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

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

First Direct Observation of Si(Al)(OH)₄(g)

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

Variation of H₂O Partial Pressure yields Ratio of Hydroxyls to Metal

Plot of log P(H₂O)/P₀ vs log P(H₂O) to determine stoichiometry of Si-O-H species.


Measurement of Equilibrium Pressures of Volatile Hydroxides
1. Transpiration Technique

PT20% Rh Transpiration Cell
And Collection Tube. Fused Quartz Collection Tubes may also be used.

- System Design
- Minimizes Kinetic and Diffusion Effects
- Can use Reactive Gas Stream e.g. H₂O/O₂

2. Boundary Layer Limited Gas Transport:

Laminar Flow, expression for turbulent flow similar

Larger hot zone => larger samples
Wider range of atmospheres possible

Vibrational mode

δ

Correct for Diffusion Effects
Model Ceramic Degradation
Estimated Thermodynamics

Computational Thermochemistry of Volatile Hydroxide Species
1. Computed Geometries and gef using Statistical Mechanics

Computed Geometry for Ti(OH)₄(g)

VIBRATIONAL FREQUENCIES for Ti(OH)₄(g)

2. Quantum Chemistry Composite Methods

Gaussian 09, revision B.01, used to compute enthalpies of formation for Ti(OH)₄(g) and Cr₂O₃(OH)₃(g). Geometries, harmonic vibrational frequencies computed with B3LYP/6-31+G(d,p) set modified by decontracting outermost 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-pVTZ 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 OK set used for H and O. Temperature corrections H°(g) = H°(g)⁺H°(g) computed using B3LYP/6-31+G(d,p) harmonic vibrational frequencies, with a flow rotor treatment of internal rotation of hydroxyl groups. Gaussian 09 (Frisch, M. J. et al., Gaussian, Inc., Wallingford, CT, 2009) CCSD(T)/CBS Computations performed at Sandia National Laboratories by I.M. Nielsen and M.D. Bauschlicher.

Summary

Comparison of Ta₂O₇, SiO₂, and H₂O/Ar with TiO(OH)₂

Enthalpies of Formation of Important Volatile Metal Hydroxides

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

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