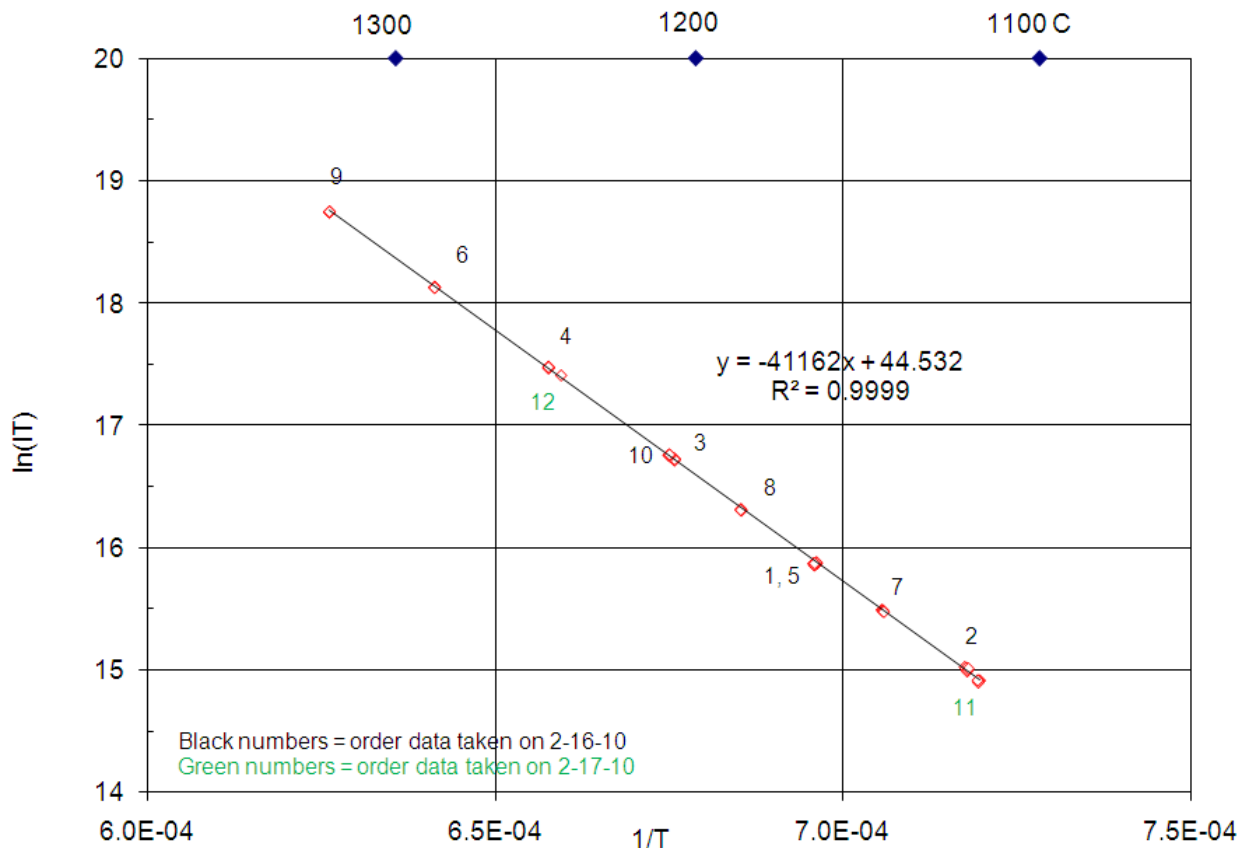

$Au(\ell) = Au(g)$

$P = kIT/\sigma \propto IT$

$$\frac{\partial \ln K_p}{\partial\left(\frac{1}{T}\right)} = \frac{\partial \ln IT}{\partial\left(\frac{1}{T}\right)} = -\frac{\Delta_V H^o}{R}$$

$\Delta_V H^o = -R*(-41.162) =$

342.20 kJ/mol

Tables = 346.33 kJ/mol

Checks temperature calibration and instrument operation
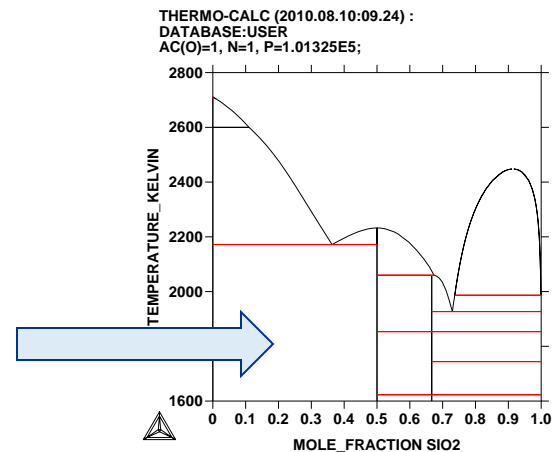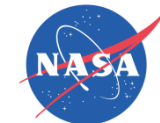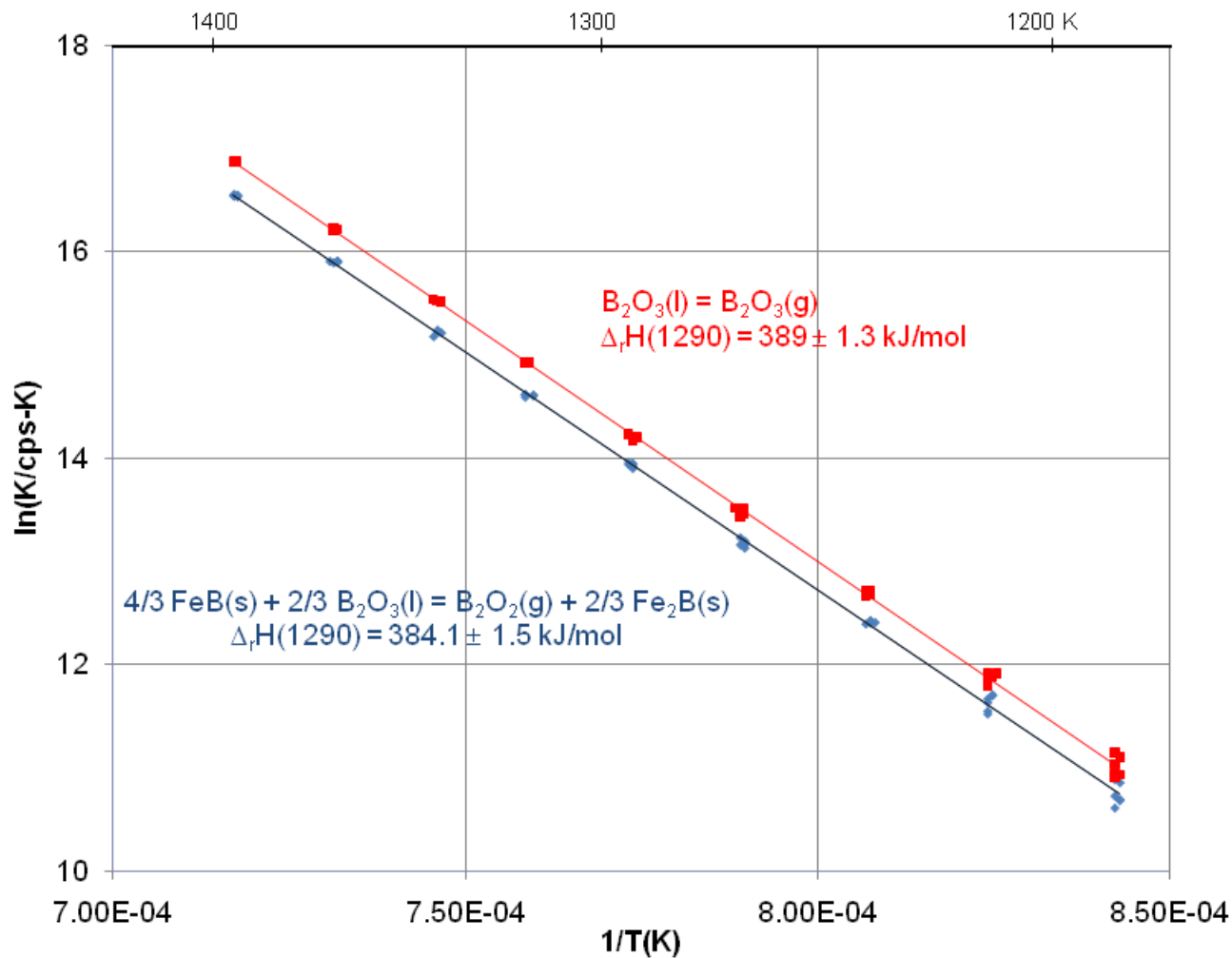
Stable over several days

Recent Studies

- Thermodynamics of vaporization of $B_2O_3(\ell)$ in a reducing atmosphere
    - Integral molar quantity
    - $B_2O_3(\ell) = B_2O_3(g)$
    - $2/3\ B_2O_3(\ell) + 4/3\ FeB(s) = B_2O_2(g) + 2/3\ Fe_2B(s)$
        - Cannot use B—phase separates
        - FeB a convenient reducing agent which mixed well with $B_2O_3(l)$

- Thermodynamics of a rare earth silicates
    - Partial molar quantity
    - Need to know the thermodynamic activity of silica in the Y_2O_3-Y_2SiO_5 two phase field.
    - Measurement of partial molar quantity.

THERMO-CALC (2010.08.10:09.24) :
DATABASE:USER
AC(O)=1, N=1, P=1.01325E5;

1:1:1 FeB:Fe$_2$B:B$_2$O$_3$ Mixture

$B_2O_3(l) = B_2O_3(g)$
$\Delta_r H(1290) = 389 \pm 1.3$ kJ/mol

$4/3\ FeB(s) + 2/3\ B_2O_3(l) = B_2O_2(g) + 2/3\ Fe_2B(s)$
$\Delta_r H(1290) = 384.1 \pm 1.5$ kJ/mol

Analysis of Data: Determine $\Delta_r H^o_{29815}$

- ' Σ Plot' method [Cubicciotti]

$$\Delta\left\{-(gef_{29815})\right\} - R\ln(I(i)T) = A + B/T$$

$$gef_{29815} = (G^o_T - H^o_{29815})/T$$

  – Plot $\Delta\left\{-(gef_{298.15})\right\} - R\ln(I(i)T) \; vs \; 1/T \quad Slope = \Delta_r H^o_{298.15}$

- 'Third Law' method

  – $T\left[\Delta\{-(gef_{29815})\} - R\ln(K)\right] = \Delta_r H^o_{29815}$

  – Obtain $\Delta_r H^o_{29815}$ for each temperature

- Use experimental Gibbs Energy Functions (gef) [JANAF]—preferred over calculated (ab initio methods)

$B_2O_3(g)$ Results: Extract $\Delta_f H^o_{29815}(B_2O_3)$

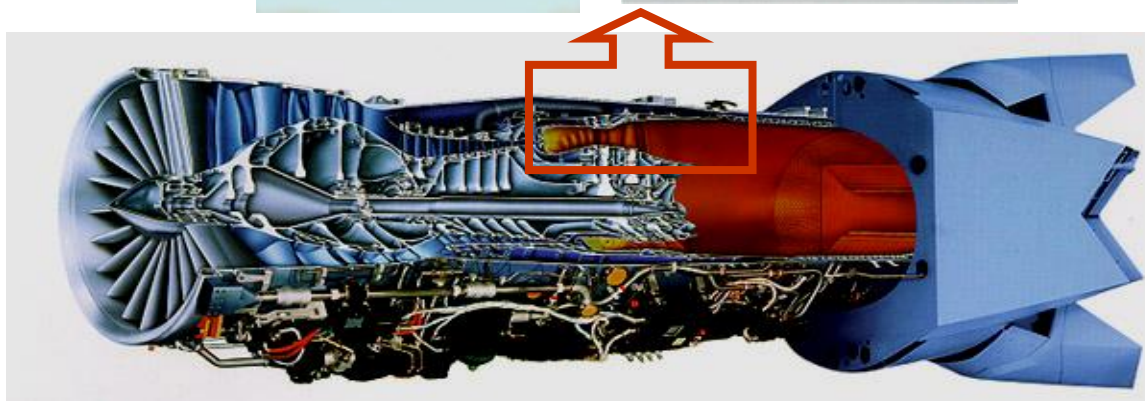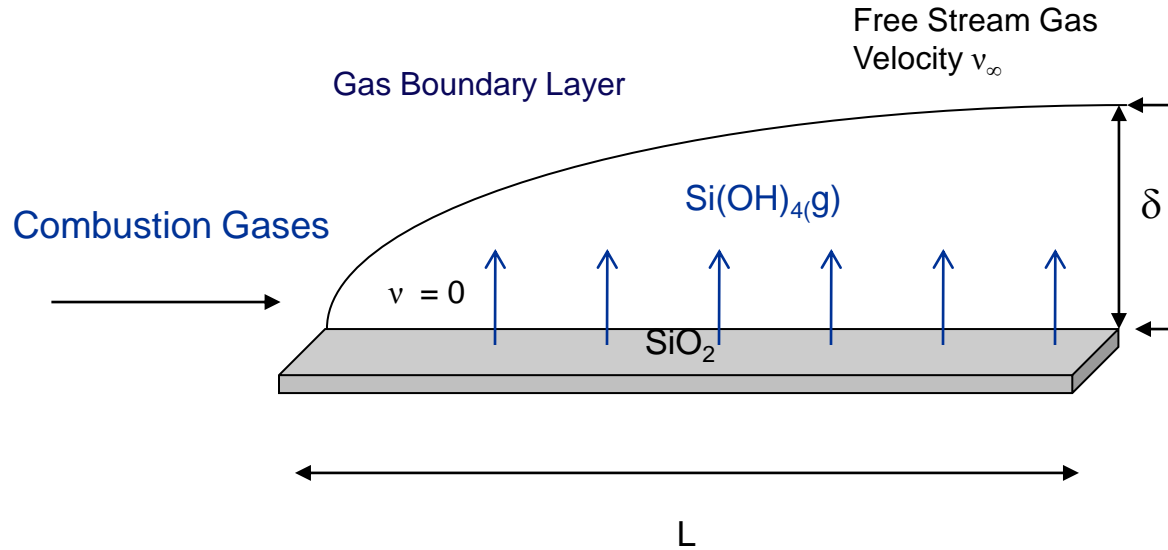| Selected Studies Investigator/method and reaction	$\Delta_f H^o_{29815}$ kJ/mol—2nd Law	$\Delta_f H^o_{29815}$ kJ/mol—3rd Law	$\Delta_f H^o_{29815}$
Hildenbrand (Torsion) et al [1963] $B_2O_3(l) = B_2O_3(g)$	-825.9	-836.0	
Scheer (Torsion) [1957] $B_2O_3(l) = B_2O_3(g)$	-848.2	-829.2	
Shultz et al. (KEMS/Weight loss) [1978] $B_2O_3(l) = B_2O_3(g)$	-841.3 ± 8.8	-837.9 ± 2.5	
Nguyen et al. (ab initio) [2009] $B_2O_3(g) = 3B(g, doublet) + 2O(g, triplet)$			-830.1
This study (KEMS) [2011] $B_2O_3(l) = B_2O_3(g)$	-843.3 ± 6.6	-823.6 ± 1.0	
This study (ab initio) [2011] $B_2O_3(g) = 3B(g, doublet) + 2O(g, triplet)$			-857.4 ± 17.2
This study (ab initio) [2011] $B_2O_3(g) + 6HF(g) = 2BF_3(g) + 2H_2O(g)$			-831.8 ± 5.3

Within 20 kJ/mol ~ 2% of 840 kJ/mol

$B_2O_2(g)$ Results: Extract $\Delta_f H^o_{298.15}\left(B_2O_2\right)$

Investigator/method and reaction	$\Delta_f H^o_{298.15}$ kJ/mol—2nd Law	$\Delta_f H^o_{298.15}$ kJ/mol—3rd Law	$\Delta_f H^o_{298.15}$
Inghram (KEMS) [1956] $2/3\ B + 2/3\ B_2O_3(l) = B_2O_2(g)$	-509.4	-444.1	
Inghram (KEMS) [1956] $2/3\ B + 2/3\ B_2O_3(g) = B_2O_2(g)$	-455.2	-458.7	
Scheer (Torsion) [1958] $2/3\ B + 2/3\ B_2O_3(l) = B_2O_2(g)$	-428.6	-462.9	
Rentzepis et al. (Collection) [1960] $C(s) + B_2O_3(l) = B_2O_2(g) + CO(g)$		-466.2	
Searcy and Myers [1957] $2MgO(s) + 2B(s) = 2Mg(g) + B_2O_2(g)$		-458.9	
Nguyen et al. (ab initio) [2009] $B_2O_2(g) = 2B(g,\ doublet) + 2O(g,\ triplet)$			-457.7
This study (KEMS) [2011] $4/3\ FeB(s) + 2/3\ B_2O_3(l) = B_2O_2(g) + 2/3\ Fe_2B(s)$	-484.8 ± 25.7	-474.6 ± 25.7	
This study (ab initio) [2011] $B_2O_2(g) = 2B(g,\ doublet) + 2O(g,\ triplet)$			-479.9 ± 17.2
This study (ab initio) [2011] $B_2O_2(g) + 6HF(g) = 2BF_3(g) + 2H_2O(g) + H_2(g)$			-456.7 ± 5.3

Measurement of Silica Activity in Coating Materials: Rare Earth Silicates

Boundary Layer Limited Gas Transport:
Model Silica Ceramic Degradation (Opila)

Free Stream Gas Velocity v_∞

Gas Boundary Layer

$Si(OH)_4(g)$

δ

Combustion Gases

$v = 0$

SiO_2

L

$$\text{Flux of Vapor Species (i)} = 0.664 \left(\text{Re}\right)^{0.5} \left(Sc\right)^{0.33} \frac{D_i P_i}{R T L}$$
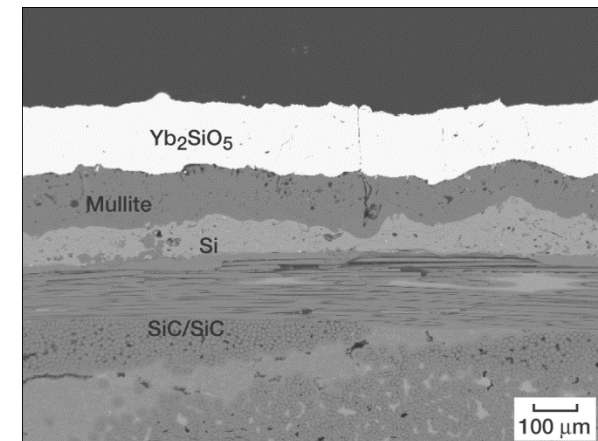
$$= 0.664 \left(\frac{v_\infty \rho_\infty L}{\eta}\right)^{0.5} \left(\frac{\eta}{D_i \rho_\infty}\right)^{0.33} \frac{D_i P_i}{R T L}$$

Laminar Flow, Expression for turbulent flow similar

Fluid parameters

Key Parameters in Boundary Layer Limited Transport Modeling

- $\underline{SiO_2}$(pure or in silicate soln) + 2 H_2O(g) = $Si(OH)_4$(g)

- Combustion environment—always 10-15% water vapor

$$K = \frac{P_{Si(OH)_4}}{a_{SiO_2}\left(P_{H_2O}\right)^2}$$

$$a_{SiO_2} = \frac{P_{SiO_2}}{P^o_{SiO_2}}$$

$$Flux = 0.664\left(\frac{v_\infty \rho_\infty L}{\eta}\right)^{0.5}\left(\frac{\eta}{D_{Si(OH)_4}\rho_\infty}\right)^{0.33}\frac{D_{Si(OH)_4}P_{Si(OH)_4}}{RTL} =$$

$$0.664\left(\frac{v_\infty \rho_\infty L}{\eta}\right)^{0.5}\left(\frac{\eta}{D_{Si(OH)_4}\rho_\infty}\right)^{0.33}\frac{D_{Si(OH)_4}}{RTL}K\,a_{SiO_2}\left(P_{H_2O}\right)^2$$

- Critical parameters to know are equilibrium constant for hydroxide formation and **activity of SiO$_2$**

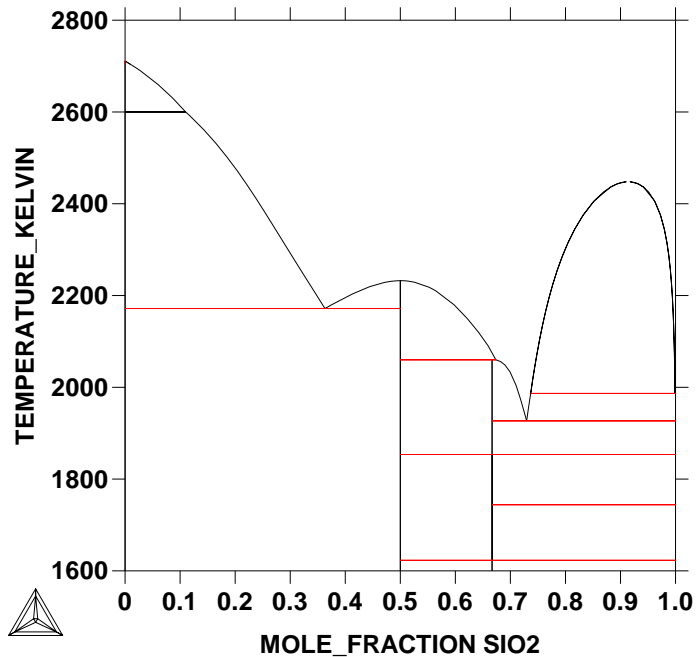- Either eliminate SiO$_2$ or reduce its activity

Environmental Barrier Coatings (EBCs) Developed for Low Thermodynamic Activity of SiO_2 (K. Lee)

- Mullite: Lower than pure silica, but not low enough

- Ba-Sr-aluminosilicate: Low silica activity
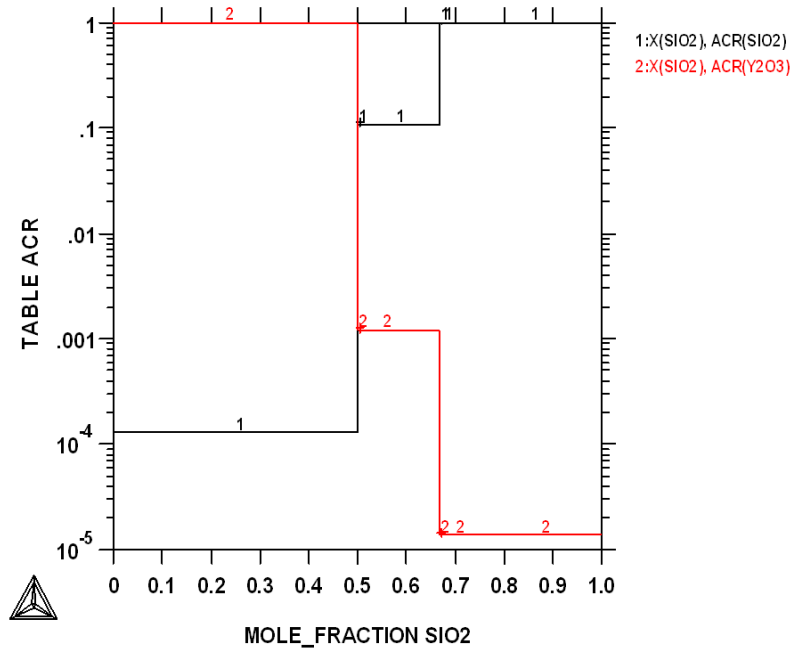
- Rare earth silicates: Low silica activity

Calculated Y_2O_3-SiO_2 Phase Diagram: Fabrichnaya-Seifert Database

THERMO-CALC (2010.08.10:09.24) :
DATABASE:USER
AC(O)=1, N=1, P=1.01325E5;

THERMO-CALC (2010.08.10:11.43) :
DATABASE:USER
AC(O)=1, T=1600, P=1.01325E5, N=1;

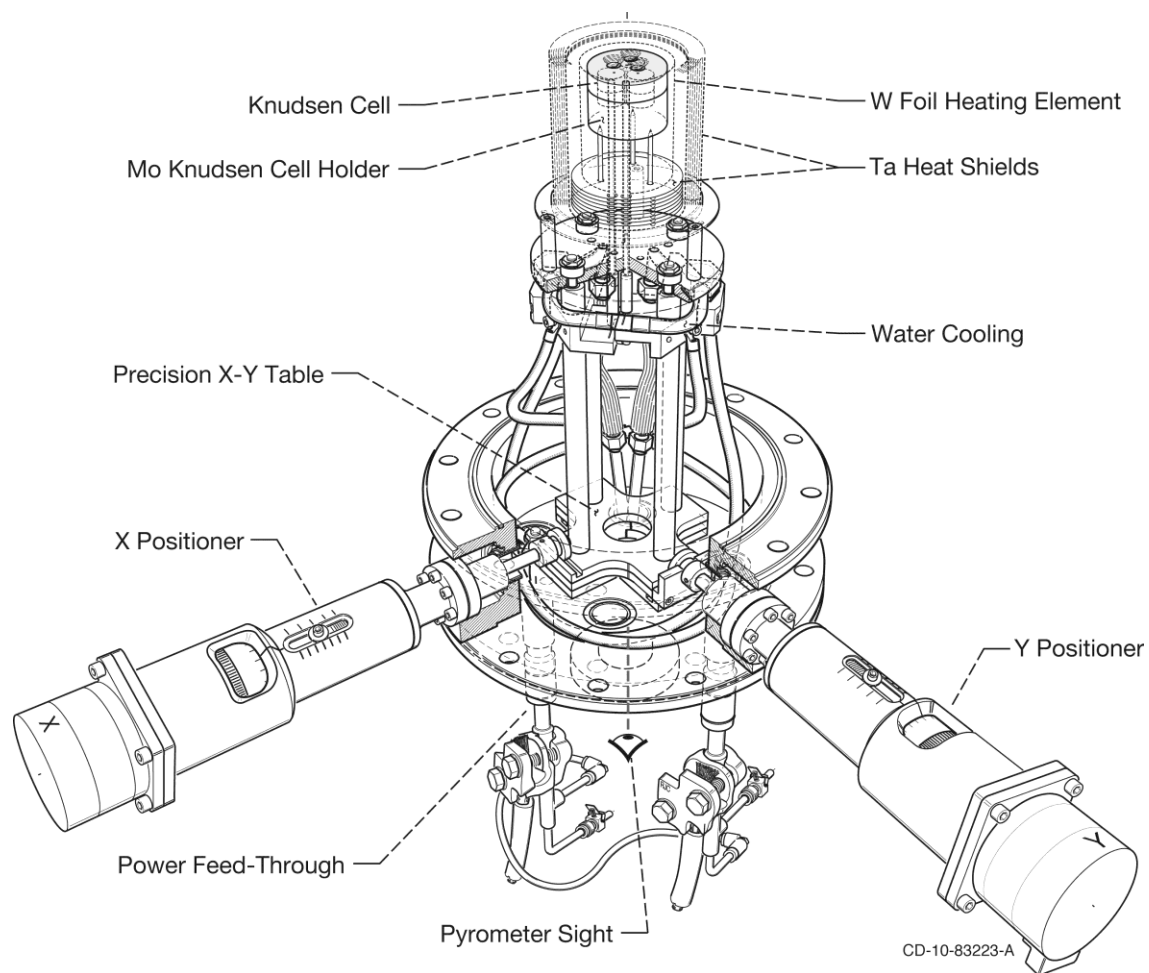1:X(SIO2), ACR(SIO2)
2:X(SIO2), ACR(Y2O3)

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

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. Tried several, selected Ta
  - Reaction depends on a(SiO_2) (underline indicates a(SiO_2) < 1)
    - $Ta + 2\underline{SiO_2} = 2SiO(g) + TaO_2(g)$

- Excess $Ta + Y_2O_3\text{-}Y_2SiO_5 + Y_2O_3$
  - Use Ta cell

- Non-equilibrium vaporization: Need to account for this with the Whitman-Motzfeld extrapolation to zero orifice size

Use Multi-Cell Flange for a(SiO$_2$)

Knudsen Cell

Mo Knudsen Cell Holder

W Foil Heating Element

Ta Heat Shields

Water Cooling

Precision X-Y Table

X Positioner

Y Positioner
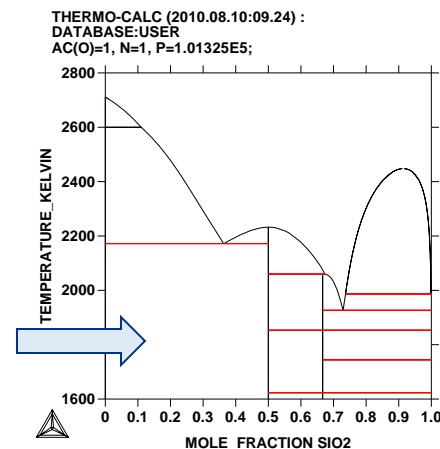
Power Feed-Through

Pyrometer Sight

CD-10-83223-A

- Three cells, computer controlled positioning in x-y plane

- Internal temperature calibration

- Internal standard

- Frequent re-calibration, if needed
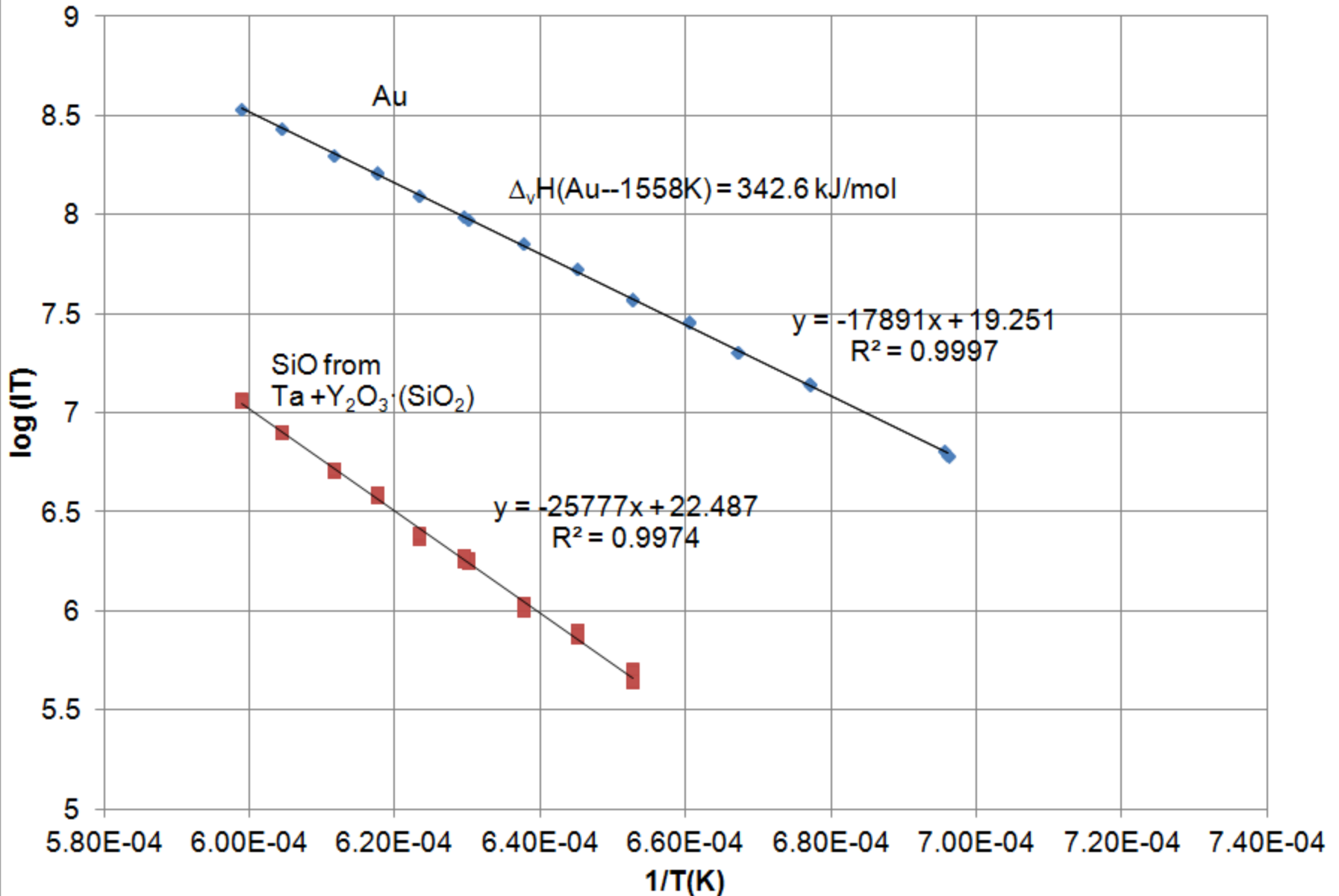
Design of E. Copland 2002

Approach

- Two cells:
  - One with Au
  - One with $3Ta + Y_2O_3 + Y_2O_3 \cdot SiO_2$

- Based on
  - $Ta + 2\underline{SiO_2} = 2SiO(g) + TaO_2(g)$

- Measure I(SiO)—convert to P(SiO)
  - $P = kIT/\sigma$ k from Au melting point
  - Need a good σ(SiO)

- Extrapolate to zero orifice size—obtain P_{eq}(SiO)

- Using P_{eq}(SiO) and FactSage (free energy minimization) calculation--determine $a(SiO_2)$ from above reaction
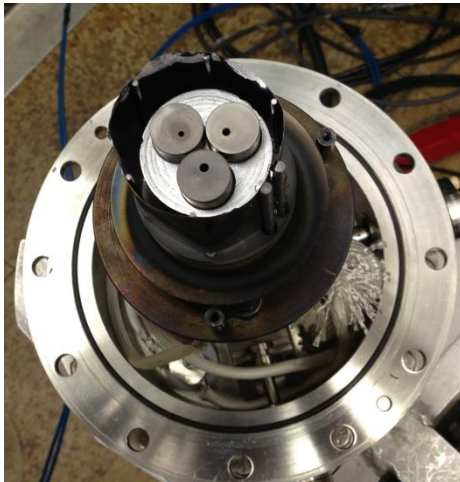
THERMO-CALC (2010.08.10:09.24) :
DATABASE:USER
AC(O)=1, N=1, P=1.01325E5;

Cell 1: Au   Cell 2:Ta + $Y_2O_3 \cdot (SiO_2)$ + Y_2O_3
1-31-12 to 2-3-12

(Raw Data)

Au

$\Delta_v H(Au\text{--}1558K) = 342.6\,kJ/mol$

$y = -17891x + 19.251$
$R^2 = 0.9997$

SiO from
Ta + $Y_2O_3 \cdot (SiO_2)$

$y = -25777x + 22.487$
$R^2 = 0.9974$

y-axis: **log (IT)**
x-axis: **1/T(K)**

Need to Correct for Non-equilibrium Vaporization

- For a Knudsen cell, apply Whitman-Motzfeld extrapolation to zero-orifice size
  - Measure vapor fluxes at different orifice sizes and extrapolate to zero-orifice size
  - Rate of vaporization = rate of effusion from orifice + rate of condensation
    - Derive

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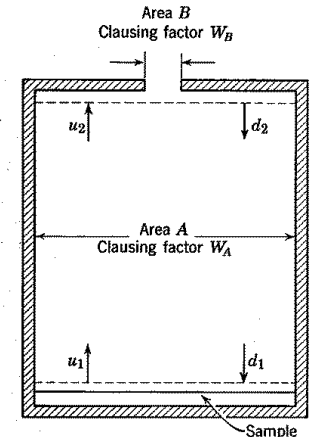
P_m = Measured pressure

P_{eq} = Equilibrium pressure

$f = W_B B/A$

α = evaporation coefficient
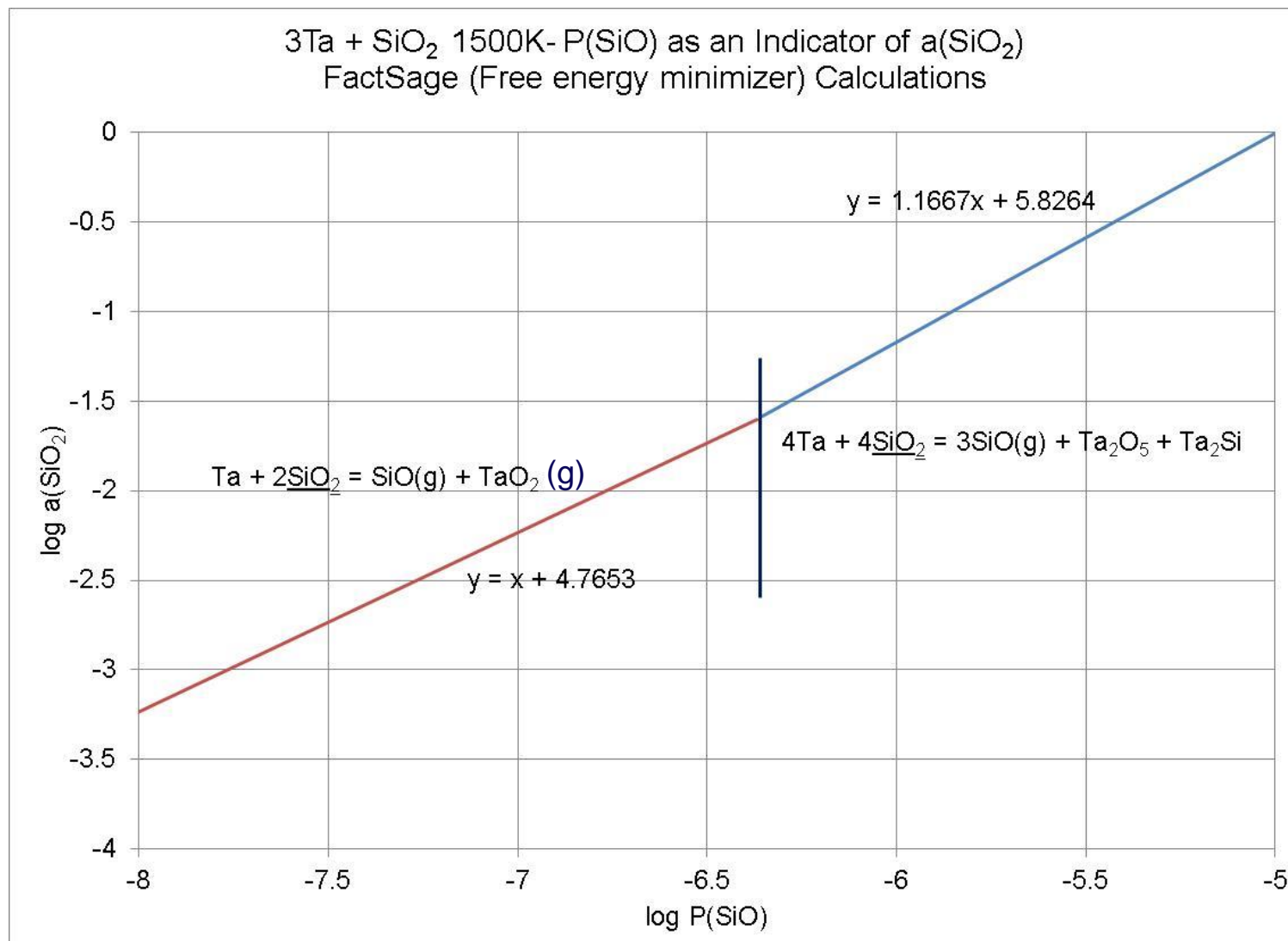
$$P_{measured} = \alpha \, P_{equilibrium}$$
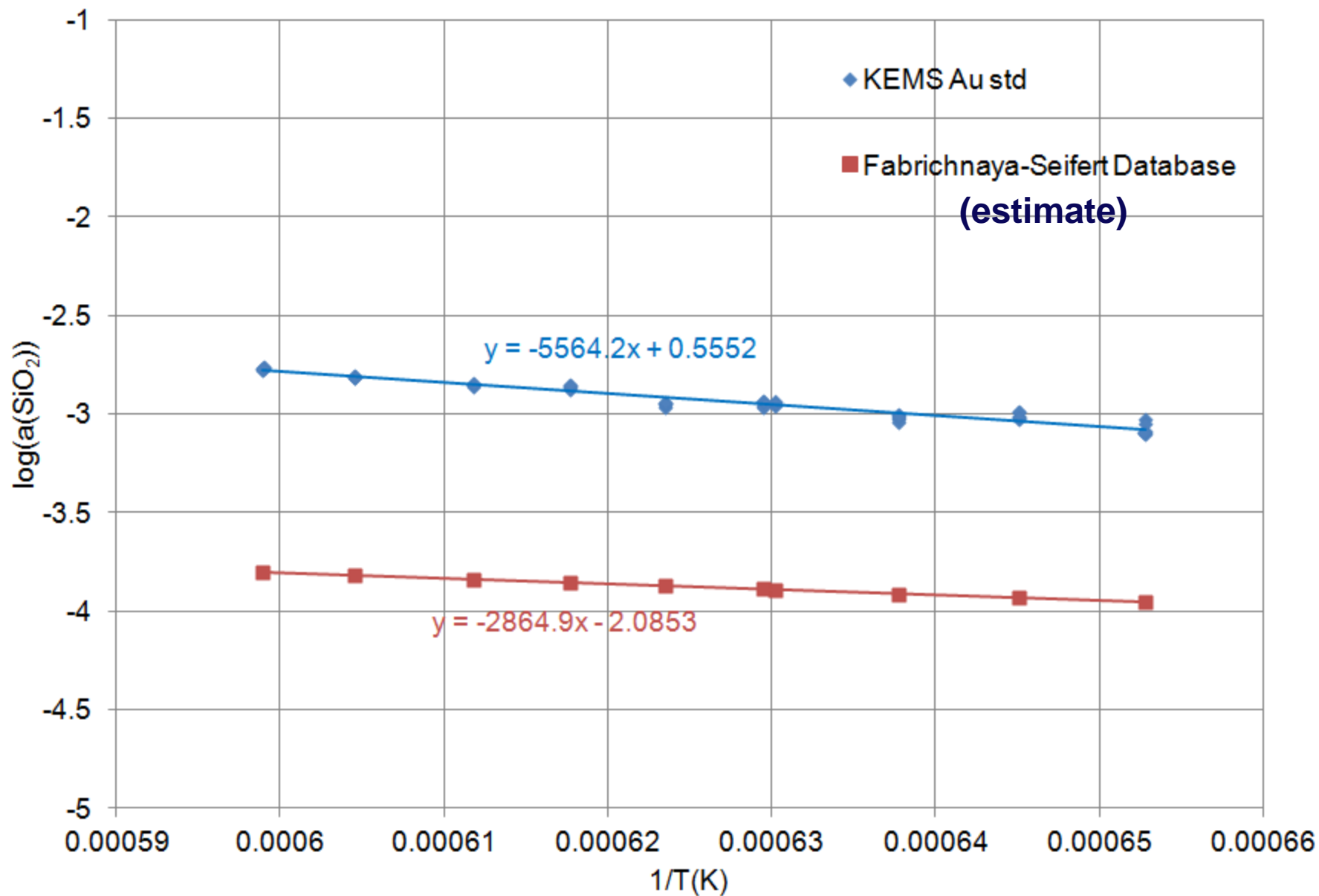
$$For\ oxides\ \alpha = 10^{-3} - 0.5\,(Searcy)$$
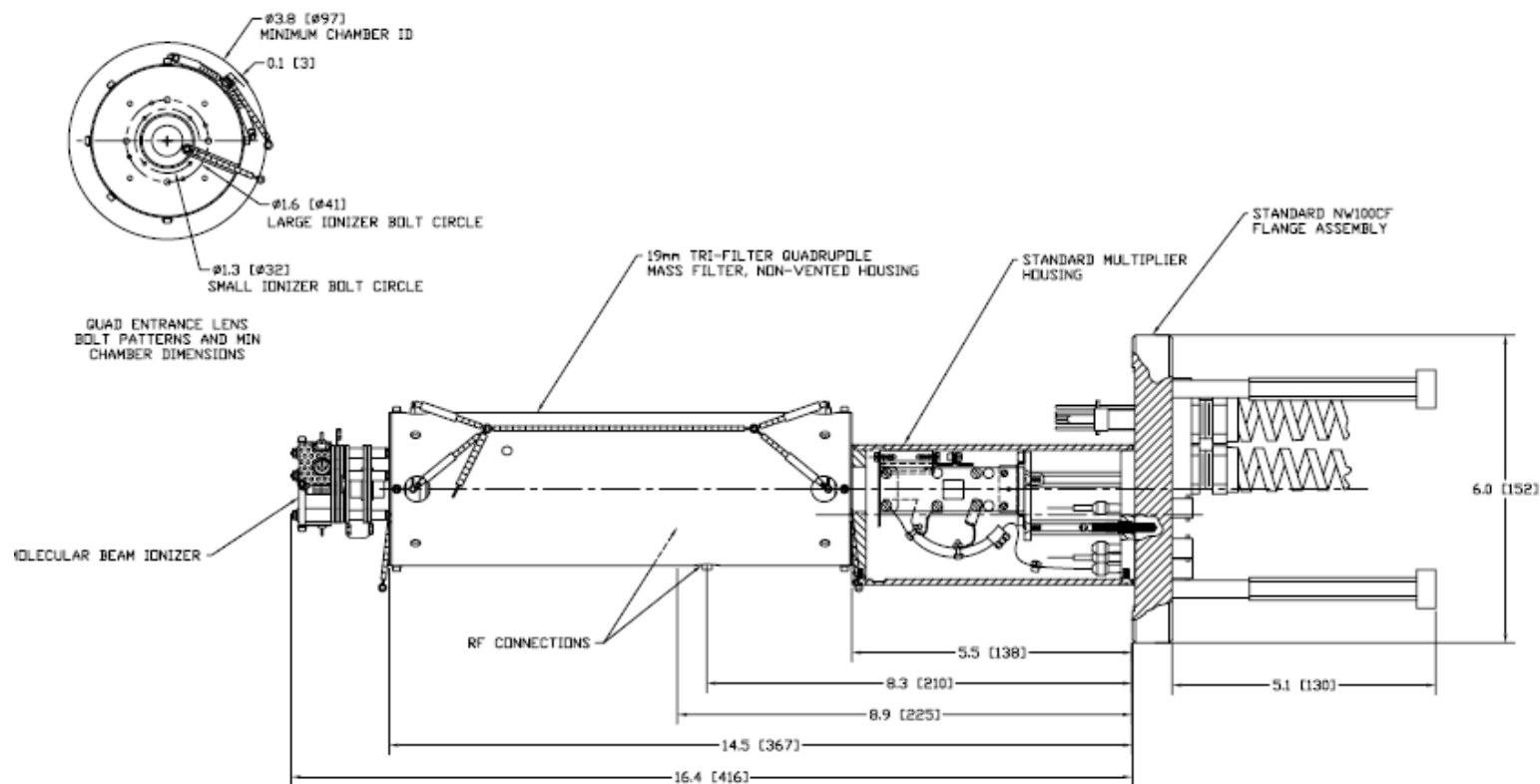
- Plot P_m vs $P_m f \Rightarrow$ intercept is P_{eq}

Calibration Curve for P(SiO) as an Indicator of Silica Activity

3Ta + SiO$_2$ 1500K - P(SiO) as an Indicator of a(SiO$_2$)
FactSage (Free energy minimizer) Calculations

$y = 1.1667x + 5.8264$

$4Ta + 4\underline{Si}O_2 = 3SiO(g) + Ta_2O_5 + Ta_2Si$

$Ta + 2\underline{Si}O_2 = SiO(g) + TaO_2$ (g)

$y = x + 4.7653$

log a(SiO$_2$)

log P(SiO)

Activity of SiO$_2$ for [(Y$_2$O$_3$).(SiO$_2$) + Y$_2$O$_3$] as f(1/T)

◆ KEMS Au std

■ Fabrichnaya-Seifert Database

(estimate)

y = -5564.2x + 0.5552

y = -2864.9x - 2.0853
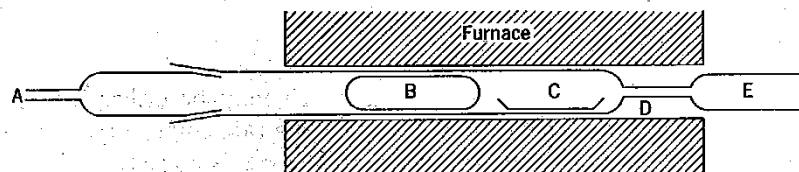
Building New KEMS Instrument with Extrel Quad

- Use existing KEMS flanges/furnaces
- On axis ionizer—maximum sensitivity
- Advantages of Quad—sensitivity, rapid mass scans
- Disadvantages of Quad—mass discrimination effects, lower resolution
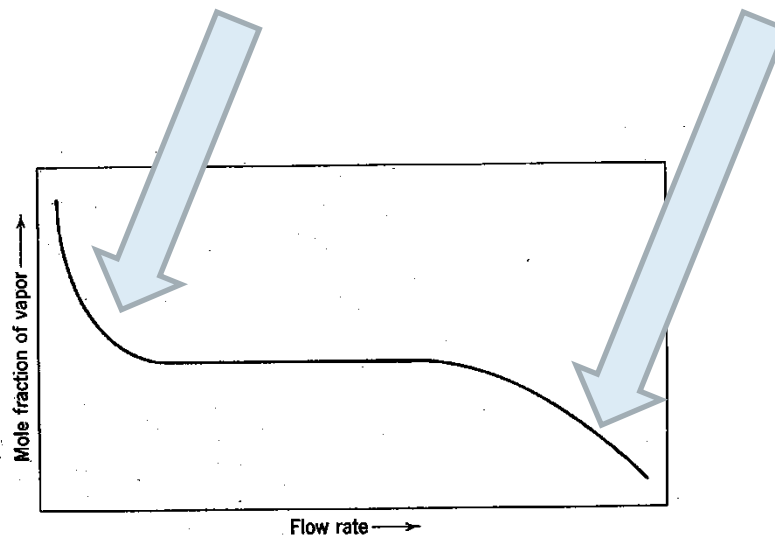
Many Applications of Knudsen Cells

- Analysis of vapor composition

- Thermodynamic data

- Thermodynamic activity in solutions

- Phase changes

- Isotope measurements

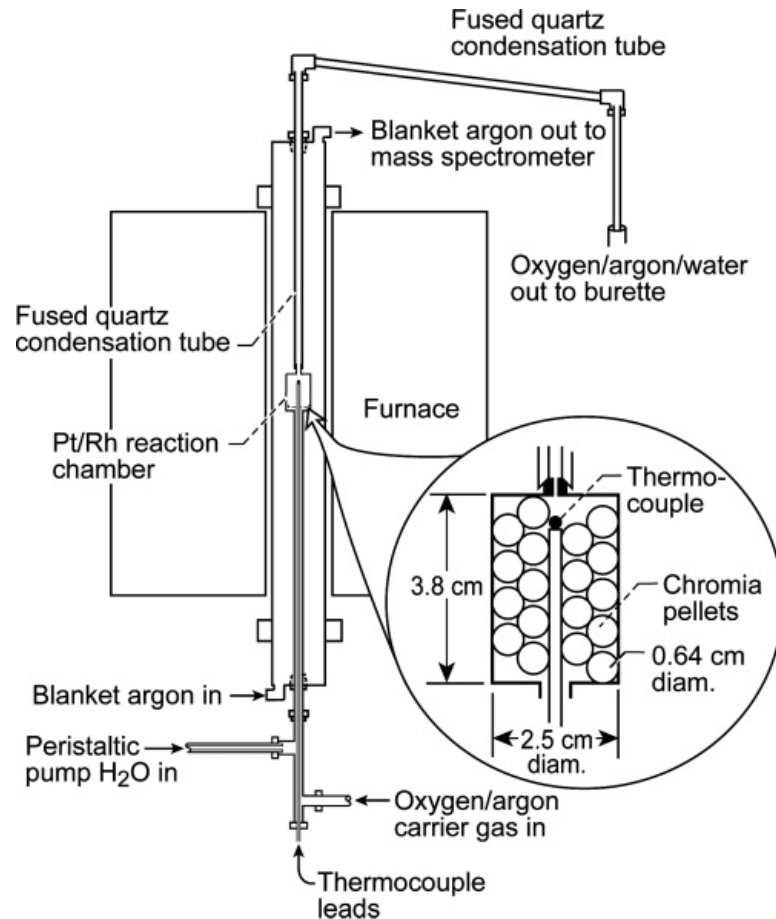- Gas leak cell for (low pressure) reactive vaporization

Transpiration

Gas mixture enters point A
Reacts with solid at C
Products collected and analyzed at E
B & D—constraints to minimize diffusion
and heat loss

Select Flow Rates and Design System to Avoid
Diffusion Limitation and Kinetic Limitation

GRC Transpiration System

$$\dot{n}(Ar) = P_1\dot{V}_1 / RT_1 \quad \text{(Point 1 Ar Inlet)}$$

$$\dot{V}_2 = RT_2(\dot{n}(H_2O) + \dot{n}(Ar)) / P_2 \quad \text{(Point 2 } H_2O \text{ inlet)}$$

$$\dot{V}_3 = RT_3(\dot{n}(H_2O) + \dot{n}(Ar) + \dot{n}(Si)) / P_3 \quad \text{(Point 3 reaction cell)}$$

$$\dot{n}(Si) << (\dot{n}(H_2O) + \dot{n}(Ar)) \quad \dot{V}_3 = \dot{V}_2$$

$$P(Si) / P(T) = \dot{n}(Si) /(\dot{n}(H_2O) + \dot{n}(Ar) + \dot{n}(Si)) = \dot{n}(Si)RT_3 / \dot{V}_3 P_3$$

- Calculate dn(Si)/dt from Si collected $\Rightarrow$ pressure of Si species
- Dependence on water vapor pressure and oxygen pressure gives identity of species
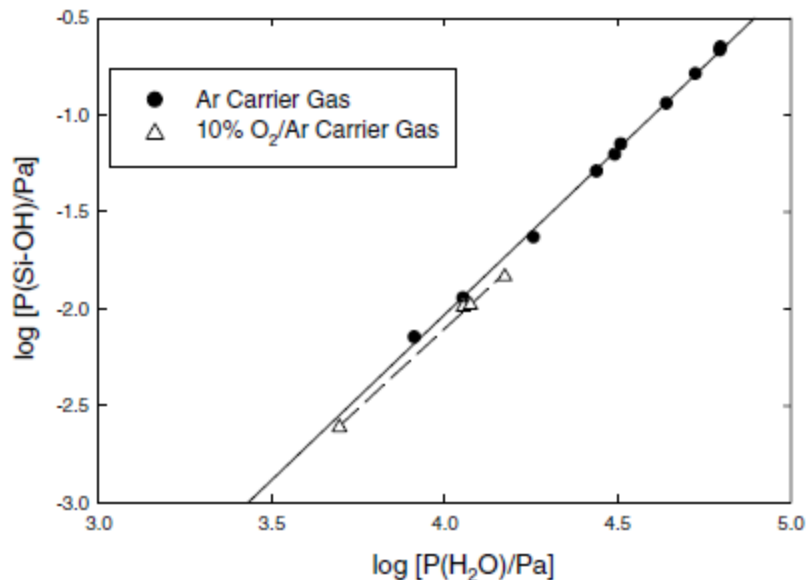
Data for $Si(OH)_4(g)$

FIGURE 4. Plot of the pressure of the Si-containing species against the water vapor at $T = 1673$ K. The solid line is for data taken with an Ar carrier gas and has a slope of (1.71 ± 0.02). The dashed line is for data taken with a 10% O_2–Ar carrier gas and has a slope of (1.65 ± 0.06).
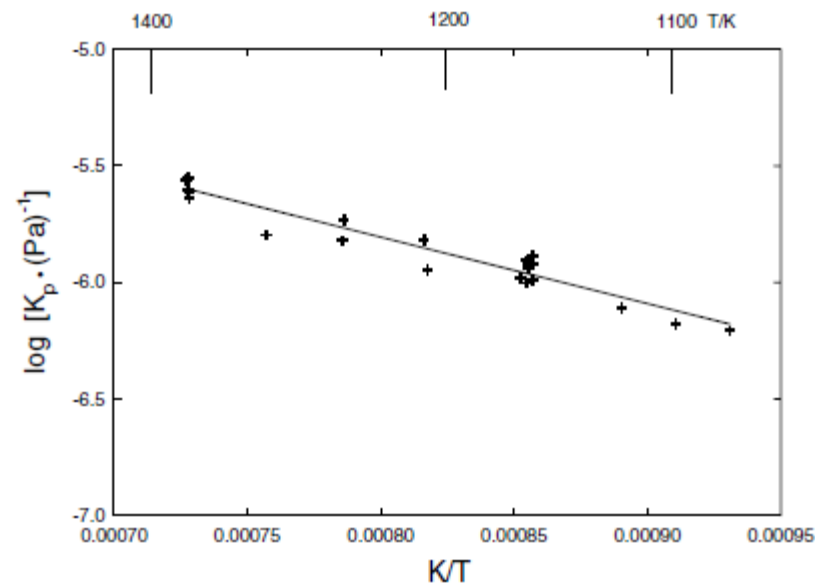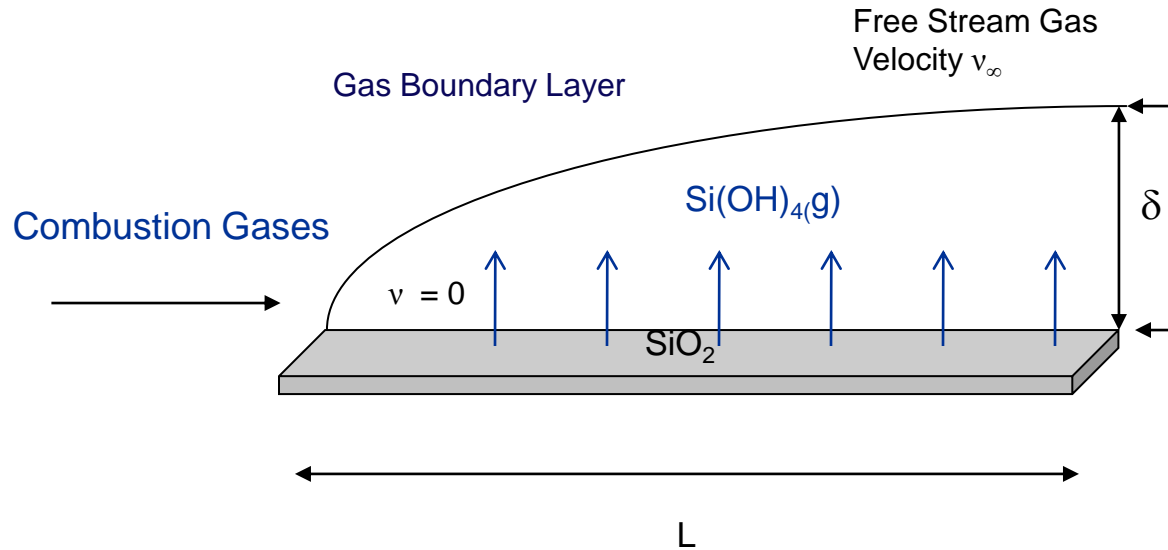
FIGURE 5. Plot of equilibrium constant for the reaction $SiO_2(cr) + 2\text{-}H_2O(g) = Si(OH)_4(g)$ as $\lg K_p$ against reciprocal temperature for $T < 1375$ K. The second law enthalpy derived from this plot is $\Delta_r H^\circ(1200\ \text{K}) = (54.6 \pm 2.7)\ \text{kJ} \cdot \text{mol}^{-1}$ and entropy change is $\Delta_r S^\circ(1200\ \text{K}) = (-67.5 \pm 2.1)\ \text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

Boundary Layer Limited Vaporization

- Useful for direct and reactive vaporization

- Have intentional, but known, diffusion limited vaporization

- Useful for approximate vapor pressures, but not accurate thermodynamic data
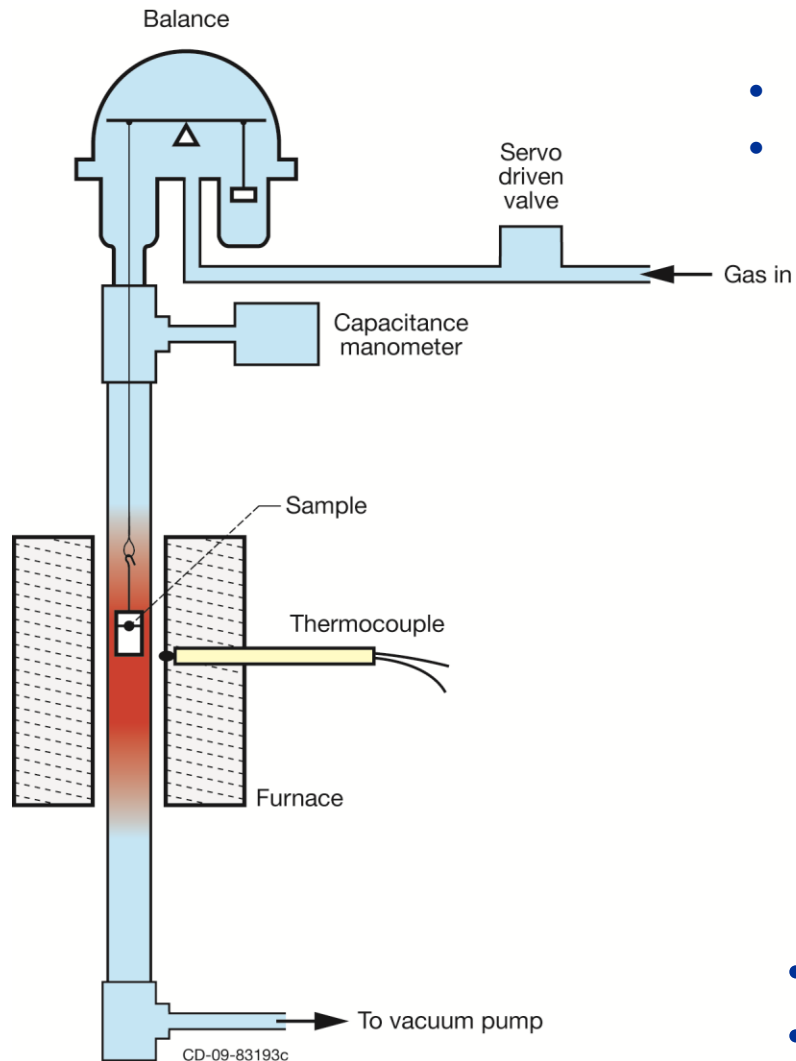
- Encountered in most applications

Boundary Layer Limited Gas Transport:
Model Silica Ceramic Degradation

Free Stream Gas
Velocity v_∞

Gas Boundary Layer

$Si(OH)_{4}(g)$

δ

Combustion Gases

$v = 0$

SiO_2

L

$$\text{Flux of Vapor Species i} = 0.664 \left(\text{Re}\right)^{0.5} \left(Sc\right)^{0.33} \frac{D_i P_i}{RT\,L}$$
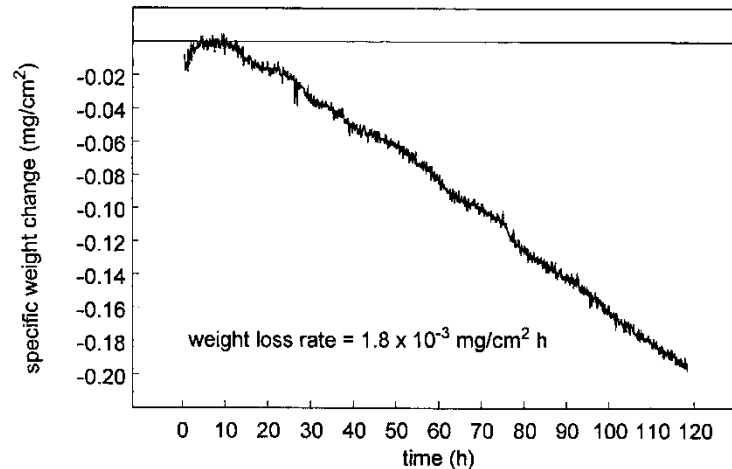
$$= 0.664 \left(\frac{v_\infty \rho_\infty L}{\eta}\right)^{0.5} \left(\frac{\eta}{D_i \rho_\infty}\right)^{0.33} \frac{D_i P_i}{RT\,L}$$

Laminar Flow, Expression for turbulent flow similar

Thermogravimetric Apparatus: NASA "Homemade"

- Large hot zone $\Rightarrow$ larger samples
- Wide range of atmospheres possible
  - $H_2O(g)$, $CO_2(g)$, $SO_2(g)$, $Cl_2(g)$, 5%H_2/Ar

weight loss rate = 1.8×10^{-3} mg/cm^2 h

- Silica coupon in 50% H_2O/O_2 (E. Opila)
- $SiO_2 + 2\,H_2O(g) = Si(OH)_4(g)$

Systems Studied: For many of these higher pressures of Water Vapor are Needed

- $SiO_2 + 2H_2O(g) = Si(OH)_4(g)$ (BL Limited; Transpiration)
  Note: Will not see this species at low pressures of $H_2O(g)$

- $Al_2O_3 + 3H_2O(g) = Al(OH)_3(g)$ (BL Limited)

- $Cr_2O_3 + H_2O(g) = CrO_2(OH)_2(g)$ (Transpiration)

- $TiO_2 + H_2O(g) = TiO(OH)_2(g)$ (Transpiration)

- $RE_2O_3 + 3H_2O(g) = RE(OH)_3(g)$ (In progress!)

Experimental Data--$\Delta_r H(298)$ (kJ/mol), $\Delta_r S(298)$ (J/mol-K) for Reaction from Oxide to Stable Hydroxide/Oxy-hydroxide Reaction based on 1 mole of Solid

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
H																	He
Li(OH) 186, 97	Be(OH) 614, 153 Be(OH)$_2$ 174, 31											BO(OH) 196, 128 B(OH)$_2$ 401, 75 B(OH)$_3$ 6.4, -15	C	NO$_2$(OH)$_2$	O	F	Ne
Na(OH) 228, 164	Mg(OH) 557, 156 Mg(OH)$_2$ 271, 52											Al(OH) 779, 199 AlO(OH) 498, 134 Al(OH)$_2$ 572, 121 Al(OH)$_3$ 188, -7.3	SiO(OH)$_2$ 718, 188 SiO(OH)$_2$ 317, 64 Si(OH)$_4$ 55, -76	P	SO$_2$(OH)$_2$	Cl	Ar
K(OH) 192, 157	Ca(OH) 562, 154 Ca(OH)$_2$ 266, 59	Sc	TiO$_2$(OH)$_2$	V	Cr(OH)) 770, 227 CrO$_2$(OH)$_2$ 61, -26	Mn(OH) 664, 268 MnO(OH) 469, 219 Mn(OH)$_2$ 442, 311	Fe(OH) 669, 229 Fe(OH)$_2$ 324, 153	Co	Ni	Cu(OH) 429, 161	Zn(OH)$_2$ 201, 55	Ga(OH) 570, 224	Ge	As	Se	Br	Kr
Rb(OH) 177, 156	Sr(OH) 507, 148 Sr(OH)$_2$ 238, 61	Y	Zr	Nb	MoO$_2$(OH)$_2$ 135, 89	Tc	Ru	Rh	Pd	Ag	Cd	In(OH) 513, 228	Sn	Sb	Te	I	Xe
Cs(OH) 157, 156	Ba(OH) 443, 138 Ba(OH)$_2$ 163, 54	La-Lu	Hf	Ta	WO$_2$(OH)$_2$ 530, 87	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

La	Ce	Pr	Nd	Pm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Green boxes: Coating Constituents. Studied at GRC: Si-O-H, Cr-O-H, Ti-O-H, Y-O-H (in progress), only ~50 to go!
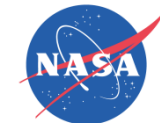
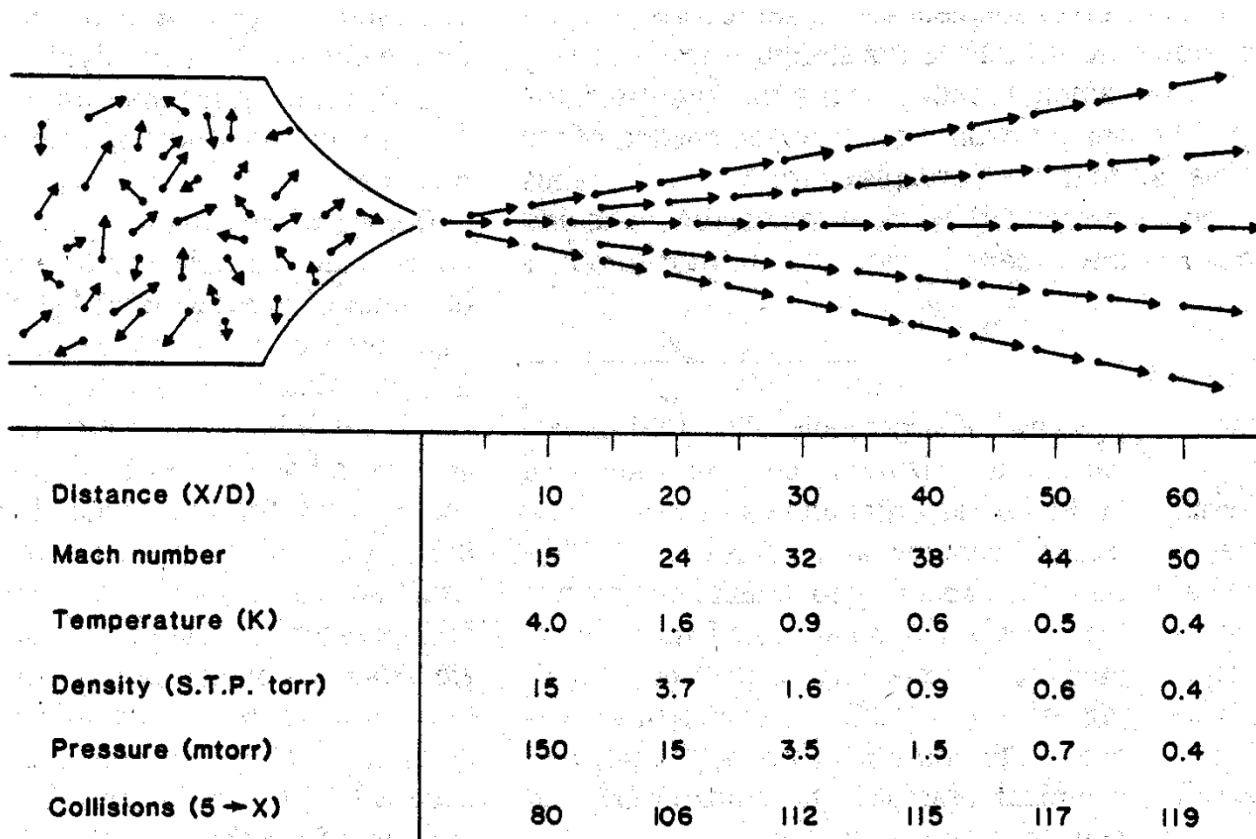How do we Identify Vapor Constituents formed at Higher Pressures?

Sampling Mass Spectrometer

- Use the a mass spectrometer to directly sample vapors from a one atmosphere process (Qualitative only!)
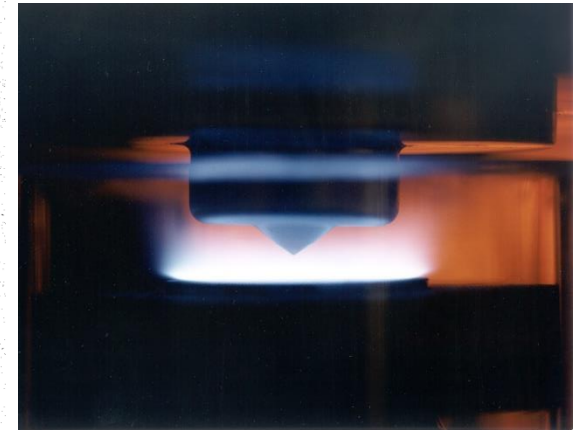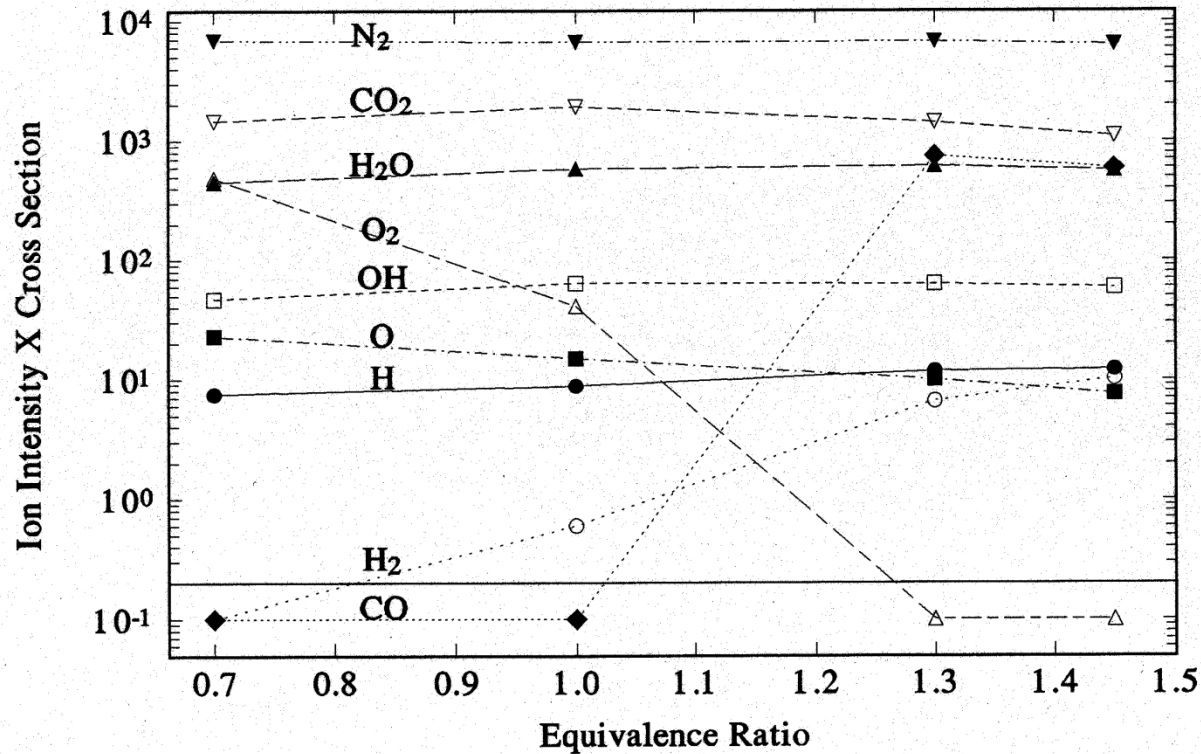 - Flame
  - Deposition process
  - Corrosion process

Free Jet Expansion Preserves
Chemical and Dynamic Integrity of Gas

Distance (X/D)	10	20	30	40	50	60
Mach number	15	24	32	38	44	50
Temperature (K)	4.0	1.6	0.9	0.6	0.5	0.4
Density (S.T.P. torr)	15	3.7	1.6	0.9	0.6	0.4
Pressure (mtorr)	150	15	3.5	1.5	0.7	0.4
Collisions (5 → X)	80	106	112	115	117	119

T. A. Miller, Science 223 (4636), 545 (1984)

Analysis of Combustion Products

Flame Chemistry

Fuel Lean:
$O_2(g)$, $CO_2(g)$, $H_2O(g)$

Fuel Rich:
$CO(g)$, $H_2(g)$, $CO_2(g)$, $H_2O(g)$

Experiments also done with seeding flame with corrosive salts, found in combustion environments

Studies of Volatile Hydroxides formed as Corrosion Products in Combustion Environments

- Combustion products always ~10% water vapor

- Water vapor can react with protective oxides

  Oxide (s,l) + H_2O(g) = Hydroxide (g) or Oxy-hydroxide (g)

  Examples:
  $$SiO_2(s) + 2H_2O(g) = Si(OH)_4(g)$$

  $$SiO_2(s) + H_2O(g) = SiO(OH)_2(g)$$

  $$Al_2O_3(s) + 3H_2O(g) = 2Al(OH)_3(g)$$

- Instrument can directly identify the species, other indirect techniques provide quantitative information on thermodynamics

First Direct Observation of $Si(OH)_4(g)$

First Direct Observation of $Al(OH)_3(g)$

AlOHms Sept. 21, 2001 11:07:54 AM

Orbiter Wing Leading Edge Deposits

- HPMS Indicated Zn, NaCl
- Zn from weathering paint on launch structure
- NaCl from coastal environment
- Zn in particular led to pinholes! Implemented launch structure wash.

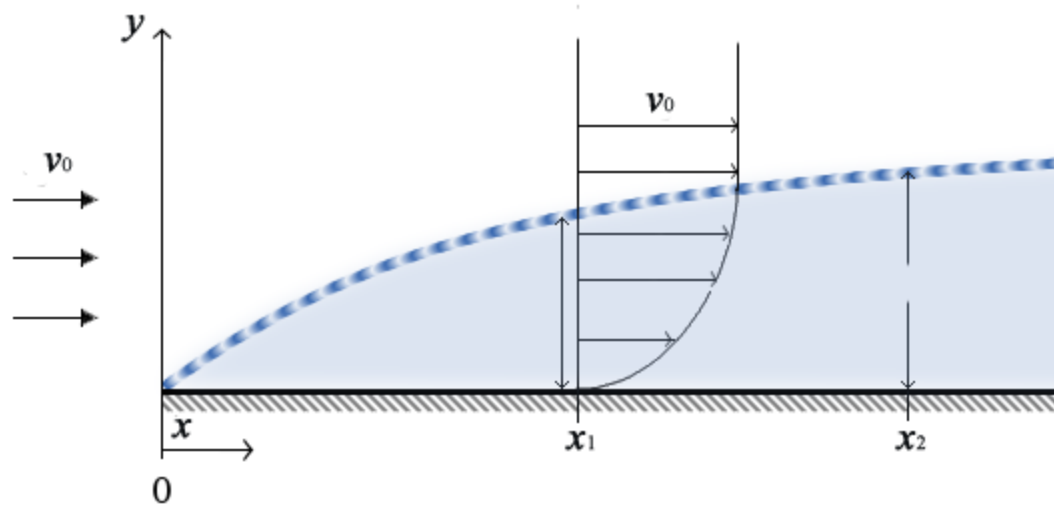# Summary: Methods used at GRC to Measure Vapor Pressure over Condensed Phases

- Knudsen cell: Molecular beam sampling from a nearly closed chamber. Limited to low pressures

- Transpiration: Downstream sampling of a vapor. Useful at higher pressures.

- Boundary Layer Limited Vaporization: Rapid test. Approximate vapor pressures. Also useful at higher pressures.

- Identify species at higher pressures with sampling mass spectrometer.

Supplemental Material

Boundary Layers: Region of Flow around an Object Affected by that Object (Viscous Drag)

Undisturbed region: v_0 or v_∞ = free stream velocity

Key Parameter: Reynold's Number (Re) = inertial force/viscous force

$$\left(\frac{v_\infty \rho_\infty L}{\eta} \right)$$

η = viscosity (g/cm-s = poise)

η/ρ = kinematic viscosity (cm^2/s)

For our typical conditions v_∞ = 400 cm^3/min*1 min/60 s*1/[π*(1.8 cm)^2] = 0.65 cm/s

η = 7 x 10^{-4} g/cm-s L = 2 cm ρ_∞ = n/V*M = P*M/RT = 1*40/(82.057*298) = 1.64 x 10^{-3} g/cm^3

Note that room temperature is used for velocity and density—corrections to temperature (1573K) cancel

Re = (0.65*1.64*10^{-3}*2/7*10^{-4}) = 3.05   Laminar; Turbulent Re > 2100

Boundary Layer Thickness Calculations

- First Need Gas Phase Diffusivity (cm^2/s)

  - Chapman-Enskog correlation

$$D_{12} = \frac{1.8\,x\,10^{-3}}{\sigma^2\,\Omega}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^{1/2}\left(\frac{T^{3/2}}{P}\right)$$

  - σ--average collision diameter (angstroms) from Svehla
  - Ω collision integral—first get force constants from Svehla and Ω from Sherwood
  - Note $T^{3/2}$ dependence and $1/P$ dependence
  - Generally at 1 atm 1-2 cm^2/s
  - Calculated for $Si(OH)_4(g)$ in Ar—1.68 cm^2/s

- Schmidt Number = viscous momentum transport/diffusion transport

  - $\rho_\infty = n/V*M = P*M/RT = 1*40/(82.057*1573) = 3.10 \times 10^{-4}$ g/cm^3 (Note now at temperature)

  - $\left(\dfrac{\eta}{D_i\rho_\infty}\right)$ $= (7*10^{-4}/(1.68*3.10*10^{-4})) = 1.34$

- Boundary Layer thickness cm

  $\delta = \dfrac{1.5L}{(\mathrm{Re})^{1/2}(Sc)^{1/3}}$ $= 1.5*2/[(3.05)^{1/2}(1.34)^{1/3}] = 1.56$

  - $\delta \propto (1/P)^{1/2}$ $\delta \propto (1/v)^{1/2}$

Thermogravimetric Apparatus

- ## Commercial Netzsch 409: Weight loss of SiC fiber