

1. FINAL REPORT

U.S. Department of Energy

Acid-Base Behavior in Hydrothermal Processing of Wastes

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Project Number:

Grant Number: DOE DE-FG07-96ER14687

Grant Project Officers: Carol van Lente

Project Duration: 9-15-96 to 9-14-00

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3. Executive Summary

A new technology, hydrothermal oxidation (also called supercritical water oxidation), is being developed to treat high level nuclear wastes. Nitrates are reduced to nitrogen; furthermore, phosphates, alumina sludge, and chromium are solubilized, and the sludge is reconstituted as fine oxide particles. Chromium is a key species to be removed from nuclear wastes. A major obstacle to development of this technology has been a lack of scientific knowledge of chemistry in hydrothermal solution above 350 °C, particularly acid-base behavior, and transport phenomena, which is needed to understand corrosion, metal-ion complexation, and salt precipitation and recovery. Our objective has been to provide this knowledge with in-situ UV-vis spectroscopic measurements and fully molecular computer simulation.

Recent UV-visible spectroscopy studies have provided major insight into the quantitative behavior of equilibrium constants of acid-base and redox reactions in supercritical water. Our recent development of relatively stable organic UV-visible pH indicators for SCW offers the opportunity to characterize buffers and to monitor acid-base titrations. For reactions which contain chromophores such as Cr(VI) and NO_x , a series of equilibrium constants has been measured, in some cases with a non-linear programming optimization model. The reaction equilibria involving the chromate and bichromate ions has been studied over a wide range of density up to 400 °C. Both temperature and density have a large effect on the equilibrium constants, ion pairing and electrostriction of water about various ions. Progressive ionic association eventually leads to K_2CrO_4 precipitation at 420 °C. UV-Vis spectroscopy was utilized to measure the decomposition of aqueous HNO_3 solutions above 300 °C, in some cases with added NaOH, H_2O_2 , and/or NaNO_2 , to form NO_2 , HNO_2 , NO, N_2O and oxygen. With constrained nonlinear optimization, areas of these bands were used to determine extinction coefficients of NO_2 and HNO_2 and, for the first time, equilibrium constants for the reactions: $\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$; $2 \text{HNO}_3 = \text{H}_2\text{O} + 2 \text{NO}_2 + 1/2 \text{O}_2$; $2 \text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2$; $2 \text{HNO}_2 = \text{H}_2\text{O} + 2 \text{NO} + 1/2 \text{O}_2$; $2 \text{NO} = \text{N}_2\text{O} + 1/2 \text{O}_2$; and $(\text{Na}^+)(\text{NO}_3^-) = \text{Na}^+ + \text{NO}_3^-$. For NO_x reaction equilibrium constants, density effects follow expected trends on the basis of reaction polarity changes and extrapolations to zero density agree with gas-phase literature values.

In our theoretical studies, we have focused on the study of the transport properties of aqueous ions in supercritical water and hydrolysis reactions that play a key role in supercritical water oxidation. We have developed a fundamental mechanism of ion transport in supercritical water that takes into account the unusual solvent dynamics at these conditions. For the first time, the effect of supercritical water density on the transition between ionic and covalent reaction mechanisms has been determined by computer simulation for a hydrolysis reaction. The effects were investigated using an empirical valence bond theory that explicitly includes the effects of solvation, particularly those on the ionic reaction pathway. Molecular dynamics simulations with free energy perturbation have been used to construct the reaction free energy surface for the dissociation of t-butyl chloride in three supercritical water densities and in ambient water, for comparison. The results of the simulations indicate that local density enhancement provides the solvation energy required to stabilize the ionic state at very low supercritical water solvent densities. These results can be explained by changes in the solvation of the pure ionic state, which is significantly lowered in energy as solvent density, and therefore dielectric constant, is increased. These results also indicate that the crossover to the covalent reaction pathway would occur at the remarkably low density of about 0.03 g cm^{-3} , significantly lower than that indicated by simple continuum models of the solvent. These results have important implications for understanding reaction pathways and yields for decomposition of wastes in supercritical water.

New chemical processes are needed to separate chromium and other metals from tank wastes. Ideally they should not utilize additional reagents which would increase waste volume or require subsequent removal. Hydrothermal oxidation can achieve these goals. Our studies of the equilibrium constants for reactions of chromate and bichromate ions are useful for understanding separation of chromium ions from these nuclear wastes after hydrothermal oxidation. Many of the DOE wastes contain high concentrations of nitrates, and the equilibrium of these species is of interest in hydrothermal oxidation. Our studies of the decomposition of aqueous HNO_3 solutions above 300°C , in some cases with added NaOH , H_2O_2 , and/or NaNO_2 , to form NO_2 , HNO_2 , NO , N_2O and oxygen are useful for designing these waste reduction processes. The fundamental understanding of ion transport is useful for controlling salt precipitation and corrosion in hydrothermal oxidation processes and for interpreting conductivity studies of equilibrium constants, primarily at ORNL.

4. Objectives

The first objective of the experimental studies has been to determine the equilibria for Cr(VI) up to 420 °C as this is a key species to be removed from nuclear wastes. A wide range of concentrations of KOH and perchloric acid were utilized to manipulate the acid-base equilibria and to understand the effects of ion solvation and ion pairing. The second objective was to measure quantitatively the equilibria between nitric acid, nitrous acid, nitrogen dioxide, nitrite and nitrate ions and oxygen. For both of these systems, chemical equilibria have not been measured previously in hydrothermal solution at these temperatures.

On the theoretical side, we have focused on the study of the transport properties of aqueous ions in supercritical water and hydrolysis reactions that play a key role in supercritical water oxidation. The motivation for the transport studies is two fold. First, although transport coefficients are fundamental to solution chemistry reaction rates, the behavior of such transport properties over wide ranges of density and temperature are not well established experimentally, particularly at the densities typically of interest (< 0.5 g/cc). Second, due to practical challenges, ionic association equilibria in SCW is typically accessed via measurements of conductivity followed by analysis through a theoretical model that incorporates ion pairing. The results of these analyses in the interesting low density region have yielded results for the limiting infinite dilution conductivity of alkali halides which are not consistent among labs. Our goal has been to determine independently via computer simulation what one should expect of these transport coefficients and to provide a fundamental understanding of behavior.

We have initiated modeling and simulation of aqueous hydrolysis reactions in SCW due to their ubiquitous presence in SCW oxidation reactions. Under ambient aqueous conditions, the first step of an S_N1 reaction occurs by initial separation into an *ion* pair, with typical further reaction of a carbocation. However, the relative stability of the ion pair and the alternative reaction path involving separation into a *neutral* radical pair depends very directly on the solvent polarity. Even in ambient water, it has been demonstrated that a free energy barrier to separation arises due to the transition from a covalent to a separated ionic state. As is widely appreciated in other contexts, SCW offers *tunable* polarity. Thus, one should expect not only that reaction barriers depend on solvent density, but also that the underlying mechanism itself will vary.

For the t-butyl chloride system, which we have used as a model system, the two most important states are a covalent state with a bonding interaction and no charge separation, and an ionic state with full charge separation as t-butyl cation and chloride anion. A fundamental understanding of transitions between these reaction pathways in supercritical water, as a function of solvent density, is useful for developing strategies to achieve efficient waste destruction in supercritical water oxidation.

5. Methods and Results

The methods and results are reported as a series of abstracts of published papers. The papers should be consulted for further details.

Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. ; Hyun, J.-K. Aqueous Ion Transport Properties and Water Reorientation Dynamics from Ambient to Supercritical Conditions. *J. Phys. Chem. B.* **1998**, *102*, 3806-3814.

Ion transport properties including the friction coefficient, Walden product (product of conductivity and viscosity), and the limiting equivalent conductance are predicted in water at elevated temperatures using a semi-continuum model. Molecular dynamics computer simulation is used to determine water rotational reorientation times in the first coordination shell compared to the bulk, and the results are incorporated into a hydrodynamic expression for the ionic friction coefficient. Along the coexistence curve of water, the effective Stokes-Einstein radius implied by the model is relatively constant, but for Cl^- , K^+ , and Rb^+ it increases at typical supercritical water conditions, where the motion of the first shell water molecules is coupled more closely to that of the ion. For Na^+ , the coupling is already quite strong at higher solvent densities. The increment to the friction coefficient in excess of the bare ion Stokes-Einstein result contributes a larger fraction of the total in supercritical water at typical densities (up to 0.29 g/cm^3) than it does in higher density subcritical water, as a result of electrostriction. The limiting equivalent conductance is found to increase approximately linearly with decreasing solvent density in the supercritical regime, in qualitative accord with the experimental extrapolations of Quist and Marshall and in contrast to the plateau with decreasing density inferred from much more recent experiments by Zimmerman *et al.*

Chlistunoff, J. B. ; Johnston, K. P. UV-Vis Spectroscopic Determination of the Dissociation Constant of Bichromate from 160°C to 400°C. *J. Phys. Chem. B.* **1998**, *102*, 3993-4003.

On the basis of direct measurements by UV-Vis spectroscopy, the dissociation constant of bichromate was found to decrease with temperature from 160 to 400 °C. For fixed Cr(VI) and KOH concentrations, the molal concentration of HCrO_4^- initially increases with temperature but decreases again in the vicinity of water's critical point where the density decreases substantially. The decrease in HCrO_4^- at high temperature and low density may be attributed to $(\text{K}^+)(\text{CrO}_4^{2-})$ ion pairs, to a high degree of electrostriction about CrO_4^{2-} , which facilitates the reaction $\text{HCrO}_4^- + \text{OH}^- = \text{CrO}_4^{2-} + \text{H}_2\text{O}$, and to ion activity coefficients.

Chlistunoff, J. B.; Ziegler, K. J.; Lasdon, L. ; Johnston, K. P. Nitric/Nitrous Acid Equilibria in Supercritical Water. *J. Phys. Chem. A.* **1999**, *103*, 1678-1688.

UV-Vis spectroscopy was utilized to measure the decomposition of aqueous HNO_3 solutions above 300 °C, in some cases with added NaOH , H_2O_2 , and/or NaNO_2 , to form NO_2 , HNO_2 , NO , N_2O and oxygen. Individual bands corresponding to HNO_2 and NO_2 were deconvoluted from the spectra up to 400 °C. With constrained nonlinear optimization, areas of these bands were used to determine extinction coefficients of NO_2 and HNO_2 and equilibrium constants for the reactions: $\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$; $2 \text{HNO}_3 = \text{H}_2\text{O} + 2 \text{NO}_2 + 1/2 \text{O}_2$; $2 \text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2$; $2 \text{HNO}_2 = \text{H}_2\text{O} + 2 \text{NO} + 1/2 \text{O}_2$; $2 \text{NO} = \text{N}_2\text{O} + 1/2 \text{O}_2$; and $(\text{Na}^+)(\text{NO}_3^-) = \text{Na}^+ + \text{NO}_3^-$.

Ziegler, K. J.; Lasdon, L.; Chlistunoff, J. ; Johnston, K. P. Optimization Models for Determining Nitric Acid Equilibria in Supercritical Water. *Computers and Chemistry.* **1999**, *23*, 421-434.

Optimization models are developed to determine equilibrium constants for dissociation, redox and disproportionation reactions involving nitric and nitrous acid, NO_2 , NO , N_2O , NO_3^- , and oxygen in supercritical at temperatures of 380°C and 400°C and at pressures of 276 to 414 bar. A constrained nonlinear programming (NLP) model of moderate size is developed to estimate equilibrium constants and extinction coefficients. This model is optimized using an implementation of the generalized reduced gradient (GRG) algorithm. Although it was only

possible to measure the absorbance of two of the twelve species by UV-Vis spectroscopy, six equilibrium constants and two extinction coefficients could be optimized. Significant improvements of these values are obtained with a Jackknife Statistical implementation. Linear extrapolation of the log K versus density plots to zero density results in values which are very close to independent gas-phase values.

Westacott, R. E.; Johnston, K. P. ; Rossky, P. J. Stability of Ionic and Radical Molecular Dissociation Pathways for Reaction in Supercritical Water. *sub. to J. Phys. Chem.* **2001**,

Molecular dynamics simulations have been used to examine the effect of supercritical water solvent density on the competition between reaction pathways for the dissociation step of a model S_N1 reaction. The effects are investigated using an empirical valence bond theory that explicitly includes the effects of solvation, particularly those on the diabatic ionic state. At low supercritical water densities, the solvent stabilization is insufficient to give rise to a local minimum on the free energy surface corresponding to a contact ion pair intermediate, although the free energy surface is completely ionic in character to solvent densities less than 0.05 g cm^{-3} . The nature of the surface is also changed by solvent density; the change from a mostly covalent (80 %) molecule to completely ionic dissociation products is decreasingly rapid as supercritical water density is decreased. Radial density functions reflect how solvation changes along the reaction coordinate and how local density enhancement provides the solvation required to stabilize the ionic products. These calculations indicate that the diabatic ionic state is lowest in free energy until extremely low supercritical water solvent density ($\sim 0.03 \text{ g cm}^{-3}$), considerably lower than would be expected if local density enhancement were ignored, as in a simple Born model calculation. The free energy difference between the two pure states at the dissociation plateau indicates that covalent products may be expected to reach approximately 22 % of the total at the lowest density (0.0435 g cm^{-3}) considered here.

6. Relevance, Impact and Technology Transfer

Treatment of High Level Waste (HLW) is the second most costly problem identified by OEM. In order to minimize costs of disposal, the volume of HLW requiring vitrification and long term storage must be reduced. Methods for efficient separation of chromium from waste sludges, such as the Hanford Tank Wastes (HTW), are key to achieving this goal since the allowed levels of chromium in the high level glass control waste loading. Chromium in sludges

most likely exists as the extremely insoluble oxides and minerals, with chromium in the plus III oxidation state. In order to solubilize and separate it from other sludge components, Cr(III) must be oxidized to the more soluble Cr(VI) state. New chemical processes are needed to separate chromium and other metals from tank wastes. Ideally they should not utilize additional reagents which would increase waste volume or require subsequent removal. Hydrothermal oxidation can achieve these goals. Our studies of the equilibrium constants for reactions of chromate and bichromate ions are useful for understanding separation of chromium ions from these nuclear wastes after hydrothermal oxidation.

Many of the DOE wastes contain high concentrations of nitrates, and the equilibrium of these species is of interest in hydrothermal oxidation. To address this, UV-Vis spectroscopy was utilized in our lab to measure the decomposition of aqueous HNO_3 solutions above 300 °C, in some cases with added NaOH, H_2O_2 , and/or NaNO_2 , to form NO_2 , HNO_2 , NO, N_2O and oxygen. Reactions involving NO, NO_2 , H_2O , HNO_3 , HNO_2 and O_2 in the gas phase play a crucial role in nitric acid production, combustion, and waste incineration. These reactions have been studied extensively in both the gas phase and for a gas phase in contact with an aqueous phase, typically at temperatures below 100 °C.

More recently NO_x chemistry has been studied in hydrothermal oxidation (HO) (also called supercritical water oxidation (SCWO)). In HO, an aqueous waste containing organics is oxidized by oxygen in supercritical water (SCW), i.e., at temperatures higher than 374 °C (typically around 500 °C and above 220 bar). Thermodynamics and kinetics favor significantly less NO_x at the relatively low temperatures in HO compared with incineration where temperatures are typically 1200 °C or more. Kinetic studies of oxidation reactions of organic compounds by nitrates suggested that the reactive species in SCW solutions of nitrates can be NO_2 . Recently, it was suggested that nitrates present in certain high level and mixed nuclear wastes could be used as an oxidizing agent instead of oxygen in the HO pretreatment of these wastes. It has been proposed that ammonium nitrate recovered from demilitarized rocket motors may be utilized as an oxidizing agent in HO. In addition, NO_x chemistry is also important in rapid hydrolysis of metal nitrates to form sub-micron metal oxide crystals.

On the theoretical side, we have completed a very important simulation study of ion transport in water under extreme conditions and also initiated a highly novel investigation of hydrolysis reactions in SCW. The motivation for the study of transport is based on the

facts that 1) transport coefficients are fundamental to solution reaction rates, but the behavior of such transport properties over wide ranges of density and temperature are not well understood, and 2) ionic association equilibria under extreme conditions in SCW is typically accessed indirectly via interpretations of conductivity measurements through ion pairing models. Although there is some variation, results suggest a linear increase in ionic diffusion constant with decreasing density at higher densities, turning over to a plateau in the most interesting region of SCW densities. We have for the first time developed a complete physical explanation of the conductivity data, using computer simulation to analyze the transport coefficients. We have demonstrated that the plateau in the data is reproduced computationally and is associated with an increasing imbalance between water-water forces and the stronger solvent-solute forces acting on the solvent in the ionic hydration shell. This shell remains intact throughout the measured density region but exerts an increasing friction on the ion with decreasing density. At densities below those measured experimentally to date, the hydration shell does begin to degrade, in accord with our earlier interpretation as solvent adsorption, and the transport rate is predicted to resume an increase. Of perhaps most importance, the calculated results have led to a suggested manner in which to analyze purely experimental data in order to best elucidate the physical content.

7. Project Productivity

The productivity matched expectations as is evident in the list of publications and presentations below for both the experimental and computer simulation studies. The productivity is further described in the sections above.

8. Personnel Supported (Ph.D. theses are available from University Microfilms)

Keith Johnston (Professor)

Peter Rossky (Professor)

Lewis Flanagan (MS. Student) "Theoretical Models of Solvation Thermodynamics in Hydrothermal Media"

Perla Balbuena (Ph.D. Student) "Structure and Dynamics of Electrolyte Solutions in Ambient and Supercritical Water: Effects on Solvation Properties and Chemical Reactions"

J.-K Hyun (Post-doc)

Kirk Ziegler (Ph.D. Student) in progress

William Wofford (Ph.D. Student) "Spectroscopic Studies of Acid-Base Behavior and pH Measurement in Supercritical Water"

Robin Westacott (Post-doc)

9 Publications

(1) Flanagan, L. W.; Balbuena, P. B.; Johnston, K. P. ; Rossky, P. J. Ion Solvation in Supercritical Water Based on an Adsorption Analogy. *J. Phys. Chem.* **1997**, *101*, 7798-8005.

(2) Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. ; Hyun, J.-K. Aqueous Ion Transport Properties and Water Reorientation Dynamics from Ambient to Supercritical Conditions. *J. Phys. Chem. B.* **1998**, *102*, 3806-3814.

(3) Chlistunoff, J. B. ; Johnston, K. P. UV-Vis Spectroscopic Determination of the Dissociation Constant of Bichromate from 160°C to 400°C. *J. Phys. Chem. B.* **1998**, *102*, 3993-4003.

(4) Chlistunoff, J. B.; Ziegler, K. J.; Lasdon, L. ; Johnston, K. P. Nitric/Nitrous Acid Equilibria in Supercritical Water. *J. Phys. Chem. A.* **1999**, *103*, 1678-1688.

(5) Johnston, K. P. ; Chlistunoff, J. B. Neutralization of Acids and Bases in Subcritical and Supercritical Water: Acetic Acid and HCl. *J. Supercritical Fluids.* **1998**, *12*, 155-64.

(6) Wofford, W. T.; Gloyna, E. F. ; Johnston, K. P. Boric Acid Equilibria in Near-Critical and Supercritical Water. *Ind. Eng. Chem. Res.* **1998**, *37*, 2045-51.

(7) Ziegler, K. J.; Lasdon, L.; Chlistunoff, J. ; Johnston, K. P. Optimization Models for Determining Nitric Acid Equilibria in Supercritical Water. *Computers and Chemistry.* **1999**, *23*, 421-434.

(8) Ziegler, K. J.; Chlistunoff, J. ; Johnston, K. P. Spectroscopic Studies of Chemical Equilibrium in Supercritical Water: Cr(VI) and NO_x Chemistry. In *Steam, Water and*

Hydrothermal Systems: Physics and Chemistry Meeting the Needs of Industry; P. R. Tremaine, Ed.; NRC Research Press: Ottawa, 2000, 441-447.

(9) Johnston, K. P. ; Rossky, P. J. Solution Chemistry in Supercritical Water: Spectroscopy and Simulation. In *Supercritical Fluids Fundamentals and Applications*; P. D. E. Kiran, C. Peters, Ed.; Kluwer Acad.: Dordrecht, 2000, 323-344.

(10) Rossky, P. J. ; Johnston, K. P. Chemistry in Supercritical Water: Insights from Theory and Simulation. In *Steam, Water & Hydrothermal Systems: Physics & Chemistry Meeting the Needs of Industry*; P. R. Tremaine, Hill, P.G., Irish, D.E., Balakrishnam, P.V., Ed.; NRC Research Press: Ottawa, 2000, 391-401.

(11) Westacott, R. E.; Johnston, K. P. ; Rossky, P. J. Stability of Ionic and Radical Molecular Dissociation Pathways for Reaction in Supercritical Water. *sub. to J. Phys. Chem.* **2001**,

(12) Westacott, R. E.; Johnston, K. P. ; Rossky, P. J. Simulation of an SN1 Reaction in Supercritical Water. *sub. to J. Am. Chem. Soc.* **2001**,

10. Interactions

"Spectroscopic and Simulation Studies of Acid-Base Equilibria in Supercritical Water Solutions" (with Perla Balbuena, Tao Xiang, Will Wofford and Lewis Flanagan) Fifth Int. Symp. on Hydrothermal Reactions, Gatlinburg, TN; July 21, 1997

"UV-visible Spectrophotometric Study of Acid-base Equilibria of Chromates in Sub- and Supercritical Water" (with Jerzy Chlistunoff) Fifth Int. Symp. on Hydrothermal Reactions, Gatlinburg, TN; July 22, 1997

"Spectroscopy and Simulation of Supercritical Water Solutions", Short Course on Supercritical Water Oxidation, Austin, TX, February 26, 1998.

"Molecular Simulation of Chemistry in Supercritical Water" (with P.J. Rossky, P. Balbuena) Am. Chem. Soc. Nat. Mtg., Dallas, TX; April 1, 1998.

"Acid-Base Behavior in Hydrothermal Processing of Wastes" DOE Workshop on Environmental Management, Chicago, IL, July 28, 1998

"Determination of Nitric Acid Decomposition Equilibria in Supercritical Water" , Am. Inst. Chem. Eng. Ann. Mtg., Miami Beach, FL, Nov. 20, 1998. (with J. Chlistunoff, K. Ziegler, L. Lasdon)

"Chemistry in Supercritical Water: Insights from Theory and Simulation" 13th. Int. Conf. On the Properties of Water and Steam, Toronto, Canada, September 15, 1999 (with Peter Rossky)

"Hydrolysis reactions in supercritical water: A computer simulation study" Am. Chem. Soc. 220th Nat. Mtg., Washington, DC, August 22, 2000 (with R. Westacott, P. Rossky)

"Chemistry in Supercritical Water: Insights from Theory and Simulation" Pacifichem., Honolulu, HI, December 15, 2000 (with P. Rossky)

"Spectroscopy and Reactions in Supercritical Water", Tokyo University, Dept. Chem. Systems Engineering, Tokyo, Japan, May 16, 1997.

"Spectroscopy and Solvent Effects on Reactions in Supercritical Fluids", U. of Delaware, Depts. of Chemistry and Chemical Engineering, Newark, DE, September 22, 1997.

"Solution chemistry in supercritical water: spectroscopy and simulation", NATO Advanced Study Institute on Supercritical Fluids, Kemer, Turkey, July 16, 1998.

"Spectroscopic Studies of Chemical Equilibrium in Supercritical Water: Cr(VI) and NO_x Chemistry", 13th. Int. Conf. On the Properties of Water and Steam, Toronto, Canada, September 15, 1999.

"Future Directions in Supercritical Fluid Science and Technology: The Third Decade", Plenary Lecture, 5th. Int. Symp. On Supercritical Fluids, Atlanta, GA, April 12, 2000.

5/97 Pacific Northwest National Laboratory, "Computer Simulation Studies of Solvation and Chemistry in Supercritical Water."

- 5/97 University of Washington, "Electronic Dynamics and Relaxation in Solution."
- 10/97 Laboratory Leon Brillouin, CEA, Saclay, France, "Thermodynamics and Chemistry in Supercritical Water Solutions"
- 2/98 Tel Aviv University, Israel, "Chemistry in Supercritical Water"
- 4/98 American Chemical Society National Meeting, Symposium on Supercritical Fluids,
"Molecular Simulation of Chemistry In Supercritical Water"
- 12/98 Symposium on "Dynamics of Small Many-Body Systems" Tokyo, Japan, "Chemistry in Supercritical Water"
- 12/98 Institute for Chemical Research, Kyoto, Japan "Ionic Solvation in Supercritical Water"
- 12/98 Kyoto University, Kyoto, Japan, "Chemistry in Supercritical Water"
- 7/99 26th International Conference on Solution Chemistry, Fukuoka, Japan, "Structure and Dynamics in Supercritical Water Solutions"
- 8/99 Gordon Research Conference on the Chemistry and Physics of Liquids, "Chemical Consequences of Solvent Clustering in Supercritical Water Solutions"
- 9/99 International Conference on Properties of Water and Steam, Toronto, Canada, Ted Whalley Lecture "Chemistry in Supercritical Water: Insights from Theory and Simulation"
- 2/00 University of Texas at San Antonio, "Chemistry in Supercritical Water: Insights from Theory and Simulation"

2/00 Angelo State University, "Chemistry in Supercritical Water: Insights from Theory and Simulation"

2/00 Austin College, "Chemistry in Supercritical Water: Insights from Theory and Simulation"

9/00 Georgia Tech University, "Chemistry in Supercritical Water: Insights from Theory and Simulation"

11. Transitions

Steve Buelow at LANL is utilizing knowledge gained in this work in their development of supercritical water oxidation technology for treating LANL nuclear wastes.

Peter Tremaine at the Memorial University of Newfoundland is extending our work on UV-vis spectroscopy in supercritical water. His work is performed for Canadian power generation companies.

Will Wofford obtained a Ph.D. in this project and started a company, Hydroprocessing Inc. He is building a commercial supercritical water oxidation plant in Brownsville, TX.

Tad Adschiri at Tohoku University is using the knowledge we gained in NO_x chemistry to develop hydrothermal synthesis technology for metal oxides.

12. Patents

none

13. Future Work

Two aspects of this project led to extremely important future work. The project enhanced the collaboration between Keith Johnston and Peter Rossky in the area of molecular simulation of supercritical fluid systems. We have new support to study carbon dioxide-water interfaces with support from NSF in an NSF Science and Technology Center and the Welch Foundation. The high temperature equipment and experimental procedures in this proposal were used to launch a

new research project in the field of high temperature synthesis of nanoparticles and nanowires in supercritical fluids. This work is supported by DOE BES.

14. Literature Cited- none (hundreds are given in our published papers)

15. Feedback. None. This program was very well managed.