Stability of Materials in High Temperature Water Vapor: SOFC Applications

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Solid oxide fuel cell material systems require long term stability in environments containing high- temperature water vapor. Many materials in fuel cell systems react with high-temperature water vapor to form volatile hydroxides which can degrade cell performance. In this paper, experimental methods to characterize these volatility reactions including the transpiration technique, thermogravimetric analysis, and high pressure mass spectrometry are reviewed. Experimentally determined data for chromia, silica, and alumina volatility are presented. In addition, data from the literature for the stability of other materials important in fuel cell systems are reviewed. Finally, methods for predicting material recession due to volatilization reactions are described.

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Motivation

- Materials in SOFC applications require stability for 10,000 to 100,000 h for desired cell operating performance
- High temperature water vapor is present on both anode and cathode sides of the cell
- Many gaseous metal hydroxide species are thermodynamically stable
- Formation of gaseous metal hydroxides can lead to consumption of thin layers of material and/or transport of metal species to other locations – poisoning cell operation
- Thermodynamic data for gaseous metal hydroxide stability are needed to predict cell degradation

Outline

- Thermodynamics of gaseous metal hydroxide formation
- Experimental techniques for determination of thermodynamic data of gaseous metal hydroxide formation
- NASA GRC experimental determination of thermodynamic stability for Cr_2O_3, SiO_2, and Al_2O_3 in high temperature water vapor
- Literature review and prediction of thermodynamic stability of Ni, CoO, SrO, CaO, La_2O_3, MnO, Pd, Pt
- Kinetics of volatilization limited by transport through laminar gaseous boundary layer

Thermodynamics of Gaseous Metal Hydroxide Formation

Generic reaction:

$MO_x + nH_2O(g) + mO_2(g) + qH_2(g) = MO_{(x+n+2m)}H_{2(n+q)}(g)$

Model SOFC environments

Anode side: $H_2O(g) + H_2(g)$

Cathode side: $H_2O(g) + O_2(g)$

Pressure dependence: $P_{MOH} = K_{eq} P^{n}_{H_2O} P^{m}_{O_2} P^{q}_{H_2}$

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

$\frac{1}{2} Cr_2O_3 + H_2O(g) + \frac{3}{4} O_2(g) = CrO_2(OH)_2(g)$

$Ni + 2H_2O(g) = Ni(OH)_2(g) + H_2(g)$

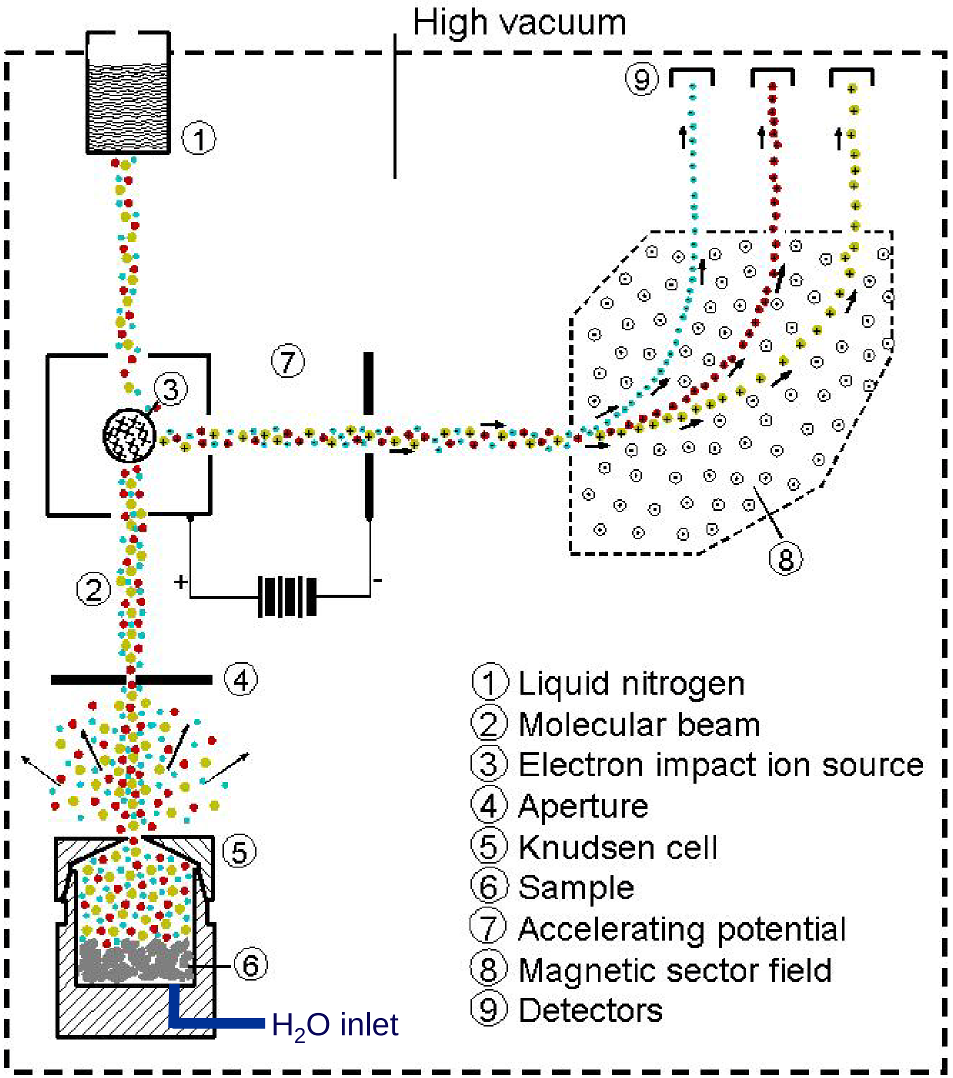
MOH(g)	n	m	q
$Si(OH)_4$	2	0	0
$CrO_2(OH)_2$	1	3/4	0
$Ni(OH)_2$	2	0	-1

Temperature dependence: $K_{eq} = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H - T\Delta S}{RT}\right)$

Experimental techniques for determination of thermodynamic data of gaseous metal hydroxide formation

- Mass spectrometry
  - Knudsen Effusion Mass Spectrometry (KEMS)
  - High Pressure Free Jet Expansion MS
- Transpiration
- Thermogravimetric Analysis (TGA)
- Flame Spectroscopy

Knudsen Effusion Mass Spectrometry (KEMS)



① Liquid nitrogen
② Molecular beam
③ Electron impact ion source
④ Aperture
⑤ Knudsen cell
⑥ Sample
⑦ Accelerating potential
⑧ Magnetic sector field
⑨ Detectors

http://www.fz-juelich.de/ief/ief-2/datapool/page/227/KEMSschematisch.jpg

- Magnetic sector analysis - accurate data
- High vacuum process
- Low water vapor partial pressures ($<10^{-5}$ bar), therefore not representative of SOFC conditions
- Data available in literature:

Si-O-H(g)

D. L. Hildenbrand, K. H. Lau, J. Chem. Phys., 101 [7] 6076 (1994).

Mn-O-H(g)

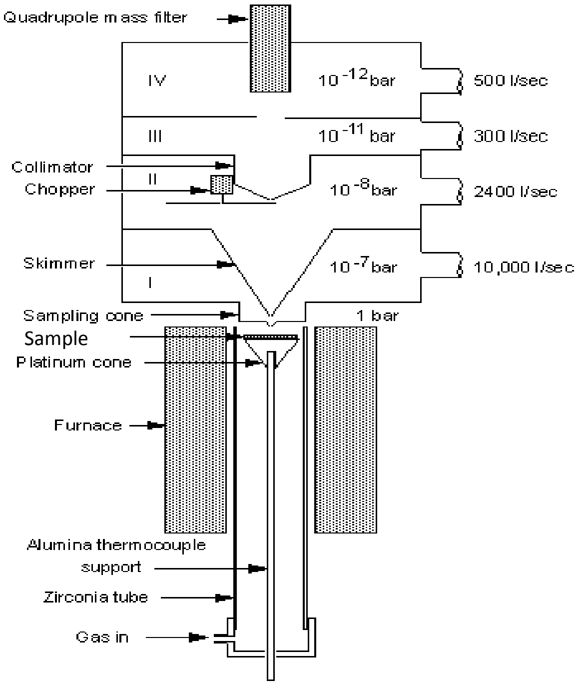
D.L. Hildenbrand, K.H. Lau, J. Chem. Phys. 100 [11] 8377 (1994).

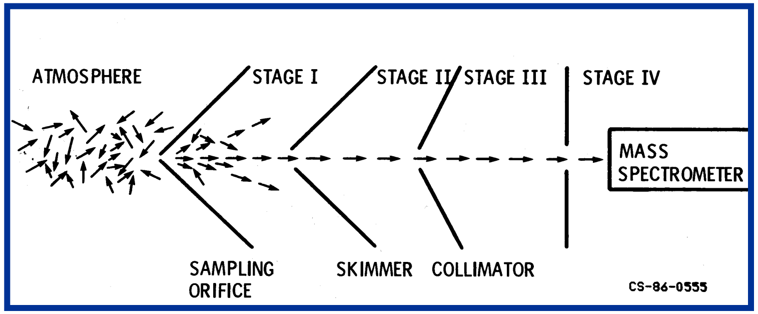
Pd-O(g)

J.H. Norman, H.G. Staley, W.E. Bell, J. Phys. Chem. 69 [4] 1373 (1965).

D.L. Hildenbrand, K.H. Lau, Chem. Phys. Lett. 319, 95 (2000).

High Pressure Free Jet Expansion Mass Spectrometry (HPMS)





High Pressure Free Jet Expansion Mass Spectrometry (HPMS)

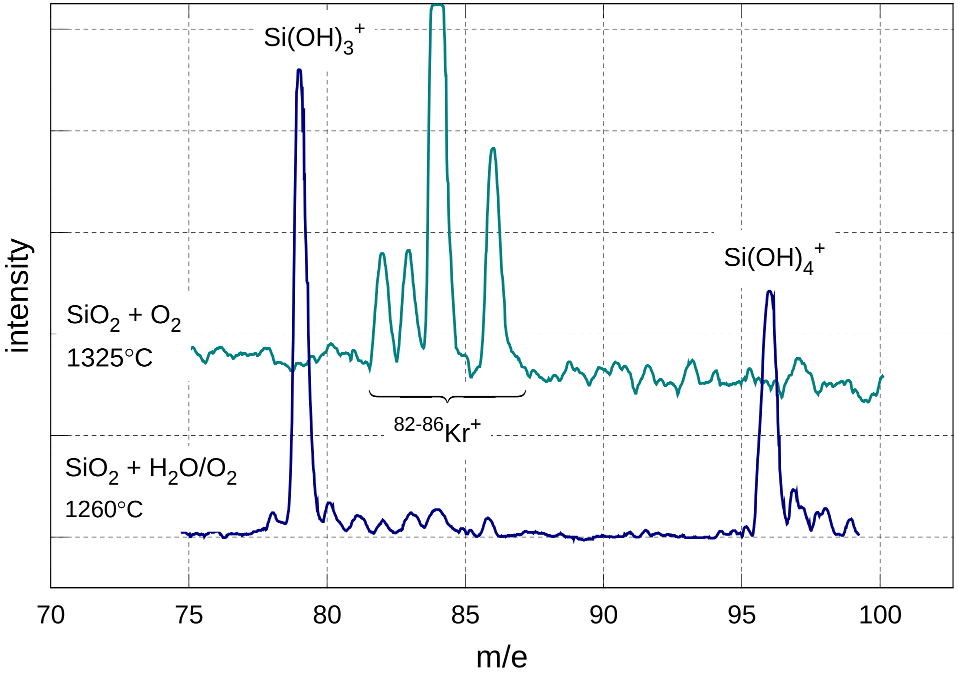
- Quadrupole analysis – quantitative data difficult
- 1 bar sampling system
- Water vapor partial pressures possible near 1 bar - representative of SOFC conditions
- Data available in literature:

Si-O-H(g)

E.J. Opila, D.S. Fox, N.S. Jacobson, J. Am. Ceram. Soc. 80 [4] 1009 (1997).

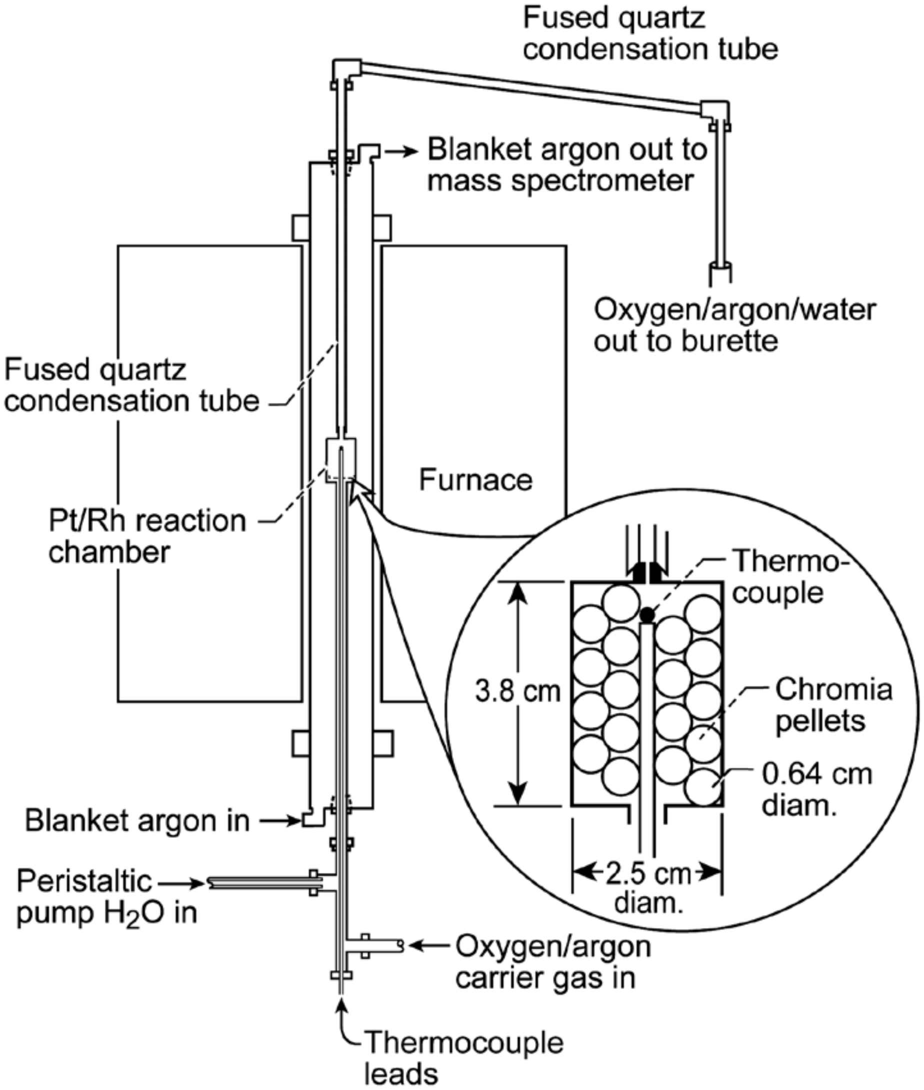
Cr-O-H(g)

G.C. Fryburg, R.A. Miller, F.J. Kohl, C.A. Stearns, J. Electrochem. Soc.124 [11] 1738 (1977).



Free jet sampling mass spectrometric identification of $Si(OH)_4$(g) from the reaction of $SiO_2 + H_2O$(g)

The Transpiration Technique



The Transpiration Technique

- Volatile species identified indirectly from pressure dependence
- Accurate pressure and temperature dependence of volatilization reaction is possible
- Water vapor partial pressures 0.1 to 1 bar - representative of SOFC conditions
- Data available in literature:

Ni-O-H(g) and Co-O-H(g)

G.R. Belton, A.S. Jordan, J. Phys. Chem. 71 [12] 4114 (1967).

Si-O-H(g)

A. Hashimoto, Geochim. Cosmo. Acta 56, 511-532 (1992).

N.S. Jacobson, E.J. Opila, D. Myers, E. CoplandJ. Chem. Thermo. 37, 1130 (2005).

Ca-O-H(g)

K. Matsumoto, T. Sata, Bull. Chem. Soc. Jpn. 54 [3] 674 (1981).

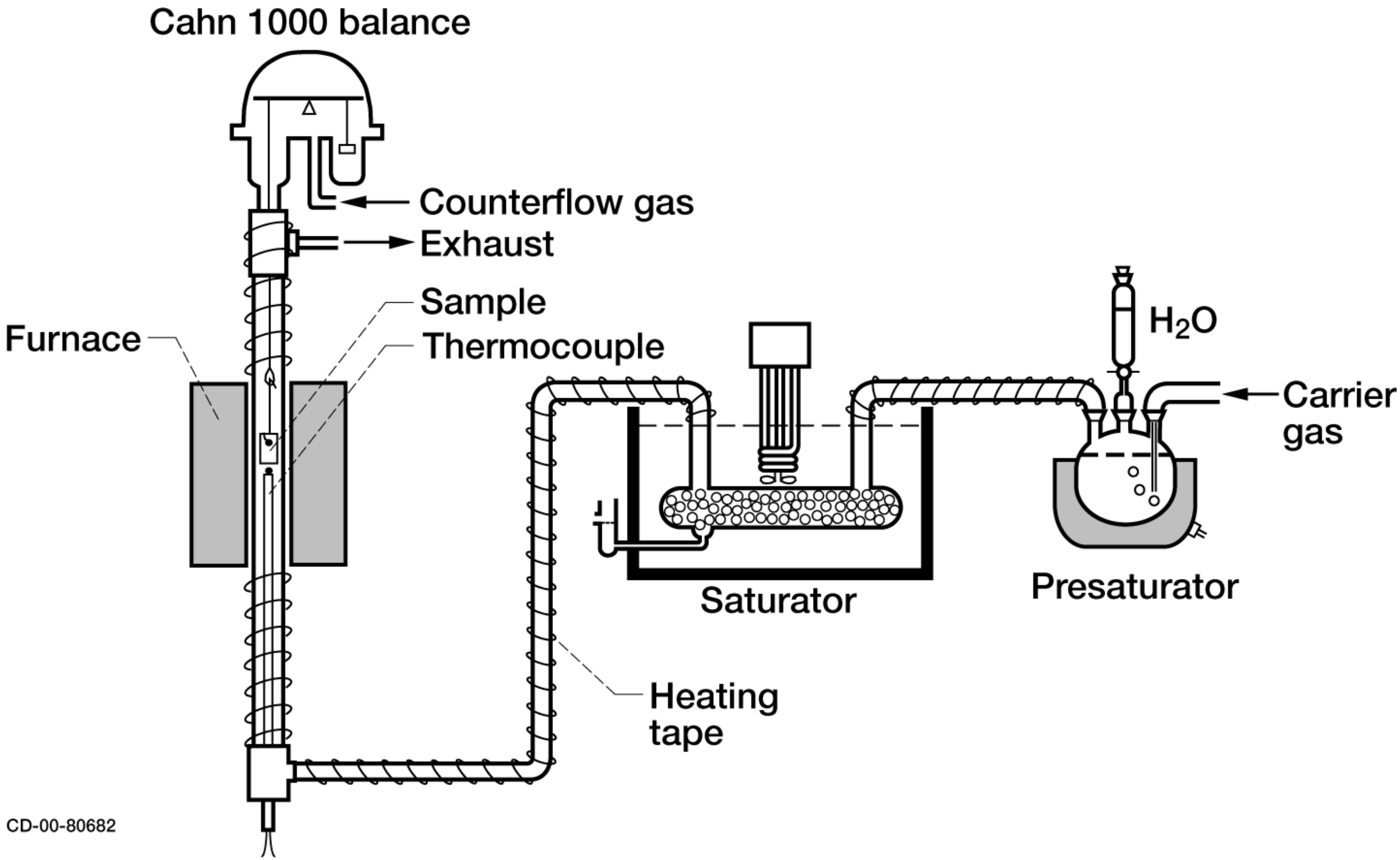
A. Hashimoto, Geochim. Cosmo. Acta 56, 511-532 (1992).

Cr-O-H(g)

E.J. Opila, D.L. Myers, N.S. Jacobson, I.B. Nielsen, D.F. Johnson, J.K. Olminsky, M.D. Allendorf, J. Phys. Chem. A. 111, 1971 (2007).

M. Stanislowski, E. Wessel, K. Hilpert, T. Markus, L. Singheiser, J. Electrochem. Soc. 154 [4] A295- (2007).

Thermogravimetric Analysis (TGA)



Thermogravimetric analysis

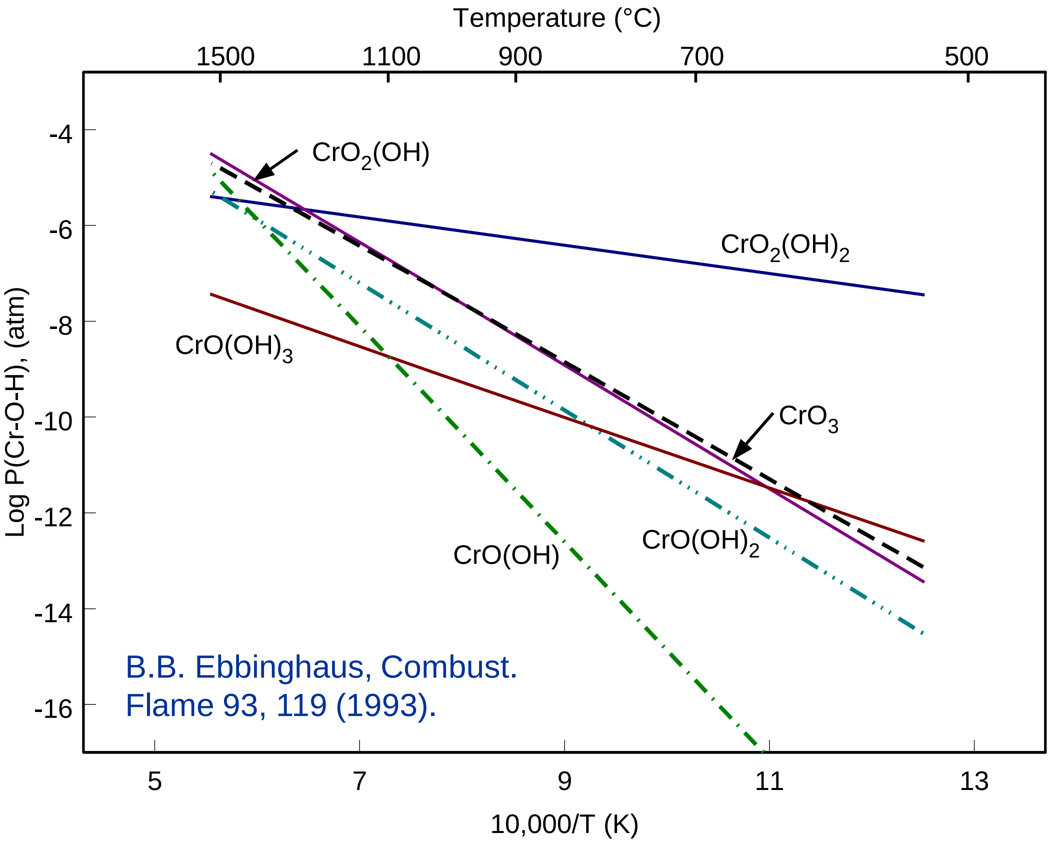
- Gas boundary layer characteristics affect volatilization rate
  - Must have well defined gas flow over sample
  - Equilibrium partial pressures of gaseous metal hydroxide calculated from weight loss assuming volatilization is limited by gaseous transport through laminar gas boundary layer
- Volatile species identified indirectly from pressure dependence
- Accurate pressure and temperature dependence of volatilization reaction is possible
- Water vapor partial pressures 0.1 to 1 bar - representative of SOFC conditions
- Data available in literature:

  Al-O-H(g)

  E.J. Opila and D.L. Myers, J. Am. Ceram. Soc. 87 [9] 1701 (2004).

The Cr-O-H system

- Cr_2O_3 in SOFC
  - Oxide thermally grown on low temperature interconnects
  - Component of $La_{1-x}M_xCrO_3$ interconnect
- Many Cr-O-H(g) vapor species



B.B. Ebbinghaus, Combust. Flame 93, 119 (1993).

The Cr-O-H system

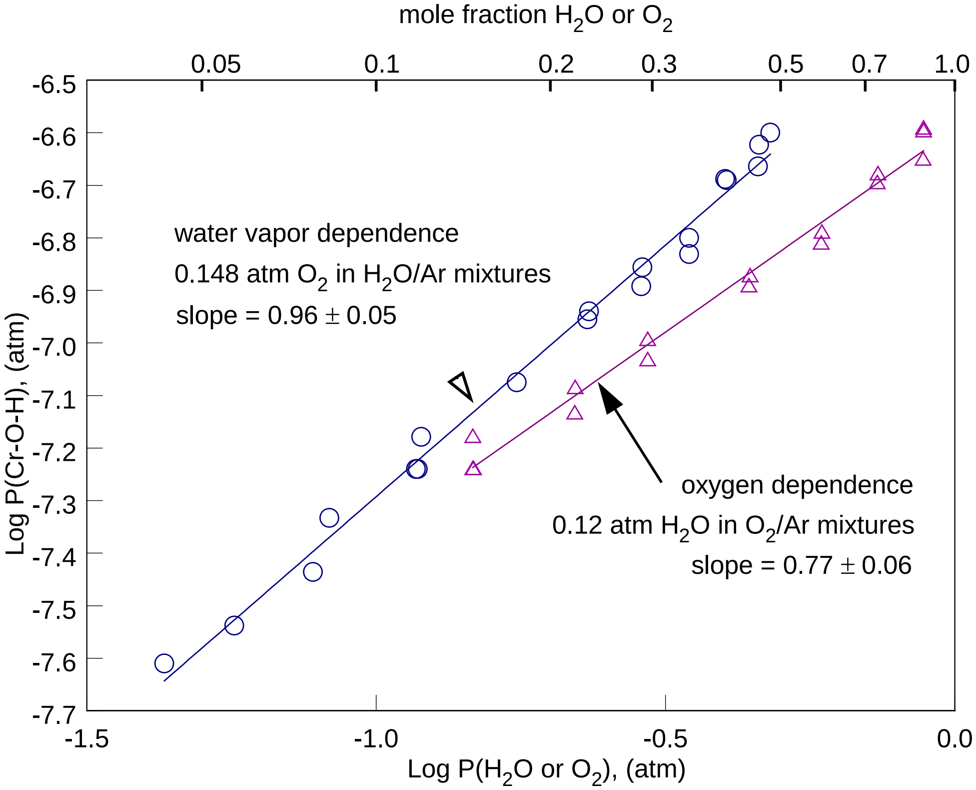
- Primary vapor species in $H_2O + O_2$ environment

$\frac{1}{2}\ Cr_2O_3(s) + \frac{3}{4}\ O_2(g) = CrO_3(g)$

$\frac{1}{2}\ Cr_2O_3(s) + H_2O(g) + \frac{3}{4}\ O_2(g) = CrO_2(OH)_2(g)$

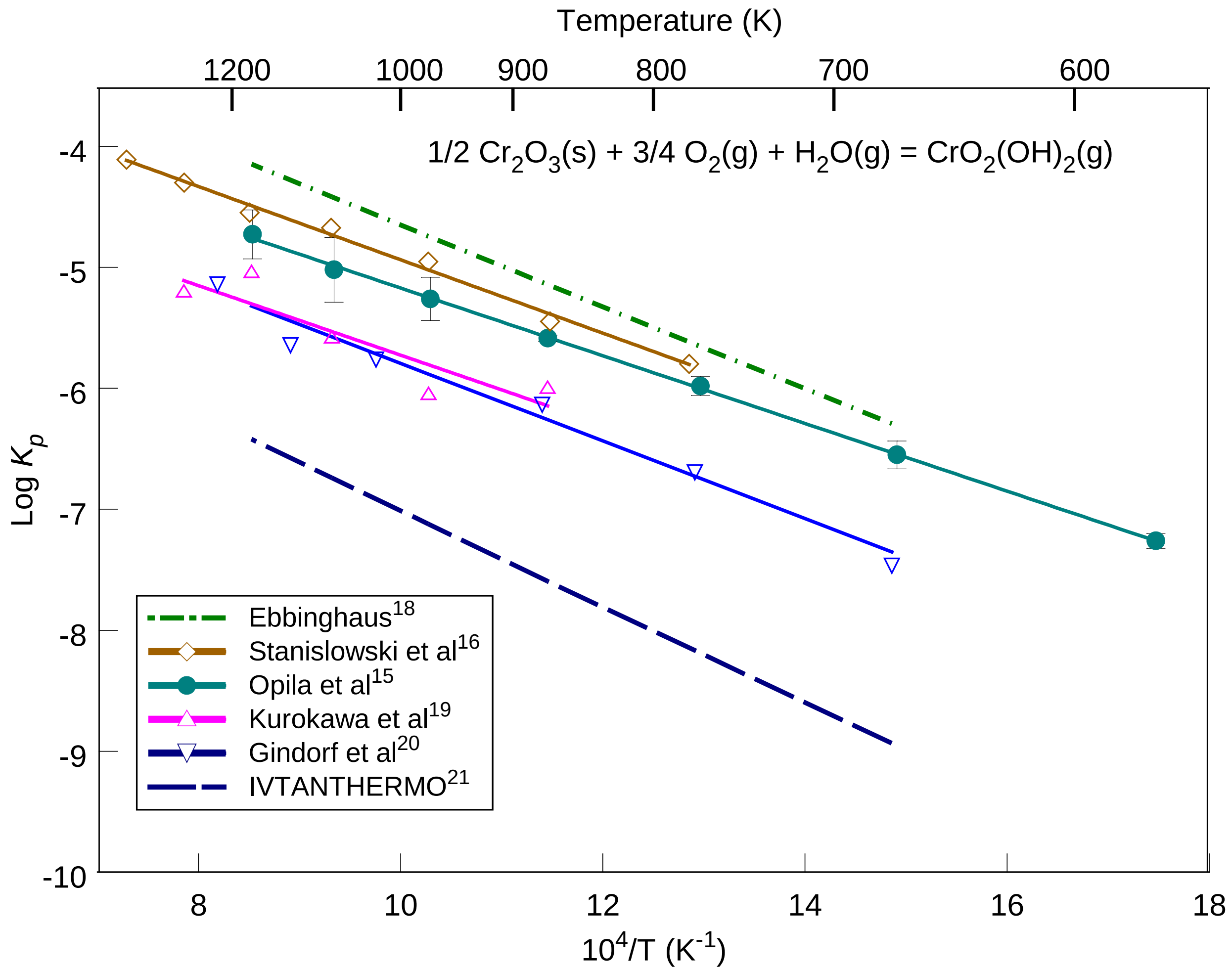
$\frac{1}{2}\ Cr_2O_3(s) + \frac{1}{2}\ H_2O(g) + \frac{1}{2}\ O_2(g) = CrO_2(OH)(g)$

- Confirmation of volatile species identity from pressure dependent transpiration experiment at 600°C



Opila et al, J. Phys. Chem. A. 111, 1971 (2007).

Temperature Dependence: $CrO_2(OH)_2(g)$ formation

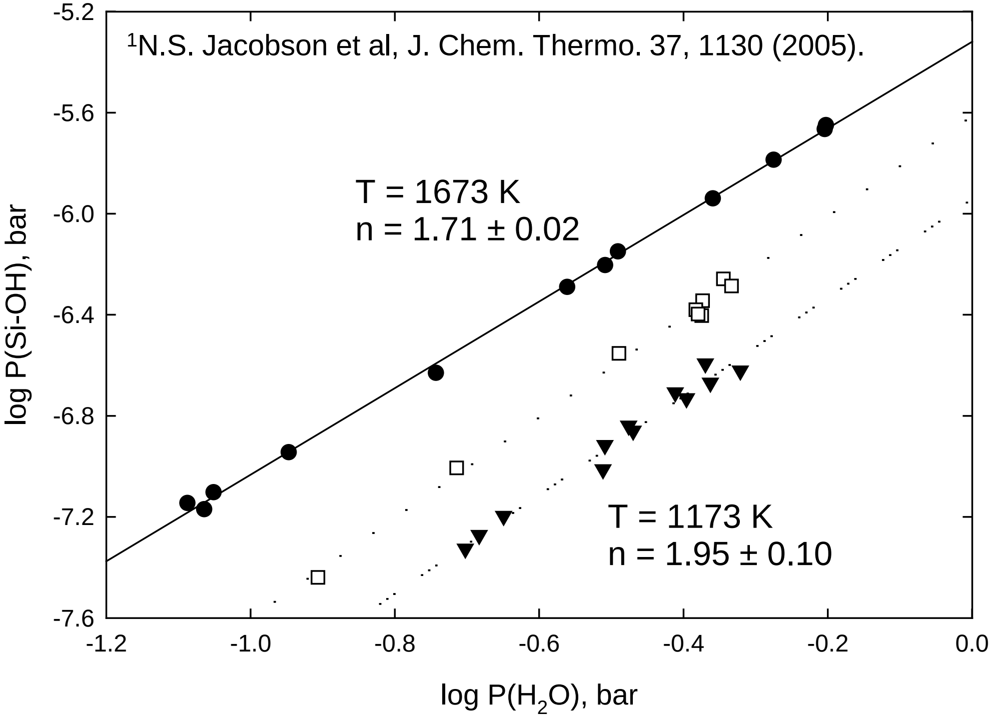


- Recent transpiration studies by Opila et al and Stanislowski et al have resolved discrepancy in thermochemical data for $CrO_2(OH)_2(g)$ formation
- Data of Opila et al: $\Delta H^\circ_{r,\ 861K}$ = 53.5 kJ/mol, $\Delta S^\circ_{r,\ 861K}$ = -45.6 J/K mol

The Si-O-H system

- SiO_2 in SOFC: constituent of sealing glasses
- Possible Si-O-H(g) vapor species and experimental method used for identification

$SiO_2(s) + 2\ H_2O(g) = Si(OH)_4(g)$	transpiration[1,2], HPMS[3]
$SiO_2(s) + H_2O(g) = SiO(OH)_2(g)$	KEMS[4]
$SiO_2(s) + ½\ H_2O(g) = SiO(OH)(g) + ¼\ O_2(g)$	KEMS[4]



[1]N.S. Jacobson et al, J. Chem. Thermo. 37, 1130 (2005).

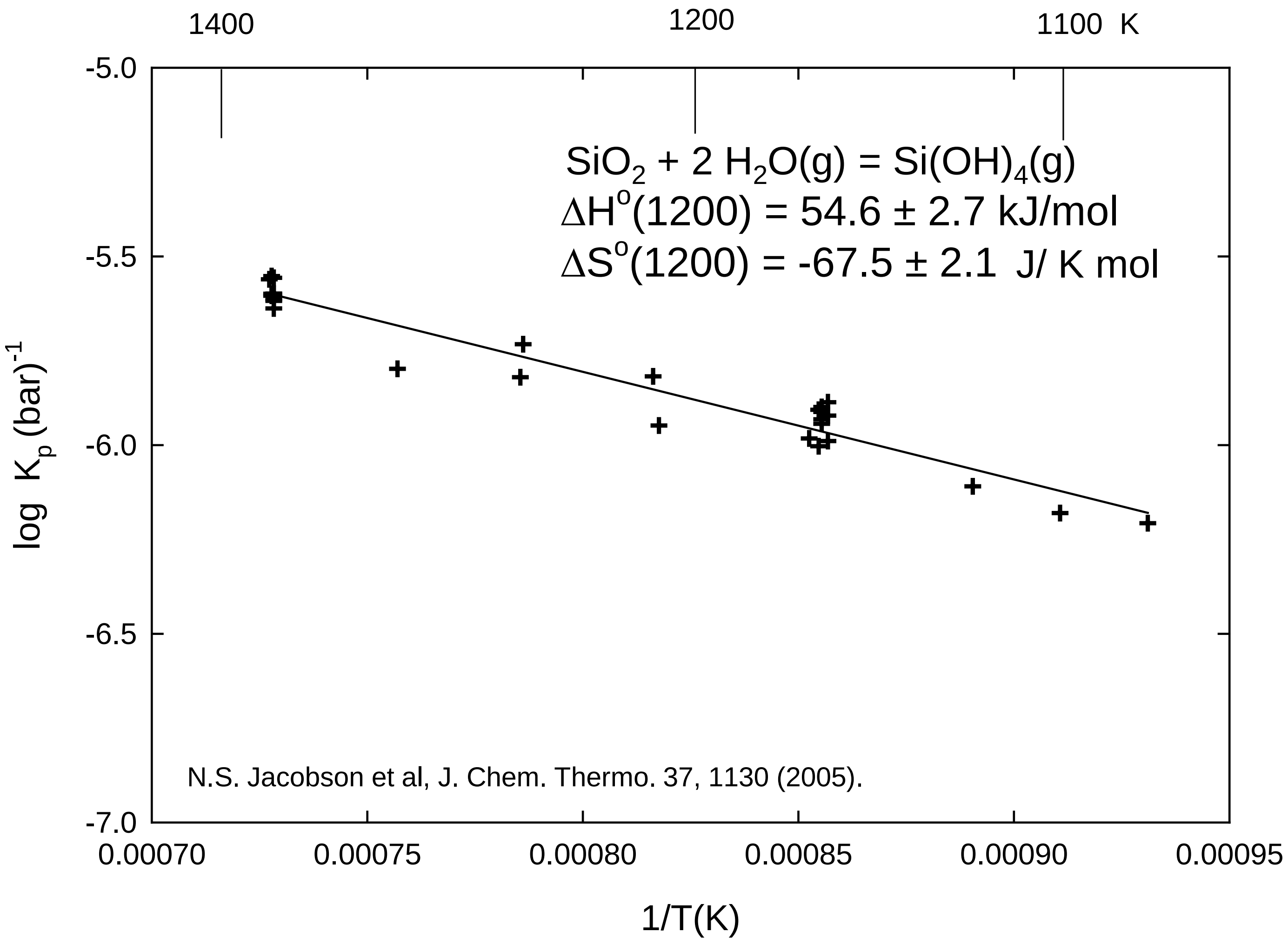
Transpiration studies show pressure dependence consistent with $Si(OH)_4(g)$ formation

[2]Hashimoto, Geochim. Cosmo. Acta 56, 511-532 (1992).

[3]Opila et al, J. Am. Ceram. Soc. 80 [4] 1009 (1997).

[4] Hildenbrand & Lau, J. Chem. Phys., 101 [7] 6076 (1994).

The Si-O-H system

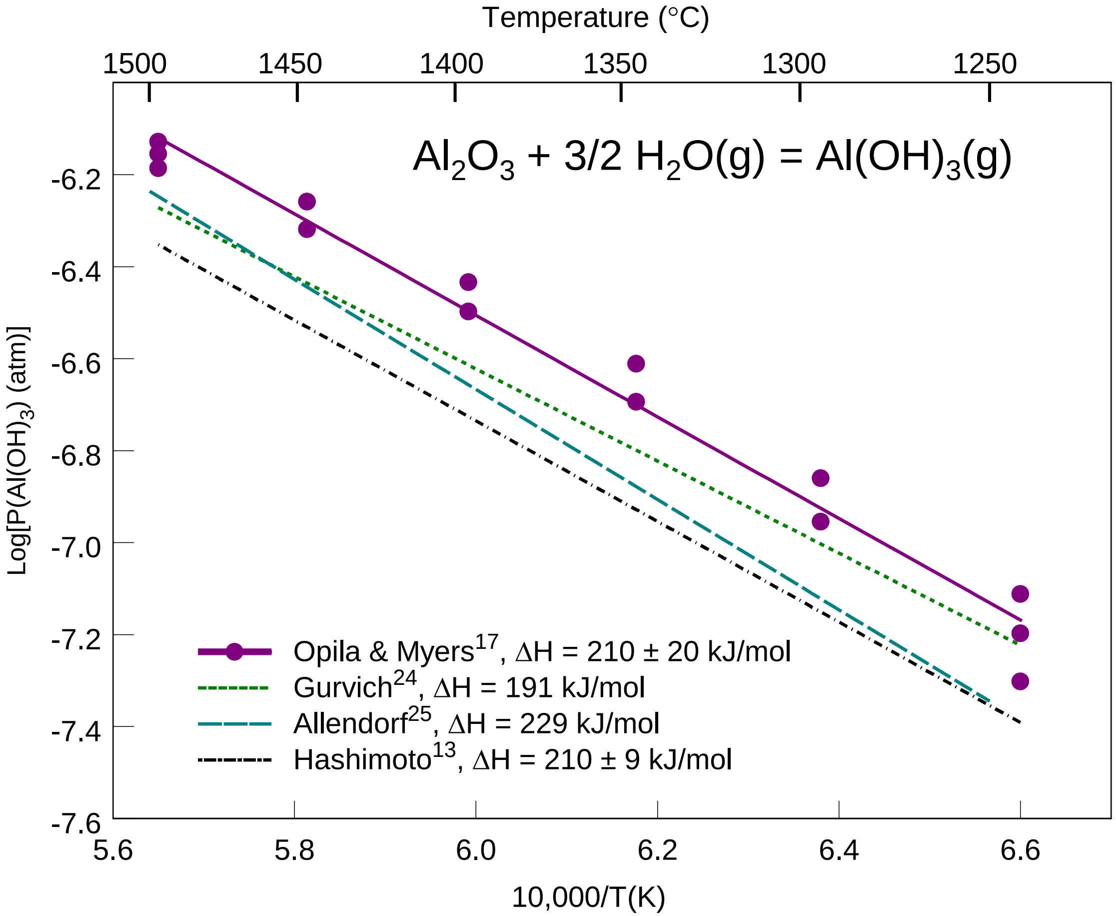


N.S. Jacobson et al, J. Chem. Thermo. 37, 1130 (2005).

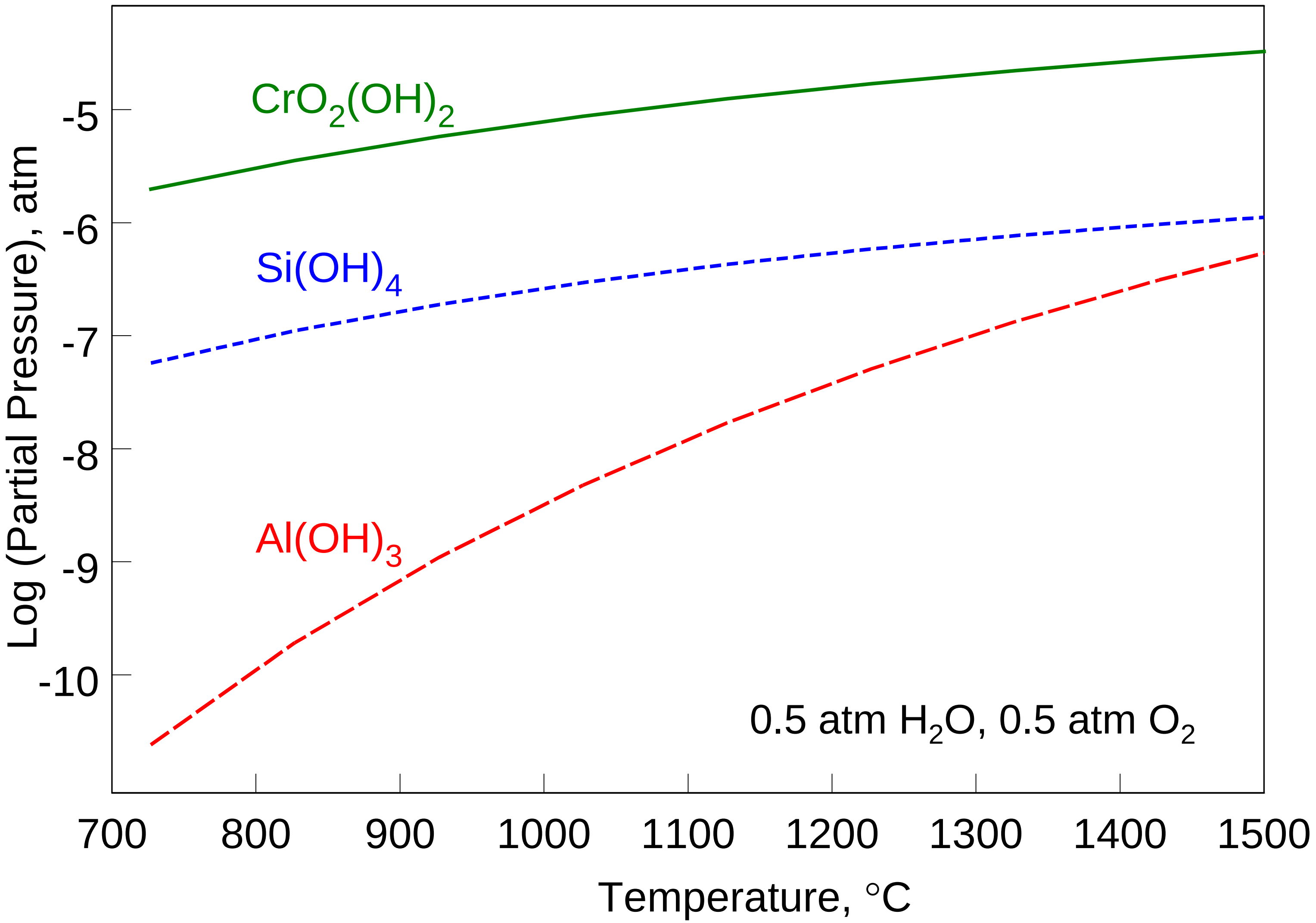
Temperature dependence for $Si(OH)_4(g)$ formation is relatively weak.

The Al-O-H system

- Al_2O_3 in SOFC: constituent of sealing glasses, insulators, and/or gas delivery components
- Al-O-H(g) vapor species identified from pressure dependence of Al_2O_3 volatility in TGA experiments and transpiration experiments with calcium aluminate



Oxide volatility comparison

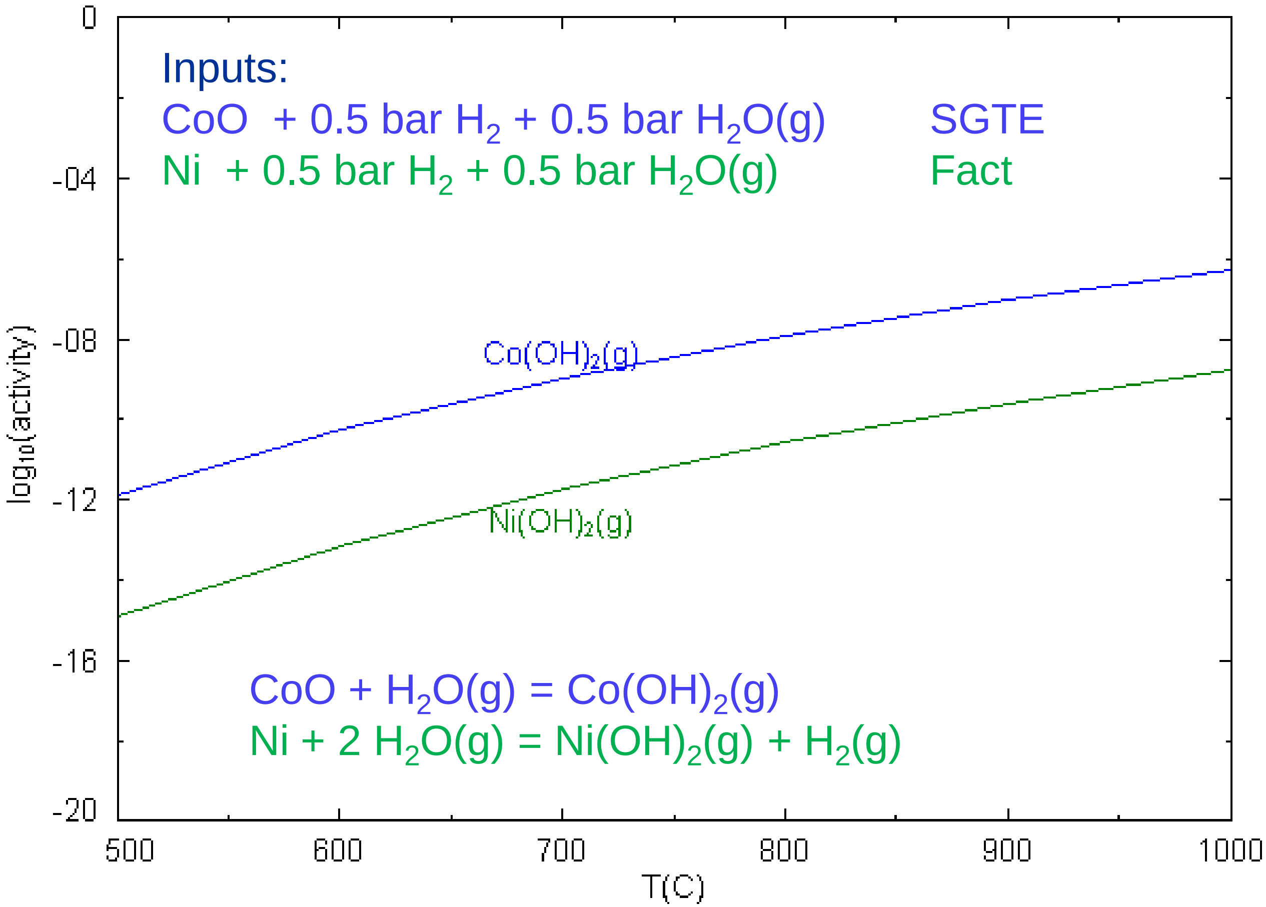


Review of thermodynamic data for materials important in SOFC systems

- Data base and literature review for M-O-H(g) data
- Data evaluation
  - Availability of data for M-O-H(g)
  - Method by which data were obtained
  - Completeness of data
  - Reliability of data
- Calculation of Ni, CoO, SrO, CaO, La_2O_3, MnO, Pd, Pt stability in model anode/cathode environments using FactSage free energy minimization program
  - Model anode environment: 1 bar 50% H_2O(g)/50% H_2(g)
  - Model cathode environment: 1 bar 50% H_2O(g)/50% O_2(g)
- Ranking/summary of volatility trends

Ni-O-H and Co-O-H systems

- Ni used in Ni/YSZ anode, Co found in interconnect alloys and CoO in coatings
- Ni-O-H vapor species include **$Ni(OH)_2$**, $Ni(OH)$, NiH, Ni_2, NiO, and Ni
- Ni-O-H and Co-O-H systems studied by transpiration method in H_2, H_2O
  - G.R. Belton, A.S. Jordan, J. Phys. Chem. 71 [12] 4114 (1967).



Inputs:

CoO + 0.5 bar H_2 + 0.5 bar $H_2O(g)$ SGTE

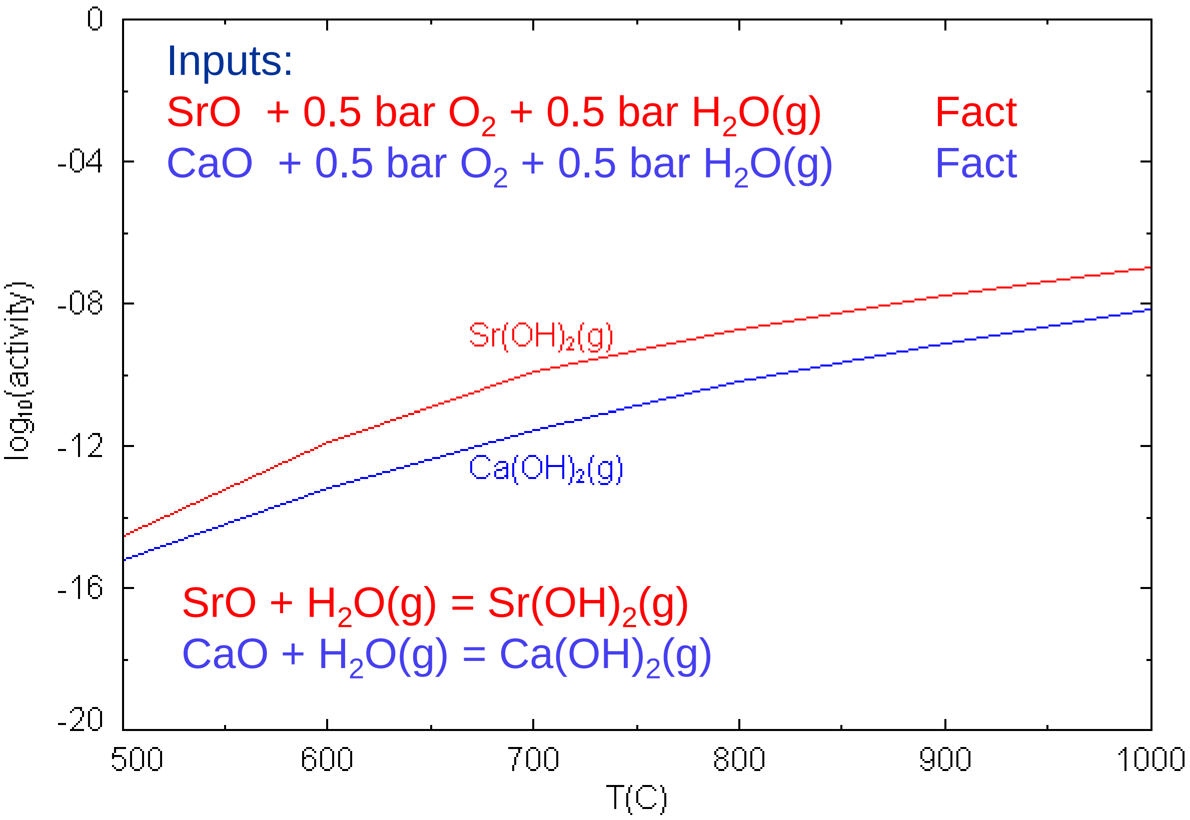
Ni + 0.5 bar H_2 + 0.5 bar $H_2O(g)$ Fact

$CoO + H_2O(g) = Co(OH)_2(g)$

$Ni + 2\ H_2O(g) = Ni(OH)_2(g) + H_2(g)$

Sr-O-H and Ca-O-H systems

- SrO found in LSM cathodes, CaO found in $La_{1-x}Ca_xCrO_{3-\delta}$ interconnects
- Sr-O-H vapor species include **$Sr(OH)_2$**, Sr(OH), SrH, Sr_2, SrO, Sr, and Sr_2O
- Ca-O-H vapor species include **$Ca(OH)_2$**, Ca(OH), CaH, Ca_2, CaO, and Ca
- Both systems studied by flame spectroscopy, Ca-O-H by transpiration


Inputs:

SrO + 0.5 bar O_2 + 0.5 bar $H_2O(g)$ Fact

CaO + 0.5 bar O_2 + 0.5 bar $H_2O(g)$ Fact

$SrO + H_2O(g) = Sr(OH)_2(g)$

$CaO + H_2O(g) = Ca(OH)_2(g)$

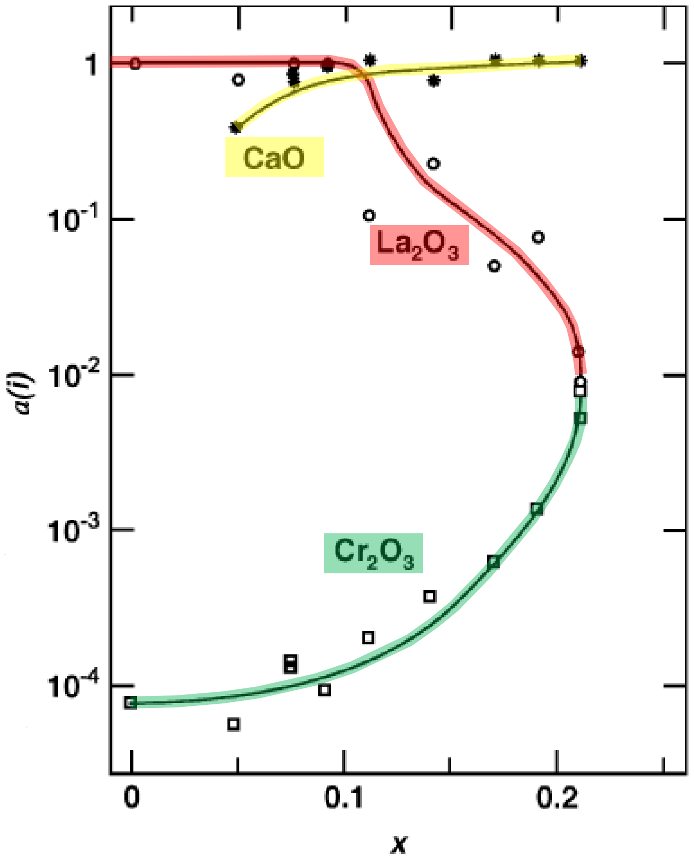
Activity of components in complex oxides

- CaO, Cr_2O_3, and La_2O_3 activities, *a(i)*, in $La_{1-x}Ca_xCrO_{3-\delta}$ interconnects can be reduced relative to pure oxides.
- Volatility will be correspondingly reduced
  $Cr_2O_3 + H_2O(g) + \frac{3}{4} O_2(g) = CrO_2(OH)_2(g)$

$$P_{CrO_2(OH)_2} = K_{eq}\, a_{Cr_2O_3}\, P_{H_2O}\, P_{O_2}^{3/4}$$

- $CrO_2(OH)_2(g)$ formation from $La_{1-x}Ca_xCrO_{3-\delta}$ (x=0 to 0.1) will be reduced by four orders of magnitude relative to pure Cr_2O_3

Thermodynamic activities of the components in $La_{1-x}Ca_xCrO_{3-d}$, x=0-0.21 at 2000K.

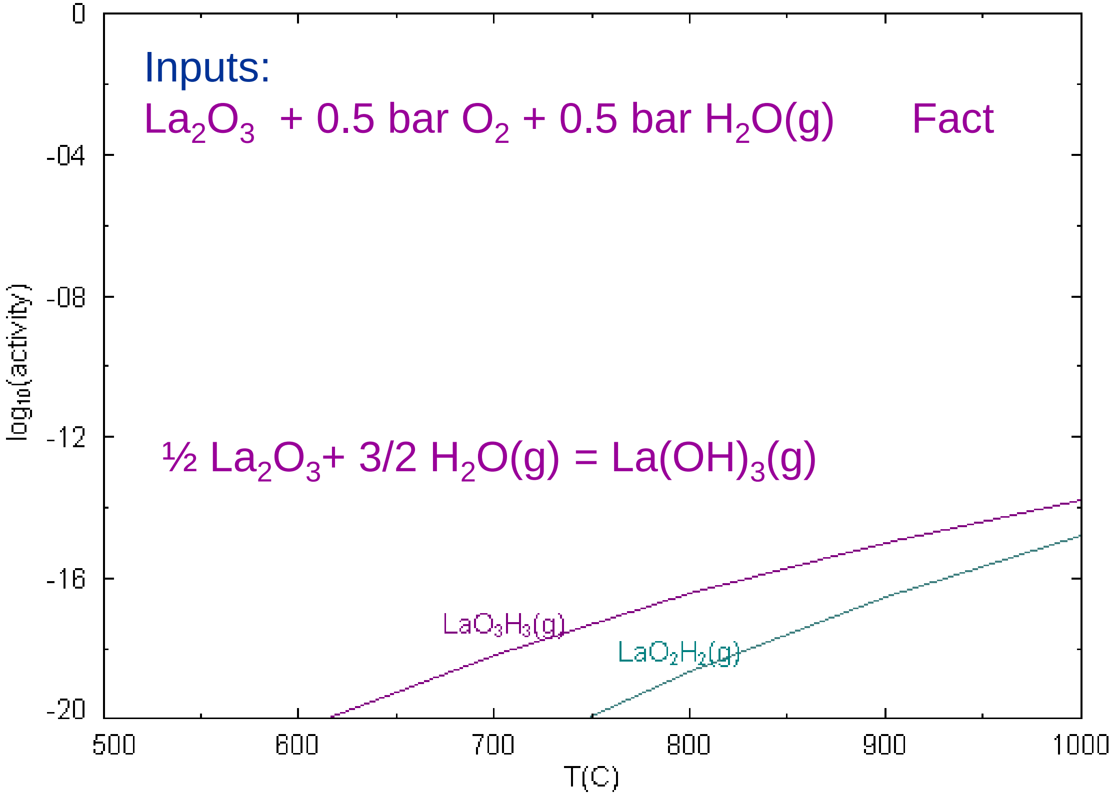


D.-H. Peck, M. Miller, K. Hilpert, Solid State Ionics 143, 391 (2001).

La-O-H system

- La_2O_3 is a component of LSM cathodes and $La_{1-x}Ca_xCrO_{3-\delta}$ interconnects
- La-O-H vapor species include **$La(OH)_3$**, $La(OH)_2$, La(OH), La_2, LaO, La, La_2O, ~~LaO_2~~, and La_2O_2
- Good review of La-O(g) system

  M. Heyrman, C. Chatillon, A. Pisch, Computer Coupling of Phase Diagrams & Thermochemistry 28, 49 (2004).
- Origin of data for $La(OH)_3$(g) unknown; $La(OH)_2$(g) and La(OH)(g) data estimated

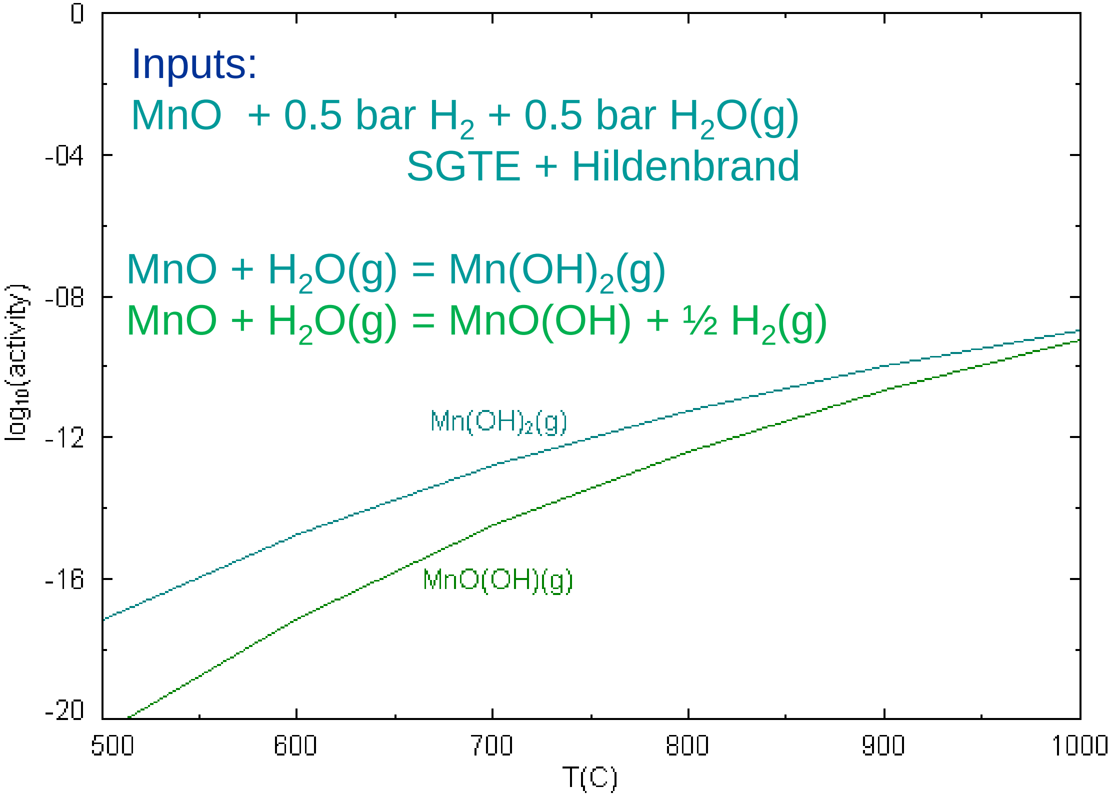

Inputs:

La_2O_3 + 0.5 bar O_2 + 0.5 bar H_2O(g) Fact

½ La_2O_3 + 3/2 $H_2O(g) = La(OH)_3(g)$

Mn-O-H system

- MnO is a component of LSM cathodes and oxide spinels formed/coated on metallic interconnects
- Mn-O-H vapor species include **$Mn(OH)_2$**, MnO(OH), Mn(OH), MnH, MnO, Mn, and MnO_2
- $Mn(OH)_2$ observed by KEMS; existence of $Mn(OH)_3$ and $MnO(OH)_2$ at higher pressures hypothesized: D.L. Hildenbrand, K.H. Lau, J. Chem. Phys. 100 [11] 8377 (1994).



Inputs:

MnO + 0.5 bar H_2 + 0.5 bar $H_2O(g)$

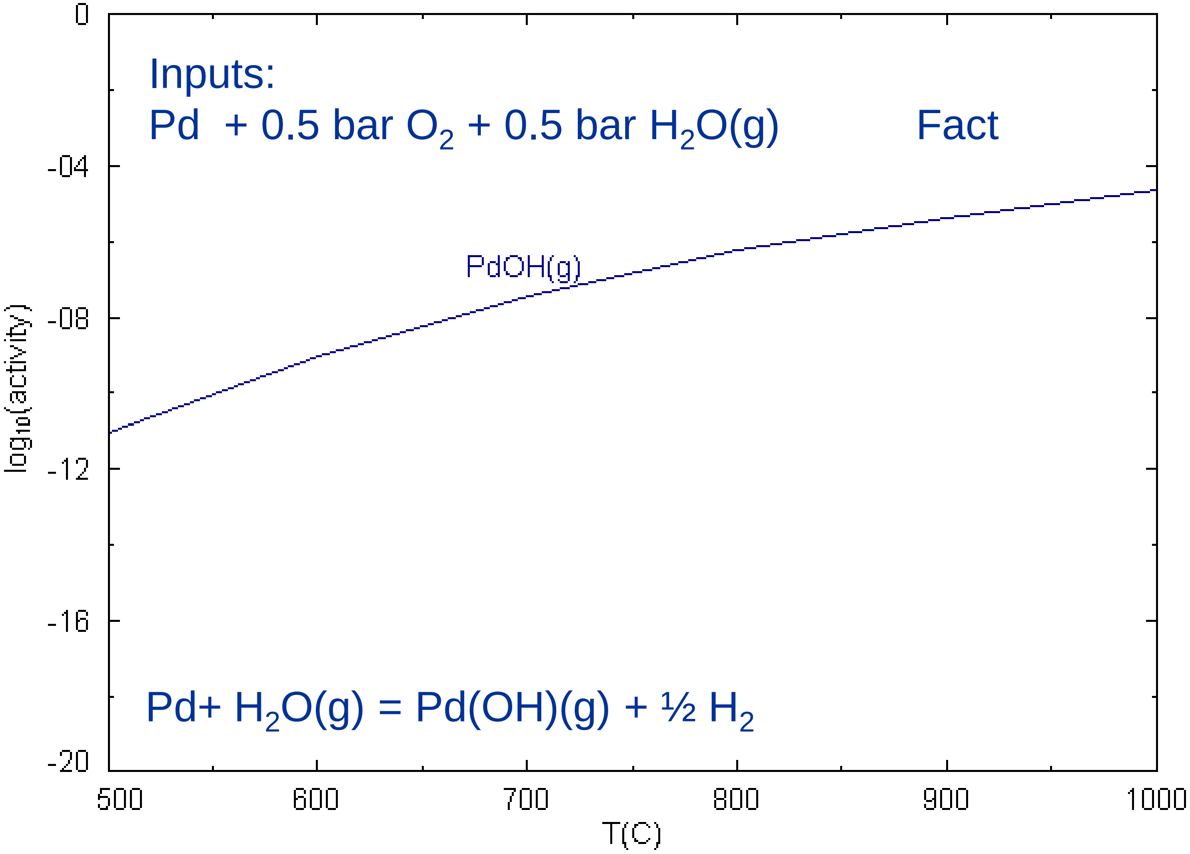
SGTE + Hildenbrand

$MnO + H_2O(g) = Mn(OH)_2(g)$

$MnO + H_2O(g) = MnO(OH) + ½ H_2(g)$

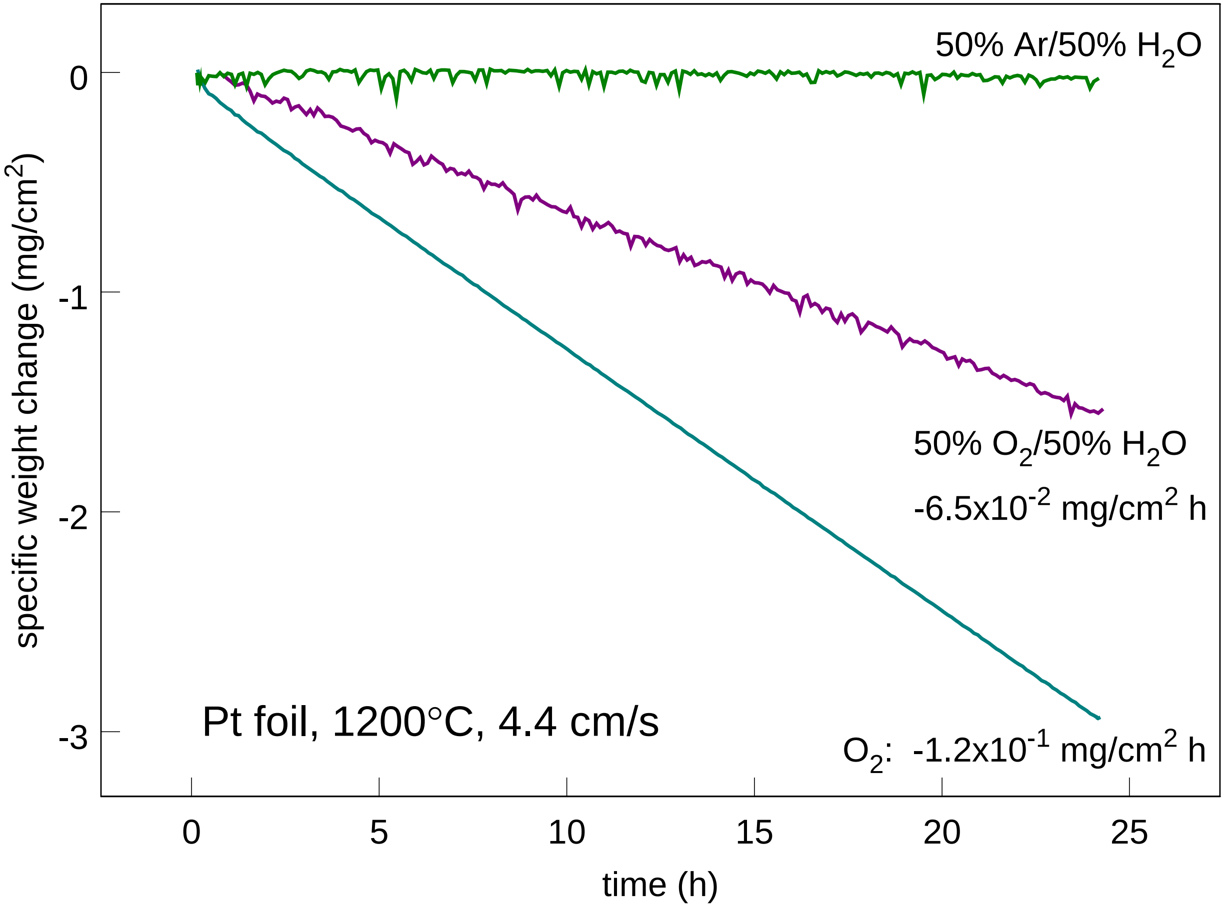
Pd-O-H system

- Pd used as current collector
- Pd-O-H vapor species include **PdOH**, Pd, $Pd(OH)_2$, PdO, and PdO_2
- No experimental data for hydroxide vapor species, data are estimated

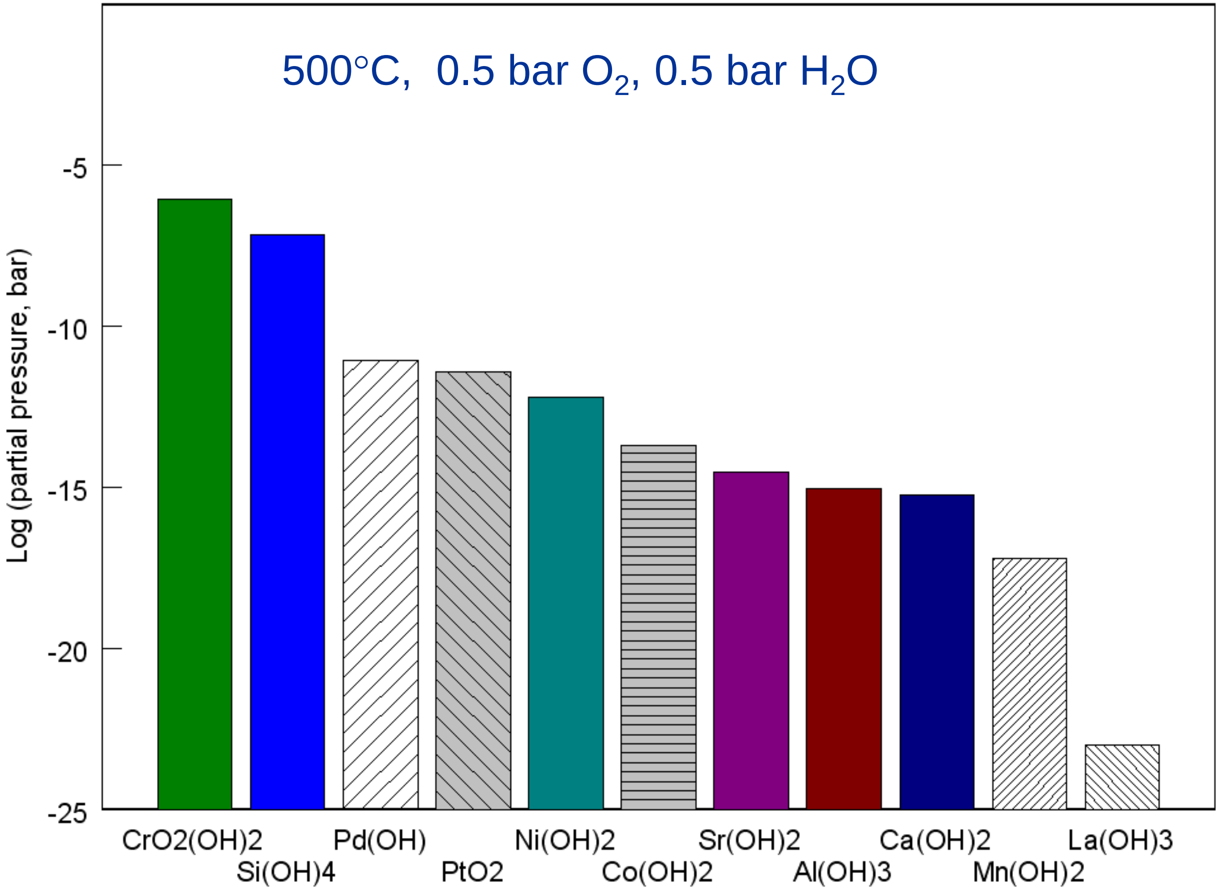


Pt-O-H system

- Pt used as current collector
- Pt-O-H vapor species include **PtO_2**, PtO, and Pt
- No data available for any hydroxide vapor species
- Experimental TGA results indicate that water vapor-Pt interactions are minimal



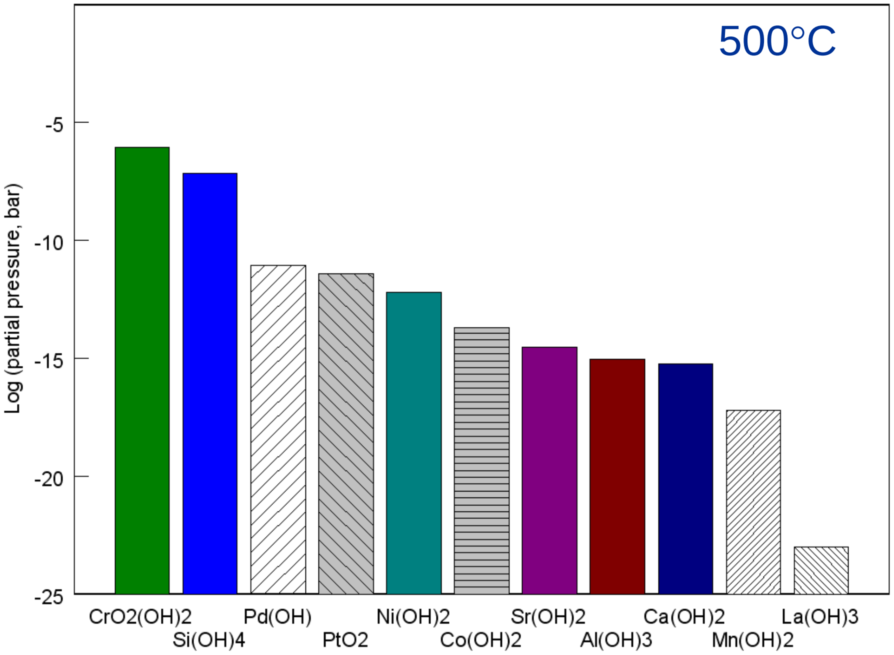
Summary of equilibrium gaseous metal hydroxide partial pressures

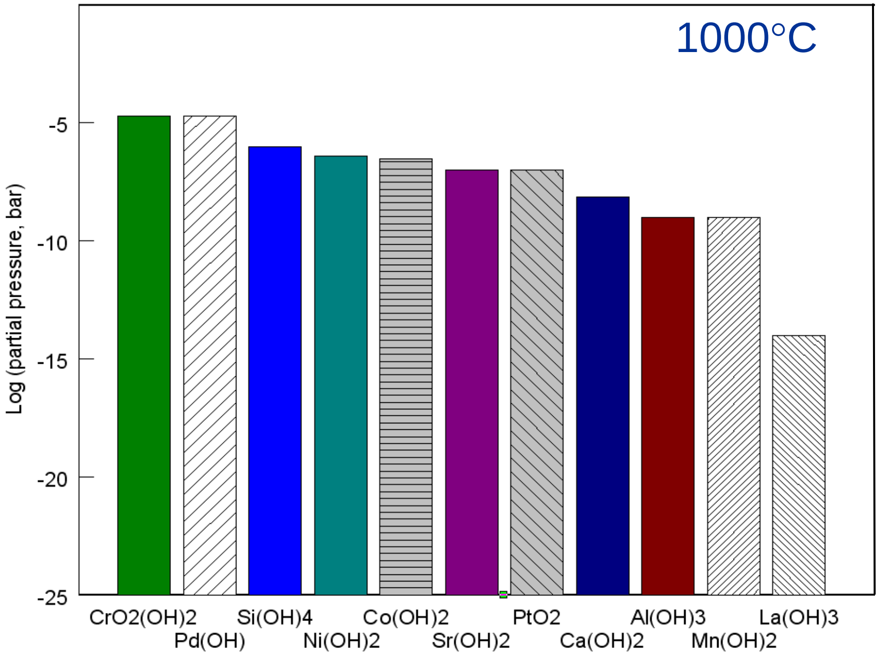


- Solid bars: good thermodynamic data
- Cross-hatched bars: thermodynamic data unreliable
- Gray cross-hatched bars: some experimental information about stability of gaseous metal hydroxides available, i.e $Co(OH)_2(g)$, $PtO_2(g)$

Summary of equilibrium gaseous metal hydroxide partial pressures: temperature effects

500°C, 0.5 bar O_2, 0.5 bar H_2O

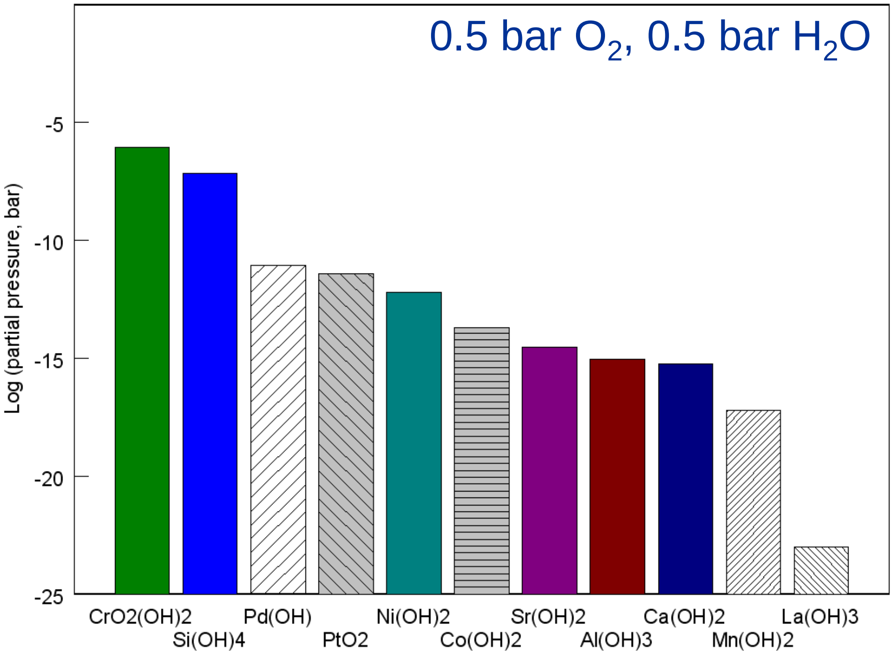


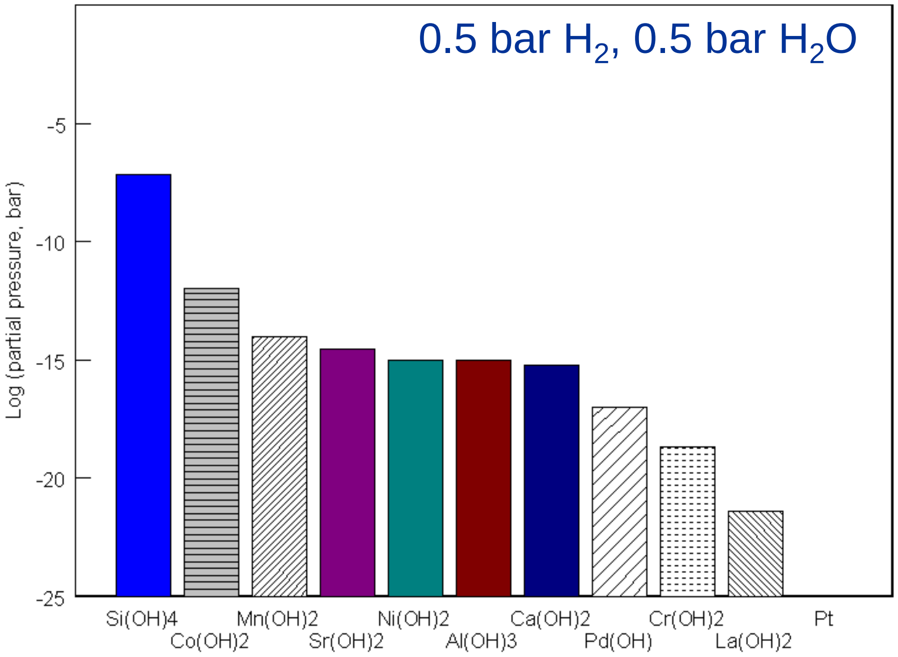


- Weak temperature dependence for $CrO_2(OH)_2$(g) and $Si(OH)_4$(g): minimal durability benefit by reducing temperature
- Stronger temperature dependence for other gaseous metal hydroxides

Summary of equilibrium gaseous metal hydroxide partial pressures: gas environment effects

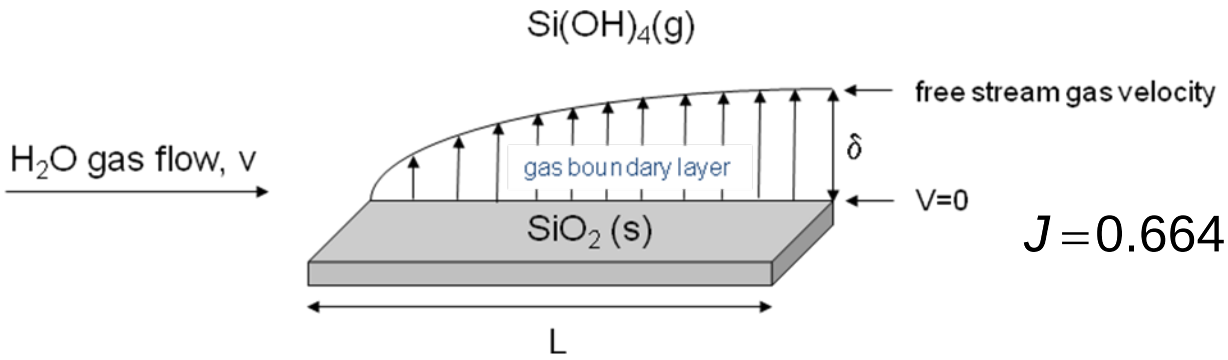
500°C





- P(MOH) dependent only on P(H_2O) do not change: Si$(OH)_4$(g)
- P(MOH) dependent on P(O_2) and/or P(H_2) can change dramatically: $CrO_2(OH)_2$(g) → $Cr(OH)_2$(g)
- MO – condensed phase reaction with environment can affect P(MOH): Ni/NiO or Co/CoO/Co_3O_4

Kinetics of volatilization limited by transport through laminar gaseous boundary layer



$$J = 0.664\left(\frac{\rho' v L}{\eta}\right)^{1/2}\left(\frac{\eta}{\rho' D}\right)^{1/3}\frac{D\rho}{L}$$

J = mass loss rate
ρ' = boundary layer gas density $\propto P_{total}$
D = interdiffusion coefficient $\propto 1/P_{total}$
ρ = $Si(OH)_4$ gas density $\propto P_{SiOH4}$
v = linear gas velocity
η = gas viscosity
L = characteristic length

Applications to SOFC

- Assumes laminar flow
- Assumes flat plate geometry - relevant for planar cell
- Related expression needed for mass transport from tube wall in flowing gas for tubular SOFC components
- More complete model needed to account for gas transport in pores of active surfaces

Summary and conclusions

- Experimental techniques are available for characterizing volatility of materials under conditions meaningful for SOFC applications
  - Thermodynamic data for prediction of materials durability can be obtained
- Accurate thermodynamic data for Cr_2O_3, SiO_2, Al_2O_3, Ni, SrO, CaO volatilization in high temperature water vapor are available
- Additional thermodynamic data are needed for gaseous hydroxides formed from La_2O_3, MnO, Pd, others?
- Component activities in complex oxides/alloys are needed to accurately predict materials durability in SOFC
- Kinetic models that accurately describe vapor transport in SOFC structures and incorporate gaseous metal hydroxide thermodynamics are needed

Acknowledgments

The thermodynamic data evaluation was made possible, in part, through funding from Rolls-Royce Fuel Cell Systems, Inc. under NASA Space Act Agreement SAA3-1031. This material is based upon work supported by the Department of Energy National Energy Technology Laboratory under Award Number DE-FE0000303.”

Fe-O-H system

- Fe found in interconnect alloys and LSF cathodes
- Fe-O-H vapor species include **$Fe(OH)_2$**, Fe(OH), FeO_2, FeO, and Fe
- Fe-O-H system studied by transpiration method in H_2, H_2O
  - G.R. Belton, F.D. Richardson, Trans. Faraday Soc. 58,1562 (1962).