Experimental and Theoretical Studies of Volatile Metal Hydroxides

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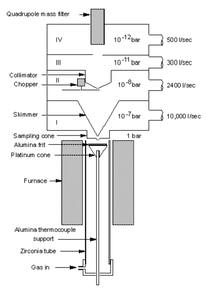
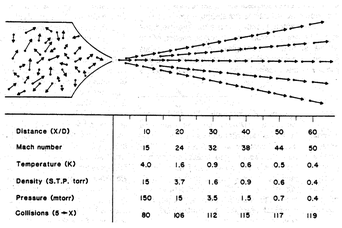
Modern superalloys used in the construction of turbomachinery contain a wide range of metals in trace quantities. In addition, metal oxides and silicon dioxide are used to form Thermal Barrier Coatings (TBC) to protect the underlying metal in turbine blades. Formation of volatile hydroxides at elevated temperatures is an important mechanism for corrosion of metal alloys or oxides in combustion environments (N. Jacobson, D. Myers, E. Opila, and E. Copland, ***J. Phys. Chem. Solids 66***, 471-478, 2005). Thermodynamic data is essential to proper design of components modern gas turbines. It is necessary to first establish the identity of volatile hydroxides formed from the reaction of a given system with high temperature water vapor, and then to establish the equilibrium pressures of the species under operating conditions. Theoretical calculations of reaction energies are an important check on experimental results. This presentation reports results for several important systems: Si-O-H, Cr-O-H, Al-O-H, Ti-O-H, and ongoing studies of Ta-O-H.

Identification of Chemical Species

1. High Pressure Sampling Mass Spectrometry

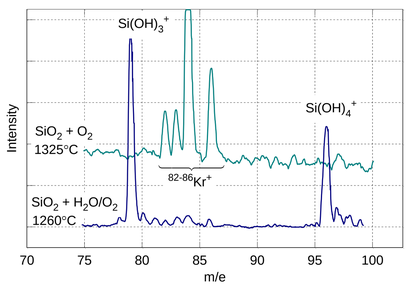




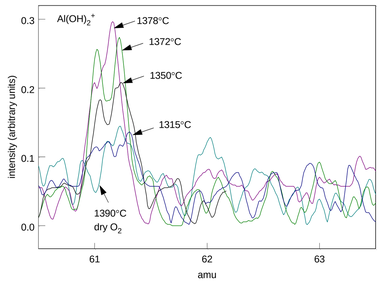
T. A. Miller, Science 223 (4636), 545 (1984)

- Free Jet Expansion Preserves Chemical and Dynamic Integrity of Gas
- Direct Sampling of Condensable Vapors

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



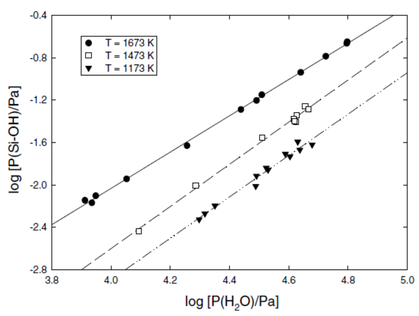
First Direct Observation of $Al(OH)_3(g)$



E.J. Opila, D.S. Fox, N.S. Jacobson, J. Am. Ceram. Soc. 80 (1997) 1009–1012

2. Pressure Dependence Measurements of Mass Loss from Coupons in Flowing Gas Streams

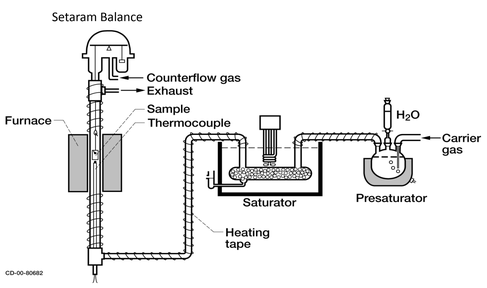
Variation of H_2O Partial Pressure yields Ratio of Hydroxyls to Metal



Plot of log P(Si-OH) vs log P(H_2O) to determine stoichiometry of Si-O-H species.

N.S. Jacobson et al. J. Chem. Thermodynamics 37 (2005) 1130–1137

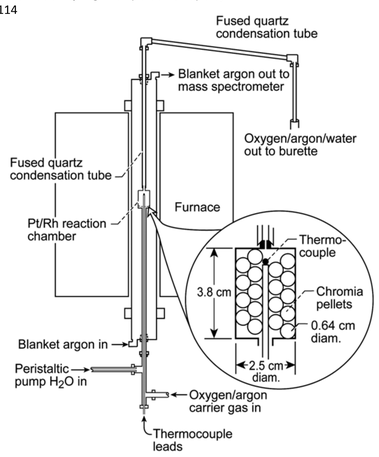
NASA Glenn Water Vapor TGA System



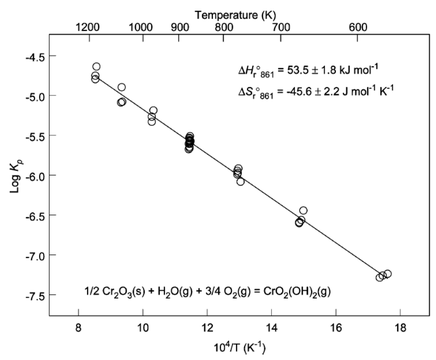
Measurement of Equilibrium Pressures of Volatile Hydroxides

1. Transpiration Technique

Merten, U. and W.E. Bell, *The Transpiration Method*, in *The Characterization of High Temperature Vapors*, J.L. Margrave, Editor. 1963, John Wiley & Sons: New York. p. 91-114



Pt20% Rh Transpiration Cell And Collection Tube. Fused Quartz Collection Tubes may also be used.



Opila, E.J., et al., J. Phys. Chem. A, 2007. **111**(10): p. 1971-1980

- System Design Minimizes Kinetic and Diffusion Effects
- Can use Reactive Gas Stream *e.g.* H_2O/O_2

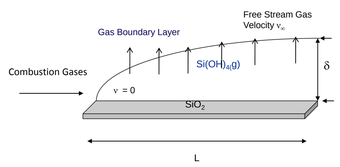
2. Boundary Layer Limited Gas Transport:

$$\text{Flux of Vapor Species (i)} = 0.664(\text{Re})^{0.5}(Sc)^{0.33}\frac{D_i P_i}{RTL}$$

$$= 0.664\left(\frac{v_\infty \rho_\infty L}{\eta}\right)^{0.5}\left(\frac{\eta}{D_i \rho_\infty}\right)^{0.33}\frac{D_i P_i}{RTL}$$

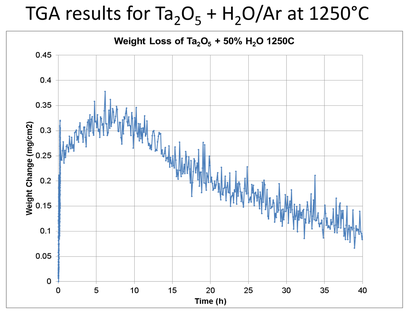
Laminar Flow, Expression for turbulent flow similar

- Larger hot zone ⇒ larger samples
- Wide range of atmospheres possible
  - H_2O(g), CO_2(g), SO_2(g), Cl_2(g), 5%H_2/Ar



- Correct for Diffusion Effects
- Model Ceramic Degradation
- Estimated Thermodynamics

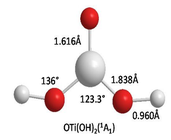
TGA results for Ta_2O_5 + H_2O/Ar at 1250°C



Computational Thermochemistry of Volatile Hydroxide Species

1. Computed Geometries and *gef*s using Statistical Mechanics

Computed Geometry for $TiO(OH)_2$(g)



Computed Geometries and Vibrational Frequencies used to compute *gef*s for Third Law Analysis:
gef= R[lnQ_t+lnQ_r+lnQ_v+lnQ_e]

VIBRATIONAL FREQUENCIES for $TiO(OH)_2$(g)

Vibrational mode	v/cm^{-1}
a1	3885.2
b2	3882.1
a1	1082.7
b2	805.3
a1	700.2
b1	529.1
a2	511.7
b2	510.3
a1	509.0
b2	234.9
a1	201.0
b1	49.1

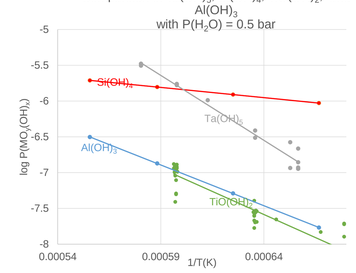
2. Quantum Chemistry Composite Methods

Gaussian 09, revision B.01, used to compute enthalpies of formation for $TiO(OH)_2$(g) and $CrO_2(OH)_2$(g). Geometries, harmonic vibrational frequencies computed with B3LYP/6-311++G(d,p), used for subsequent calculations. Electron correlation using CCSD, CCSD(T). Bauschlicher ANO basis set used for transition metals, obtained from Basis Set Exchange at the Environmental Molecular Science Laboratory at Pacific Northwest National Laboratory; cc-pVTZ for H and O.
MP2 theory for inclusion of Ti 3s and 3p core orbitals; Bauschlicher ANO set for transition metals modified by decontracting outermost six s, seven p, and seven d functions.
Correction for basis-set incompleteness estimated using large-basis-set MP2 energies with completely decontracted Bauschlicher ANO basis set on Ti and aug-cc-pVQZ set on H and O.
Scalar relativistic effects accounted for at the MP2 level using Douglas-Kroll-Hess second-order relativistic correction. Bauschlicher ANO set modified by decontracting entire s and p spaces used for transition metals; cc-pVTZ_DK set used for H and O.
Temperature corrections $H°_{298.15} - H°_0$ computed using B3LYP/6-311++G(d,p) harmonic vibrational frequencies, with a free rotor treatment of internal rotation of hydroxyl groups.

Gaussian 09: Frisch, M. J. et al., Gaussian 09, revision B.01; Gaussian Inc.: Wallingford, CT, 2009
CrO2(OH)2 Computations performed at Sandia National Laboratories by I.M. Nielsen and M.D. Allendorf : Opila, E.J., et al., **J. Phys. Chem. A, 2007 111**(10): p. 1971-1980; TiO(OH)2 Computations performed at OU Supercomputing Center for Education & Research (OSCER) at the University of Oklahoma, see Nguyen et al. NASA TM-2014-218372.

Summary

Comparison of $Ta(OH)_5$, $Si(OH)_4$, $TiO(OH)_2$, and $Al(OH)_3$ with $P(H_2O)$ = 0.5 bar



Enthalpies of Formation of Important Volatile Metal Hydroxides

Species	Method of Identification of Volatile Hydroxide Species	Method of Determining Thermodynamic Data	$\Delta_f H°_{298}$
$Si(OH)_4$(g)	Flow Rate Dependence, HPMS	Transpiration, Third Law	-1351.3±1.7 kJ/mol
$SiO(OH)_2$(g)	Flow Rate Dependence	Transpiration, Second Law	-836±40 kJ/mol
$Al(OH)_3$(g)	Flow Rate Dependence	Boundary Layer	$\Delta_f H°_{1630}$=-210±20 kJ/mol
$CrO_2(OH)_2$(g)	Flow Rate Dependence	Transpiration, Third Law	-741±6 kJ/mol
		Computational	-792±20 kJ/mol
$TiO(OH)_2$(g)	Flow Rate Dependence	Transpiration, Third Law	-403±13 kJ/mol
		Computational	-820±50 kJ/mol
$Ta(OH)_5$(g)	Flow Rate Dependence, HPMS	Boundary Layer	$\Delta_f H°_{1600}$=-151 kJ/mol

$Al(OH)_3$ data from: Opila and Myers, *J. Am. Ceram. Soc. 87*(9), 1701-1705 (2004)

Challenges:

- Low Equilibrium Partial Pressures of Species of Interest
- Boundary Layer Methods Provide Estimates of Thermodynamic Values Only
- Computational Methods Involving Transition Metals are Challenging – limited availability of suitable basis sets

Acknowledgements

Dr. Elizabeth Opila, University of Virginia
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