

PHYSICAL CHEMISTRY AND THE ENVIRONMENT

T. H. Dunning, Jr.
B. C. Garrett

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Pacific Northwest Laboratory
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*Physical
Chemistry
and
the
Environment*

A Symposium at the

206th National Meeting of the
American Chemical Society

22-27 August 1993
Chicago, Illinois

Organized by:

Thom H. Dunning, Jr. and Bruce C. Garrett
Molecular Science Research Center
Pacific Northwest Laboratory, Richland, WA

with Charles E. Kolb, Jr.; Robert W. Shaw;
Gregory R. Choppin; and Albert F. Wagner

From the ozone hole and the greenhouse effect to plastics recycling and hazardous waste disposal, society faces a number of issues, the solutions to which require an unprecedented understanding of the properties of molecules. We are coming to realize that the environment is a coupled set of chemical systems, its dynamics determining the welfare of the biosphere and of humans in particular. These chemical systems are governed by fundamental molecular interactions, and they present chemists with an unparalleled challenge. The application of current concepts of molecular behavior and of up-to-date experimental and computational techniques can provide us with insights into the environment that are needed to mitigate past damage, to anticipate the impact of current human activity, and to avoid future insults to the environment.

Environmental chemistry encompasses a number of separate, yet interlocking, areas of research. In all of these areas progress is limited by an inadequate understanding of the underlying chemical processes involved. Participation of all chemical approaches – experimental, theoretical and computational – and of all disciplines of chemistry – organic, inorganic, physical, analytical and biochemistry – will be required to provide the necessary fundamental understanding. The Symposium on "Physical Chemistry and the Environment" was designed to bring the many exciting and challenging physical chemistry problems involved in environmental chemistry to the attention of a larger segment of the physical chemistry community.

The symposium on "Physical Chemistry and the Environment" was organized into six sessions: General, Atmospheric Chemistry, Contaminated Soils & Groundwater, Toxic Waste Destruction, Treatment of Nuclear Wastes, and Pollutant Formation in Flames. Each session consisted of two types of presentations:

- (i) overviews that reduced important environmental problems to the underlying questions in physical chemistry and
- (ii) presentations that provided exemplary examples of research in physical chemistry that address current environmental problems.

Summaries of the presentations given in each of these sessions were prepared by the session chairpersons. These summaries follow.

General Session

Chairman: Dr. Thom H. Dunning, Jr., Pacific Northwest Laboratory

The symposium was opened by Dr. Thom H. Dunning, Jr. (Molecular Science Research Center, Pacific Northwest Laboratory). Dr. Dunning noted that the U.S. Department of Energy is faced with enormous challenges in cleaning up its weapons sites and laboratories. Cost estimates range up to \$1 trillion with clean up times estimated to exceed 30 years. Superfund sites under the jurisdiction of the U.S. Environmental Protection Agency face similar problems. Remediation of contaminated sites involve the resolution of both political and scientific issues. The most serious scientific and technical problems are (1) an inadequate understanding of the fate of hazardous wastes in the environment and (2) a lack of effective, efficient, cost-effective technologies for cleaning up contaminated sites. Physical chemistry is an integral part of the solution of these problems.

The first talk in the session, "Challenges and Opportunities in Environmental Chemistry: An Important Intersection of Fundamental Research

and National Needs," was given by Dr. Kenneth G. Hancock (Chemistry Division, National Science Foundation). Dr. Hancock also noted that the nation, indeed the world, faces serious environmental problems. A number of U.S. government agencies fund research in environmental chemistry, including the National Science Foundation. NSF's role is to build the knowledge base. The Chemistry Division at NSF has long advocated a strong program in environmental chemistry, beginning with the publication of the report "Chemistry and the Environment 1988" (J. W. Frost, D. M. Golden, Eds.) and continuing with the workshop on environmental chemistry organized by T. Dunning and T. Spiro in March 1992. Dr. Hancock noted that environmental chemistry poses a wide range of exciting challenges in gas-phase chemistry, solution chemistry, surface and interfacial chemistry, photochemistry, and theory & modeling. Solution of these problems will require engagement of the entire academic chemistry community.

The next talk entitled "DOE Basic Research Programs for Environmental Restoration and Waste Management" was given by Dr. Robert S. Marianelli (Chemical Sciences Division, Office of Energy Research, U.S. Department of Energy). Dr. Marianelli noted that over the past few years the U.S. Department of Energy has shifted its focus from weapons production to environmental restoration (clean up) and waste management (treat and store). The DOE has more than 4000 contaminated sites, cubic kilometers of contaminated soils, many square miles of contaminated aquifers, etc. It is clear that basic research will be required to address the scientific and technological needs of the DOE effort, and that this work must go all the way down to the molecular level. The DOE's scientific and technological needs include better risk analysis and management, improved laboratory analysis and *in situ* characterization, new chemical separations techniques, *in situ* techniques for remediating contaminated soils and groundwater, etc. At present the DOE does not have a coordinated, focused, basic research effort to support these needs.

Dr. Robert W. Shaw (Chemical and Biological Sciences, U.S. Army Research Office) spoke on "Physical Chemistry and the DOD Environmental Quality Plan." Shaw began by noting that the U.S. Army Research Office is anticipating an additional \$13 million to support research in environmental chemistry this fall. While there are many elements to the Department of Defense's Environmental Quality Plan, cleaning up DOD's bases and laboratories and safely destroying chemical munitions and warfare agents are clearly the most pressing problems. Here it is critical to develop a better understanding of the biodegradation of pollutants and of the chemical processes involved in

the destruction (especially combustion) of contaminants, especially chemical agents such as nerve gases that are flame retardants. Work being supported by ARO includes research on the pyrolysis and reactions of nerve gas simulants (Cornell), chemical/photochemical catalysis of hydrocarbon fuels by TiO₂ (Texas), and supercritical water oxidation (MIT, Delaware, and Texas).

The final talk of the session, "The Importance of Physical Chemistry in CFC/Ozone Issues," was presented by Dr. David A. Dixon (Central Research & Development Department, E. I. DuPont de Nemours and Company, Inc.). Dixon noted that the chemical industry is now responsible for the complete life-cycle of the chemicals that it uses and produces, including the ultimate fate of any chemicals released into the environment. This is a daunting task that requires a wealth of physical chemistry data: thermochemistry, reaction mechanisms and kinetics, photochemical cross sections and quantum yields, etc. A case in point are the chlorofluorocarbons (CFCs) which, over the past decades, have found innumerable uses as refrigerants, foaming agents, propellants, etc. Unfortunately, the very property that made them so valuable in these applications, their inertness, was also their Achilles' heel - they rose unhindered through the troposphere to be photodissociated in the stratosphere where the released chlorine atoms are now involved in the destruction of ozone. Since the CFCs have been banned by international protocol and the chemical industry has been forced to develop more benign alternatives on an ever shortening time scale, industry has been forced to rely heavily on innovative approaches to the development of new products, including the intensive use of advanced molecular modeling techniques to screen proposed CFC replacements.

Atmospheric Chemistry

Chairman: Dr. Charles E. Kolb, Jr., Aerodyne Research, Inc.

The keynote presentation in this session, "Physical Chemistry and Atmospheric Chemistry: A Developing Partnership," was given by Prof. James G. Anderson (Department of Chemistry, Harvard University). Dr. Anderson outlined how advances in physical chemistry, atmospheric dynamics and advanced technologies are driving research in global atmospheric chemistry. He used the stratospheric ozone depletion problem to illustrate how physical chemical issues such as gas-phase free radical reaction rate constants and product branching ratios at low (180-250K) temperatures, heterogeneous (gas/particle) reaction mechanisms and rates, and photochemical cross sections and quantum yields define the concentrations of critical ozone depleting HO_x, ClO_x, BrO_x and NO_x free radicals and their impact on local stratospheric ozone levels. Spectroscopic studies in both the laboratory and atmosphere allow the identification of key reactants and reaction intermediates, thus permitting the confirmation of critical chemical pathways.

Dr. Anderson also noted that advancing understanding of stratospheric meteorology (atmospheric dynamics) leads to the definition of three separate stratospheric regimes, polar, mid-latitude and tropical, each with its own chemical characteristics and time scales. Recent airborne measurements in the polar and mid-latitude regimes have confirmed the importance of heterogeneous processes on polar ice particles and sulfuric acid aerosols in influencing the relative abundance of the various free radical families. These results have changed our perception of the relative importance of the various free radical-

driven catalytic cycles in reducing ozone levels. Current aircraft technology largely limits *in situ* chemical measurements to altitudes below 19 km. However, Dr. Anderson highlighted advances in aeronautics, materials, and compact computerized laser and spectroscopic measurement systems that will soon allow less expensive, but more definitive, measurements up to 25 km. This can be accomplished by remotely piloted vehicles using robotic, real-time instrumentation to monitor key chemical reactants and reaction intermediates.

The next talk, "Quantitative IR Spectroscopy for Atmospheric Chemistry Applications," was presented by Dr. Mark S. Zahniser (Aerodyne Research, Inc). Zahniser discussed how quantitative infrared spectroscopy can be used to measure the concentrations of atmospheric radical and reservoir species in both the laboratory and the atmosphere. Using the HO₂ radical as an example, he demonstrated how laboratory fast-flow reactor techniques are used to prepare known concentrations of very reactive species and how tunable infrared lasers coupled to multipass optical cells can be used to accurately determine vibrational/rotational line and band strengths and pressure broadening coefficients. Armed with these fundamental parameters, measurement systems can be designed to quantify atmospheric concentrations of many important reactive species down to ~10 parts-per-trillion (ppt). Of special interest to theorists, Zahniser noted that *ab initio* calculations of infrared band strengths for diatomic radicals such as OH, ClO and BF agree with measured values to within ~15%,

however calculated values for polyatomic radicals such as HO₂, CH₃ and CF₂ are usually off by factors of at least 2 to 3.

New astigmatic off-axis resonator mirror geometries with 182 and 370 passes allow absorption path lengths up to 0.6 km in limited volume sampling cells. This same mirror geometry is also applicable to open path sampling between an aircraft wing and fuselage to avoid any sampling loss of "sticky" gasses such as HCl, HNO₃, HOCl, or HO₂.

Prof. Margaret A. Tolbert (Department of Chemistry and Biochemistry, University of Colorado, Boulder) gave a presentation on "Heterogeneous Processes in the Stratosphere." In this talk the composition and formation mechanisms of polar stratospheric clouds (PSCs) were reviewed. Type 1 PSCs were identified with nitric acid/water ices, most probably nitric acid tri-hydrate (NAT) and type 2 were identified as predominately water ice. Reaction probabilities of key stratospheric reservoir gases, N₂O₅, ClONO₂, HCl and HOCl on these surfaces were also reviewed. N₂O₅ and ClONO₂ react with condensed H₂O to form HNO₃. These reactions proceed much faster on water ice than on NAT. HOCl, also produced by the ClONO₂ + H₂O(c) reaction, and ClONO₂ itself reacts with HCl on ice surfaces to produce Cl₂. The N₂O₅ reaction also proceeds rapidly with the H₂O contained in liquid sulfuric acid aerosols of up to 80 wt.% H₂SO₄. However, the ClONO₂ + H₂O(c) reaction is slow at high levels of H₂SO₄, speeding up significantly as the aerosol water content increases. Infrared spectroscopy is now widely used to characterize films of acidic liquids and ices characteristic of the stratosphere. It is now being extended to characterize aerosol compositions in both laboratory simulations and in the stratosphere.

Prof. A. R. Ravishankara (NOAA Aeronomy Laboratory and Department of Chemistry, University of Colorado, Boulder) in his presentation

entitled "How Long Do Molecules Live in the Atmosphere?" discussed the concept of an atmospheric lifetime for individual trace chemical species. It was noted that these lifetimes are controlled by chemical or physical removal processes at either the Earth's surface or in the atmosphere. Most atmospheric removal processes involve irreversible oxidation steps. Atmospheric lifetimes control the concentration of atmospheric species, their partitioning between the troposphere and stratosphere and the recovery time of the atmosphere from a natural or anthropogenic perturbation of a trace species concentration. Species such as hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs) being introduced as substitutes for ozone depleting chlorofluorocarbons (CFCs) generally have lifetimes controlled by reaction with OH in the lower atmosphere. Rate constants in the 10⁻¹³ to 10⁻¹⁵ cm³ s⁻¹ range result in lifetimes of months to decades. These rate constants are low and need to be accurately determined. CFCs and bromofluorocarbons (Halons) generally have lifetimes controlled by UV photolysis in the stratosphere and the lifetimes range from ~10 to ~100 years. Perfluorocarbon compounds are resistant to homogeneous reactions, hydrolysis and photolysis; thus, CF₄ has an atmosphere lifetime currently estimated at 50,000 years.

Prof. William L. Chameides (School of Earth and Atmospheric Sciences, Georgia Institute of Technology) spoke on "Multi-Phase Atmospheric Chemistry and its Impact on Air Quality and Climate." Multi-phase processes in the lower atmosphere were reviewed from the viewpoint of a modeler. Characteristic time scales for the interaction of gaseous species with cloud droplets, typical level of background aerosols, and the ocean were presented. The physicochemical parameters controlling interaction with cloud droplets are the mass accommodation coefficient, the Henry's law constant, and the first order rate constant for chemical conversion (usually hydrolysis). The latter two parameters also control

uptake of gaseous trace species by the ocean. Chameides then presented models for a relatively well understood process, cloud droplet oxidation of SO_2 by H_2O_2 , HO_2 and O_3 , and a less understood process, nucleation of new $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ particles in the marine boundary layer. The latter process is plagued with poorly understood oxidation kinetics of the CH_3SCH_3 precursor species and poorly known $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ homogeneous nucleation kinetics. He provided a list of challenges for physical chemists, which included the two topics just noted as well as the need for studies of hydrolysis mechanisms and rate constants for moderately soluble species, theoretical predictions of trace gas mass accommodation coefficients on aqueous surfaces, the aqueous phase chemistries of Cl_2^- and Br_2^- important in sea salt aerosols produced by breaking waves, and ways to better characterize chemical processes in highly ionic (deliquescent) aerosols. The latter includes the specification of activity coefficients and the description of chemistry in the interfacial monolayer between the vapor and liquid phases.

The final talk, "Surface Studies of Simulated Stratospheric Water/Acid Ices," was a con-

tributed presentation by Dr. Bryan F. Henson, working with co-author Dr. Jeanne Robinson (Chemical and Laser Sciences Division, Los Alamos National Laboratory). Henson described the use of second harmonic generation (SHG) spectroscopy to characterize the surface composition and morphology of water ice and acid/ice films used for laboratory simulation of polar stratospheric clouds. The SHG signal of water ice surfaces is independent of temperature over the range of 140-240 K, but acid/ice surfaces produce strongly temperature-dependent SHG signals. After calibration by traditional BET surface absorption studies, toluene-doped ice surfaces can be used to characterize ice surface areas as a function of growth conditions. Ice surfaces deposited from H_2O vapor at 95K have a much higher surface area than those grown at 180K. Ice growth kinetics appear to be "Langmuir-like." Irreversible phase transitions between amorphous and crystalline ice can also be characterized by SHG. A tunable IR laser with a visible laser to produce a tunable "fingerprint" sum generation frequency laser might be used to better characterize the surface composition of acid/ice mixtures.

Contaminated Soils & Groundwater

Chairman: Dr. Bruce C. Garrett, Pacific Northwest Laboratory

The overview presentation in this session, "Research Needs and Opportunities in Contaminated Soils, Sediments and Natural Waters," was given by Prof. Sam J. Traina (Department of Agronomy, The Ohio State University). It was emphasized that soils are complex; they are multiphase and spatially varied. Important solids in soils include minerals, organic materials (e.g., humic materials), and precipitates. Important processes in soils and groundwater include sorp-

tion/desorption and precipitation/dissolution on solids, ionic and organic complexation in solution, and transformation (or mineralization) by biomass. Traditional approaches based on macroscopic measurements have been used in the past to quantify contaminants and speciation, but were limited to giving this type of chemical composition data. Microscopic measurements are needed to deduce information about mecha-

nisms and rates of processes as a function of pH and temperature.

Prof. Traina discussed some examples of the comparisons of microscopic (*e.g.*, spectroscopic) methods with macroscopic (*e.g.*, ultracentrifuge and titration) methods. Studies of liquid speciation of a model humic material indicated that the spectroscopic studies were capable of reproducing the results of ultracentrifuge studies more efficiently. In studies of solid speciation, macroscopic data can often be understood by using a number of molecular models. For example, macroscopic studies of anion speciation on minerals often cannot distinguish outer sphere complexes (where the ion retains its solvation shell), inner sphere complexes (where the ion is directly bound to an adsorption site), and precipitation in which the ion forms a complex. In a detailed study of Pb substitution in apatite, spectroscopic studies indicate the complete dissolution and reprecipitation of the complex. In summary, Traina saw a great potential for application of physical chemistry methods to provide needed molecular level information.

The next talk, "Laser Studies at Acid-Base Equilibria and Vibrational Spectroscopy at Aqueous Interfaces," was given by Prof. Kenneth B. Eisenthal (Department of Chemistry, Columbia University). Second harmonic generation (SHG) and sum frequency generation (SFG) spectroscopic methods were used to differentiate structure and dynamics at aqueous interfaces from those in the bulk materials. In the first part of his talk, Eisenthal presented results of studies of acid-base equilibria of substituted phenol at the air/water interface. Aliphatic tails were added to the phenol as hydrophobic groups to increase the concentration of the solute molecules at the interface. As a function of the number "n" of CH₂ groups in the normal hydrocarbon tail, the SHG signal was found to increase monotonically above n = 3. The pK_a was directly measured to be 11.7 at the interface compared with 10 in the bulk.

Eisenthal also presented studies of the SiO₂/H₂O interface. First, studies of proton transfer into the water from the surface silanol groups were found to require third order corrections to the SHG signal to account for effects of large electric fields extending into the bulk at high pH. Next, SFG spectroscopy was used to study vibrational spectra of CD₃CN at the SiO₂/H₂O interface. At low concentrations the CN frequency is blue shifted but as the concentration increases the frequency shifts back indicating an orientation shift (phase transition) at about one monolayer coverage at the interface.

Prof. Steven M. George (Department of Chemistry and Biochemistry, University of Colorado, Boulder) gave the presentation "Surface Science Studies on MgO(100) and SiO₂ Surfaces." Ultra-high vacuum studies of the absorption of NH₃ and CO₂ on MgO (100) were presented. Laser induced thermal desorption (LITD) studies of the uptake of NH₃ on MgO(100) at constant NH₃ pressure showed little temperature dependence and fit a model of precursor mediated adsorption kinetics. LITD studies at fixed NH₃ coverage was not first order indicating that lateral interactions between the adsorbed NH₃ molecules are repulsive. The desorption energy was measured to be 12-15 kcal/mol. LITD studies of CO₂ on MgO(100) were also found to be consistent with the model of precursor mediated adsorption kinetics and gave a value of 7-9 kcal/mol for the desorption energy. A high pressure doser inside the UHV chamber was used to study the dehydroxylation of hydroxyl covered surfaces (silanol terminated) to form Si-O-Si (siloxane) termination at the surface and the reverse process, hydroxylation of the siloxane surface. The siloxane surfaces were found to be surprisingly resistant to hydroxylation. Methanol coverage was found to be a good probe of the OH coverage of the SiO₂ surfaces.

The presentation "Theoretical Investigations of the Physics and Chemistry of the Mineral Water

Interface" was given by Dr. Anthony C. Hess (Molecular Science Research Center, Pacific Northwest Laboratory). The periodic Hartree Fock (PHF) method for calculating the electronic structure of extended systems was described. The PHF method is particularly well suited to studies of insulating and semi-conducting materials and their surfaces and has the advantage over cluster models of describing an infinite system rather than a truncated model. Results were presented for the interaction of Cl_2 and H_2O with the MgO (001) surface. Physisorption energies of 8 kcal/mol and 12 kcal/mol were reported for Cl_2 and H_2O respectively using an *a posteriori* correlation correction of the Hartree-Fock energies. A study of the surface structure of (0001) $\alpha\text{-Al}_2\text{O}_3$ was then presented including the influence of H_2O on the resulting surface structure. Large relaxations were found to occur on the clean surface of this compound with the surface Al atoms relaxing back toward the plane of the first layer of O atoms. The structure of the surface was found to assume a nearly planar geometry with respect to the unrelaxed bulk structure. It was then reported that the addition of H_2O to the unrelaxed (0001) surface formed a chemisorbed complex (water oxygens over surface aluminums) of approximately 27 kcal/mol. Preliminary relaxation data were then discussed which indicated that surface Al atoms in the chemisorbed $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ complex underwent a similar relaxation to approximately the same extent as found on the clean surface. A comparison of the correlation-corrected physisorption of CO on MgO (001) was then discussed. These calculations indicated that theoretical and experimental evaluations of the binding energy were within 2 kcal/mol of each other (calculated: 7 kcal/mol; experiment: 9 kcal/mol).

Prof. Cliff T. Johnston (Department of Soil Science, Purdue University) spoke on "Chemisorption of Aromatic Hydrocarbons on

Clay Minerals." He discussed the abiotic transformation of aromatic hydrocarbons on minerals and, in particular, focused on single electron transfer reactions between metal atoms and dimethoxybenzene on montmorillonite. Spectroscopic methods were used to probe the reaction to form radical organic cations. The methoxy groups on the benzene ring were used to block polymerization. The surface of the mineral stabilizes the radical organic cation. Reaction is found to be immediate on dry montmorillonite but is reversed upon adding water. The IR spectra of the matrix isolated cation was found to agree well with theoretical calculations of vibrational frequencies and intensities by Vala (University of Florida).

The final talk in the session was the contributed presentation "Modeling the Chemistry at Mineral Interfaces" by Dr. Carol A. Scamehorn (Molecular Science Research Center, Pacific Northwest Laboratory). She presented results of periodic Hartree Fock calculations on H_2O interactions with surfaces of MgO . For a clean (100) surface two energetically favorable arrangements of water were found, one with the water O directly over the Mg and the other with the H atoms on the water pointing down towards the O atoms on the surface. Coverage effects were studied and attractive lateral interactions were found when the water orientation (O down versus H's down) was alternated and the H_2O planes twisted by 90° for adjacent water molecules. The effects of surface defects on the binding and energetics of hydroxylation were also studied. Binding was found to increase from the clean surface to an edge site to a corner site. Although hydroxylation was not energetically favorable on the clean surface, it was found to be exoergic by 7.3 kcal/mol and 67.3 kcal/mol for the edge and corner sites. Analysis of the charge distributions indicates that surface O atoms at defects are the reactive sites.

Toxic Waste Destruction

Chairman: Dr. Robert W. Shaw, Army Research Office

Prof. Joseph F. Bunnett (Professor Emeritus of Chemistry at the University of California, Santa Cruz) gave the overview presentation in this session, "All About Disposal of Chemical Wastes, in Forty Minutes." Prof. Bunnett has served on the NAS Subcommittee on Alternatives to Incineration for Chemical Weapons Destruction. He spoke of the need for more accurate categorization of chemical waste and emphasized the importance of industrial processes that generate less waste or, better, use waste as an input. He gave the example of tires ground up in Portland cement and observed that tires resemble coal in their elemental composition and so could be used as fuel in high temperature furnaces. Because regulations have been developed to handle specific situations, they may become obsolete when the situation changes. Clearly, it is important for regulations to evolve along with our scientific understanding. The Army's plan for incineration of chemical weapons was well considered from a scientific and engineering point of view, but communication with the public was poor. Now the effort is stalled. Canada did a good job of informing their public about plans for chemical weapons destruction. Viable alternatives to incineration exist; these include wet air oxidation, supercritical water oxidation, biodegradation.

The next talk, "Destruction of Explosives and Propellants by Hydrothermal Processing," was presented by Dr. Steven J. Buelow (Chemical and Laser Sciences Division, Los Alamos National Laboratory). Dr. Buelow is the head of a large group working on hydrothermal processing. He reported on the Los Alamos program on high temperature water processing of explosives and propellants; the hydrothermal process conditions range from 25-600C and 1-1000 atm. He

pointed out that the solubility of salts at high temperatures can be increased by increasing pressure (density). Although the Los Alamos group has shown complete mineralization of a wide range of energetic materials, a principal problem is their (lack of) solubility in the input stream. So they have explored the use of organic solvents, slurries of particles, pre-processing in alkali, *etc.* Organic solvents are more expensive, are a fire hazard, and may be toxic. Slurries require particles to be $< 300 \mu\text{m}$ for pumping and carry the risk of explosives settling in feed lines. In addition, heterogeneous chemistry may make process control difficult. Alkaline hydrolysis, however, produces water soluble, non-explosive products. The Los Alamos group has worked out mechanisms for hydrolysis. Dr. Buelow also reported laser spectroscopic studies of these systems, employing coherent anti-Stokes Raman spectroscopy and Raman scattering to probe water structure and reaction intermediates.

Prof. Paul L. Houston (Department of Chemistry, Cornell University) gave a presentation on "Radical-Molecule Reactions Important in the Combustion of Chemical Warfare Agents." The distribution of weapons storage and problems of chemical weapons destruction were described and the series of decisions made by the Army were reviewed. Prof. Houston is a member of the Army Center for Combustion Diagnostics at Cornell; he described the Cornell research program to elucidate the combustion chemistry of chemical agents and to develop monitors for the process. One activity involves the use of crossed molecular beams to study the products from collision of typical combustion radicals (*e.g.*, OH) with simulant molecules. Products are detected by single photon VUV tuned to the ionization

threshold to reduce parent fragmentation for subsequent detection by mass spectrometry. Prof. Houston presented spectra for DMMP – a common simulant for nerve agents.

The presentation "Photocatalytic Oxidative Degradation of Organic Compounds on Aerated TiO₂ Suspensions" was given by Prof. Marye Anne Fox (Department of Chemistry, University of Texas, Austin). Prof. Fox is a member of the Army Center on Molecular Interactions and Reaction Dynamics in Supercritical Water at the University of Texas, Austin. She described the formation of electron/hole pairs when photons strike semiconductor particles and their migration to form highly reductive and oxidative sites on particle surfaces. This work originated from attempts to use solar energy to make fuel (H₂ and O₂) from water. TiO₂ is the most efficient semiconductor particle because of its high oxidative turnover and quantum efficiency. This technology has been demonstrated in the field – metal oxides have destroyed pesticides in an agricultural field. Organic compounds containing heteroatoms and conjugated molecules are especially well degraded. Prof. Fox has shown that a mustard simulant containing sulfur passes to the sulfoxide and then to the sulphone, moving from more to less toxic products.

Dr. Carl F. Melius (Combustion Research Facility and Center for Computational Engineering, Sandia National Laboratories, Livermore) spoke on

"Solvent Effects on the Chemical Reaction Mechanisms of Hazardous Waste Removal." He discussed the difference between gas and condensed phase reactions. The presence of condensed phases creates new reaction paths (because of near neighbors) and reaction rate changes (transition state structure and reactant free energy changes). His calculations show the stabilization of intra-molecular charge separation by solvation. Dr. Melius remarked that the solvation environment in supercritical water resembles that in an incinerator – a high temperature, but dense gas. Using his BAC-MP4 method, Dr. Melius has begun calculating the thermochemistry for chemical agents: bond dissociation energies, the first bonds to break, and H abstraction sites. He has also begun exploring possible structures of bioengineered enzymes that resist deactivation by chemical agents.

The final talk in the session was the contributed presentation "Sunlight-Assisted Oxidation of Oil and Organics on Water Using Bouyant TiO₂-Coated Oleophilic Hollow Glass Microbubbles" by Prof. Adam Heller (Department of Chemical Engineering, University of Texas, Austin) Prof. Heller reported on likely paths for mineralization of organic contaminants in water by glass beads coated with TiO₂. He based his analysis on research by Troe *et al.*, who described combustion as radical chain reactions leading to smaller and smaller products.

Treatment of Nuclear Wastes

Chairman: Professor Gregory R. Choppin, Florida State University

Dr. Teresa B. Fryberger (Office of Environmental Restoration and Waste Management, U.S. Department of Energy) gave the introductory pre-

sentation "Radionuclide Separations and Processing for Defense Waste Management." An overview was presented of the DOE's program in

"Efficient Separations and Processing." The purpose of the program is to develop advanced chemical separations technologies that reduce the total volume of high level waste that needs to be disposed of in a geological repository. The separations would also seek to improve the quality and volume of the low level waste. The impact should be a considerable reduction in the expense, as well as the safety concerns, associated with the waste disposal systems. The talk outlined the types of problems to be addressed and the time schedule for the development of the separations.

The next presentation "Selective Chelators for Actinide Complexation" was given by Dr. P. H. Smith (Los Alamos National Laboratory). Dr. Smith outlined the development of selective chelating polymers for the removal of actinides from aqueous media. He reviewed the design criteria used in their program to systematically study the defined chelate parameters that control metal ion selectivity. A combination of model calculations and laboratory parameter studies has led to the development of a system which preferentially binds Th(IV) over Fe(III).

The presentation "An Ab Initio Study of the Selective Binding of Alkali Metal Cations to 18-Crown-6" was given by Dr. David F. Feller (Molecular Science Research Center, Pacific Northwest Laboratory). He described *ab initio* calculations that correctly predicted the selective binding of alkali metal cations by 18-crown-6 ether. In these studies both the gas-phase and the aqueous-phase systems were examined theoretically and only the predictions from the aqueous-phase studies agreed with those reported in the literature – in fact, the aqueous-phase selectivity order differs dramatically from the gas-phase order. The specificity derives from a subtle interplay between the binding of the ion to water and to the crown ether. These calculations show significant promise for the application of *ab initio*

methods to problems in the design of selective ligating species.

Prof. Frank J. Millero (Rosenstiel School of Marine and Atmospheric Science, University of Miami) spoke on "The Use of Models to Account for Ionic Interactions in Brines." In the United States a repository for actinide waste is being developed in salt beds near Carlsbad, New Mexico. For approval of the repository it is necessary to show the extent to which the actinide elements might be soluble and migrate in the brines associated with these salt beds. Prof. Millero described developments in the use of a Pitzer model for estimating the activity coefficients of the major anions and cations associated with the brines. He also described the extension of this model in an ion pairing mode for the minor components of the brines. The activity coefficients of the metals obtained from such calculations can be used to estimate the effect of the brines on the solubilities of the various actinide species in the repository. Dr. Millero's talk reflected the value of research in concentrated electrolyte solutions to the nuclear waste problems.

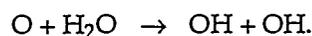
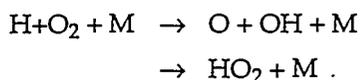
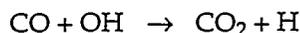
The final talk of the session "Use of Polyelectrolyte Models to Humic Acid-Metal Binding" was given by Prof. Gregory R. Choppin (Department of Chemistry, Florida State University). The role of humic acid in the redox and complexation behavior of actinides in natural waters was described. The data reflect a complex system in which the binding constants depend on the pH of the system and the disassociation kinetics of the metal from the humic acid is dependent on pH and on the time of binding prior to disassociation. The talk indicated how these phenomena can be interpreted qualitatively in terms of the site binding versus condensation models used to explain polyelectrolyte phenomena in biological and other systems. The emphasis was on the value of the application of standard polyelectrolyte models to understand the

complicated humic acid interactions with metals in natural waters.

Pollutant Formation in Flames

Chairman: Dr. Albert F. Wagner, Argonne National Laboratory

Prof. Fred L. Dryer (Department of Mechanical and Aerospace Engineering, Princeton University) gave the introductory presentation "Observations on the Chemistry of Combustion Emissions under Post Flame Conditions." Both premixed and diffusion flame combustion devices have a zone in which CO from the combusted fuel is further oxidized to CO₂. This zone has several important characteristics: (1) its chemistry influences the trace species that are the emitted pollutants of the device and (2) the temperature and pressure variations of this zone can be very large (*e.g.*, up to 60 atm in an internal combustion engine) which can change the chemistry substantially. The reactions of the major species are

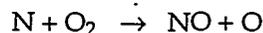
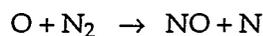


The branching ratio of the middle chain-propagating reaction is sensitive to pressure and temperature and results in great variations in the combustion characteristics.

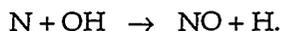
Prof. Dryer has mimicked the behavior of this zone by measuring concentration profiles of a CO/H₂O/O₂ combustion system in the presence of NO_x, halogen, unburned alkanes and other pollutants in a variable pressure flow reactor. Illustrative findings are (1) trace amounts of HCl or halogenated hydrocarbons suppress CO com-

bustion by chain termination steps involving Cl radical attack on HO₂ species, (2) trace NO can enhance combustion under fuel lean conditions, and (3) trace amounts of NO and HCl produce non-additive effects because the chemistry of species like NOCl, which is present in neither the HCl nor NO case alone, can significantly affect combustion. This last synergistic effect of multiple pollutants was stressed in the talk.

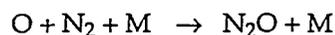
The next presentation "How NO_x Is Formed in Combustion" was given by Dr. James A. Miller (Combustion Research Facility, Sandia National Laboratories, Livermore). Dr. Miller reviewed the mechanisms by which NO_x species are created in combustion and go on to contribute to smog, acid rain, and ozone loss in the stratosphere. There are four important mechanisms. The Zeldovich mechanism that is important at high temperatures involves the reactions

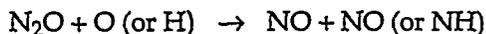


or



These reactions can be circumvented by reducing the maximum temperature of combustion. This can usually be done with minor effects on the efficiency of the combustion device. In the lower temperature Zeldovich-like mechanism, the important reactions are





(at 1 atm and 1800 K, the first reaction is the dominant attack of O on N₂). The prompt NO mechanism includes the reaction



followed by reactions of HCN and N to make NO. The CH + N₂ reaction has been the subject of detailed molecular calculations and some consensus between experiment and theory on the rate has been achieved. In the fuel nitrogen mechanism, amines or N-ring compounds (e.g., pyridines) in fuels are thought to burn as Fuel-N → HCN (very fast) followed by HCN + radicals → NCO, NH_x, NO, and N₂ (interconnected reactions). Both theoretical and experimental work has helped to sort out much of these interconnected rates. However, connections between NH_x and NO, as an example, are still not fully understood.

Prof. Selim M. Senkan (Department of Chemical Engineering, University of California, Los Angeles) gave the presentation "Flame Chemistries and Kinetics of Chlorinated Hydrocarbons." Professor Sankan showed that the number of environmental laws are growing exponentially with time and this motivates understanding halogen chemistry with some urgency. His flame experiments with microprobes can analyze the growth of chlorinated combustion products under different conditions. In broad terms, his work shows that the burning of partially chlorinated C₁ species under fuel rich conditions produces little highly chlorinated products. Under fuel lean conditions he finds that large amounts of highly chlorinated products are produced. Semi-empirical electronic structure calculations have been used to map out bond strengths in C₁ and C₂ partially chlorinated species. With C₁, as chlorination increases, the calculations indicate that the C-H bond strength drops by over 10 kcal/mole. With C₂ species, α-CH bond

strengths decrease with chlorination (as in the C₁ species) but β-CH bond strengths increase. This information can be used in group additivity calculations to predict the products expected in attacks on partially halogenated hydrocarbons. Key to successful predictions is the fact that H can form a strong bond with Cl while O, OH, and to some extent Cl, cannot. With the above bond strengths, one would expect that, for C₁ species, H attack (as in fuel rich flames) would remove a Cl from the C₁ species leading to less halogenated products. However, in fuel lean flames, O and OH and Cl would remove an H from the C₁ species, leading to more highly chlorinated products. In C₂ species, the same is true with O, OH, and Cl taking the H off the α-C. Much more work along these lines is required, including more accurate thermochemistry, especially for radicals and aromatics, and further higher temperature studies of rates.

The presentation "Formation of PAH and Soot in Flames" was given by Prof. Jack B. Howard (Department of Chemical Engineering, Massachusetts Institute of Technology). Professor Howard talked about the formation of 10+ member rings in the sooty combustion of hydrocarbon fuels. He pointed out that the C/H ratio in soot can vary substantially with some sooting conditions producing fullerenes as 20% of the soot. However, all soot involved fused ring species. His measurements are carried out in stirred plugged reactors. In a broad sense, he distinguishes four stages in soot growth: (1) formation of one ring, (2) formation of 2-5 rings, (3) formation of large rings, and (4) formation of macroscopic soot particles. The stages are interlinked by growth (e.g., addition of acetylene) or loss (e.g., ring opening by OH attack) processes. As an illustration of his work, Prof. Howard discussed the growth of naphthalene. Several different reactions were included in a kinetics model for the growth of naphthalene. The data in this model came from separate kinetics studies by others in which the growth of naphthalene from smaller

species was all that was possible. The results did not adequately represent his measured naphthalene concentrations, leading to the conclusion that naphthalene formation via the destruction of larger ring species, as well as via the growth from smaller ring species, is important.

The final talk entitled "Effects of Fuel Structure and Operation Conditions on Exhaust Gas Reactivity from a Spark-Ignited Engine" was given by Dr. E. W. Kaiser (Research Laboratory, Ford Motor Company). Dr. Kaiser discussed studies of unburned hydrocarbons in internal combustion engines as a function of fuel content. The motivation for this work is the California Air Quality Standards for cars; the standard will establish limits on the amount of "smog creating" unburned fuels emitted from the exhaust. This is determined by measuring the species in the unburned fuels and weighing their concentration by an index relating to their role in promoting smog. Thus, higher concentrations of unburned hydrocarbons with little smog impact (*e.g.*, methane) can be tolerated over lower concentrations of species that are important in smog chemistry. Dr. Kaiser's experiments used single component fuels (*e.g.*, pure methane or pure benzene), an internal combustion engine without a catalytic converter, a fuel/oxygen ratio typical of operating automobile engines, and measurements of the hydrocarbons in the exhaust stream. A catalytic converter is not used because as much as 50% of unburned hydrocarbon emissions in federal government tests occur when the car has not warmed up sufficiently for the catalytic converter to be effective. No oxygenated fuels (*e.g.*, ethanol) were used. In typical car engines, as much as 4% of the fuel sprayed into the chamber

ends up in the crevices bounded by the chamber walls, the piston rings, and the piston sides. Flame propagation inside the volume created as the piston drops away from the top of the chamber tends to stop at the crevice edge, leading to unburnt fuels. That gas is ultimately pulled out into the growing volume above the piston, is partially combusted, and is expelled from the chamber during the upstroke of the piston. In Dr. Kaiser's experiments less than 4% of the fuel became unburned hydrocarbons in the exhaust, indicating that under all circumstances some of the crevice gas gets burned. However, the amount burned, the amount converted to lower weight hydrocarbons, and the amount left as the original fuel changes substantially with the nature of the fuel. When the measurements are done under conditions in which the different fuels give the same engine power output, variations in particle emissions are still seen. However, when the smog reactivity index is included, all alkane fuels tend to look the same according to the California Air Quality Standards. The same can be said for aromatic fuels, although as a class they produce far more pollution. The mechanism of the combustion of crevice fuels as they are drawn out into the chamber is poorly understood. It is thought that only the heavy fraction (greater than C_6 species) can be absorbed in the oil on the chamber walls. It is not known if diffusion from the walls into the chamber's interior volume is important. It is not known if partial combustion within the chamber or in the exhaust manifold is important. Much more work has to be done to understand why different fuels produce different amounts and different species in the unburnt hydrocarbons.