A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

**Chemical Technology Division
Oak Ridge National Laboratory**

**RESEARCH PROGRAMS FOR
DIVISION OF CHEMICAL SCIENCES
OFFICE OF BASIC ENERGY SCIENCES
DEPARTMENT OF ENERGY**

DISCLAIMER

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

MASTER

CONTENTS

	<u>Page</u>
Agenda for 1988 Chemical Sciences Review	iv
Personnel Directory	v
Chemistry of Actinides and Fission Products.	1
Interactions of Solvents, Solutes, and Surfaces: Adsorption and Supercritical Extraction.	11
Chemical and Physical Principles in Multiphase Separations.	19
Chemical Kinetics of Enzyme Catalyzed Reactions.	29
Biographical Sketches	38

AGENDA FOR 1988 CHEMICAL SCIENCES REVIEW

Building 4500N, Room 246

Thursday, April 14, 1988

12:00 noon	Lunch	R. K. Genung <i>et al.</i>
1:00 pm	Overview of the Chemical Technology Division and Chemical Sciences Research	R. K. Genung J. R. Hightower, and C. D. Scott

Separation Chemistry of Actinides and Fission Products

1:30	Synergistic Solvent Extraction Studies of the Actinides and Lanthanides	D. J. Pruett
------	--	--------------

Interactions of Solutes, Solvents, and Surfaces

2:00	Theoretical Modeling and the Experimental Study of Supercritical Solutions	H. D. Cochran
------	---	---------------

The Effects of External Fields on Multiphase Separations

2:30	Experimental and Theoretical Studies of Mass Transfer in Circulating-Oscillating Droplets	T. C. Scott
3:00	Staff visits	
5:00	Adjournment	

Friday, April 15, 1988

Kinetics of Enzyme-Catalyzed Reactions

8:30 am	Mechanistic and Catalytic Studies with Chemically Modified Photosynthetic Membranes	E. Greenbaum
9:00	Elucidation of the Mechanism of Synergism Between Purified Cellulase Components	J. Woodward
9:30	Staff visits	
11:00	Executive session	R. K. Genung and Management Staff
12:00 noon	Lunch	
1:00 pm	Staff visits	

Personnel Directory

Chemistry of Actinides and Fission Products

<u>Name</u>	<u>Room</u>	<u>Bldg.</u>	<u>Telephone</u>
J. T. Bell	B-6	4500N	574-4934
J. R. Hightower	204	4501	574-6777
D. J. Pruett	224	4501	576-2771
S. A. Sherrow	B-36	4500N	576-8024
L. M. Toth	B-32	4500N	574-5021

Interactions of Solvents, Solutes, and Surfaces: Adsorption and Supercritical Extraction

P. R. Bienkowski	15-B	4505	574-5769
H. D. Cochran	211	4501	574-6821
C. D. Scott	27	4505	574-5775

Chemical and Physical Principles in Multiphase Separations

C. H. Byers	209	4501	574-4653
O. A. Basaran	217	4501	574-8782
T. C. Scott	205	4501	574-5962

Chemical Kinetics of Enzyme Catalyzed Reactions

E. Greenbaum	A-4	4500N	574-6835
J. Woodward	B-10	4500N	475-6826

Chemistry of Actinides and Fission Products

**KC 03 02 02 0; FWP ERKCTOS
D. J. Pruett, S. A. Sherrow, and L. M. Toth**

This task is concerned primarily with the fundamental chemistry of the actinide and fission product elements. Special efforts are made to develop research programs in collaboration with researchers at universities and in industry who have need of national laboratory facilities. Specific areas currently under investigation include: (1) spectroscopy and photochemistry of actinides in low-temperature matrices; (2) small-angle scattering studies of hydrous actinide and fission product polymers in aqueous and nonaqueous solvents; (3) kinetic and thermodynamic studies of complexation reactions in aqueous and nonaqueous solutions; and (4) the development of inorganic ion exchange materials for actinide and lanthanide separations. Recent results from work in these areas are summarized here.

Chemistry of Actinides and Fission Products

KC 03 02 02 0; FWP ERKCT05

D. J. Pruett, S. A. Sherrow, and L. M. Toth

The primary purpose of this program is to explore the fundamental chemistry of the actinide elements and their fission products. Emphasis is placed on the photochemistry, coordination chemistry, and separation chemistry of these elements, especially as they relate to problems in waste management, environmental control, and the nuclear fuel cycle. The chemistry of other elements is often examined in parallel with that of the actinides and fission products in order to develop a better understanding of the periodic behavior of the elements. Special efforts are made to explore areas that can not or will not be examined elsewhere, and to use the unique facilities that are available at ORNL for handling hazardous and radioactive materials.

The program is divided into two broad areas: Spectrophotometric Studies, carried out by L. M. Toth and S. A. Sherrow, and Chemical Studies, carried out by D. J. Pruett. Specific areas of interest include: (1) spectroscopy and photochemistry of actinides in low-temperature matrices, with particular emphasis on isotope effects; (2) small-angle scattering studies of hydrous polymers in aqueous and nonaqueous solvents; (3) the characterization of the structures and properties of pure and mixed actinide polymers; (4) photochemical studies of U, Np, and Pu in aqueous solution; (5) kinetic and thermodynamic studies of complexation and redox reactions in aqueous and nonaqueous solutions; (6) the determination of solvation numbers in aqueous and nonaqueous solutions; (7) the properties of complexes with macrocyclic ligands; (8) the development of inorganic ion exchange materials for actinide and lanthanide separations; and (9) studies of fundamental properties of aqueous and nonaqueous solvent systems in support of these primary fields of investigation.

Currently, there are six areas of active investigation: (1) small-angle scattering studies of hydrous polymers; (2) spectroscopic studies of matrix-isolated actinide compounds; (3) synergistic effects of macrocycles on the solvent extraction of actinides and lanthanides; (4) coordination chemistry of actinides and lanthanides in nonaqueous systems; (5) extraction chemistry of actinides and lanthanides in alkaline solution; and (6) inorganic ion exchange materials for actinide and fission product separations. Progress in each of these areas is summarized here.

PHOTOCHEMICAL STUDIES (L. M. Toth and S. A. Sherrow)

Small-Angle Scattering Experiments (L. M. Toth)

The first stage of the small-angle x-ray scattering (SAXS) experiments on Th(IV) hydrous polymers has been completed. These studies have been conducted on 0.01 M Th(NO₃)₄ aqueous suspensions and organic extractants that were equilibrated with the aqueous phases. Assuming spherical geometries, fresh Th(IV) polymer suspensions consist of particles that vary in size from 25 to 84 Å, whereas aged (by reflux) Th(IV) polymer suspensions consist of particles that range in size from 16 to 174 Å. The decrease in size

of the small extreme on aging (i.e., the 25-Å particles becoming 16 Å) is consistent with a dehydration and shrinkage process during conversion of hydroxyl bridges to oxygen bridges between Th atoms.

These suspensions have been shown to be extracted by 0.5 M dibutylphosphate in n-dodecane, NDD, but not by 0.1 M trioctylphosphine oxide in NDD or 0.1 M dihexyl-[(diethylcarbamoyl)-methyl]phosphonate in NDD. The particle size distribution in the organic extractant was similar to that in the aqueous phase showing that there was no size segregation as a result of extraction.

Attempts to alter the size of the polymers by growing them in the presence of UO_2^{2+} produced no differences in particle size distribution; it has since been realized, though, that the 0.5/1 ratio of UO_2^{2+} /Th(IV) would probably have to be increased by 10x before measureable effects could be obtained, if at all. It is probable that the tendency of the UO_2^{2+} and Th^{4+} ions to hydrolyze in the same pH region, namely pH = 3-4 and the subsequent precipitation of UO_2^{2+} interferes with the extensive interaction of UO_2^{2+} with Th^{4+} . (It should be recalled that the significant chain inhibition reaction was noted with the UO_2^{2+} /Pu $^{4+}$ system in which Pu $^{4+}$ begins to hydrolyze in the pH = 1-2 region.)

With the development of modeling routines at Argonne National Laboratory (ANL), the above SAXS data for Th(IV) have been analyzed with respect to geometry and particle size by fitting the scattering data using Fournet functions for various geometries. A nonlinear regression analysis was used for obtaining diameters and/or length-to-diameter ratios (when less symmetrical geometries were tested). As a result of these analyses, it was apparent that the complications caused by the polydisperse nature of the colloid (i.e., the polymer suspension consists of particles of widely varying sizes) would not permit a satisfactory fit of the SAXS data to a given model which assumed a particular geometry of uniform-size particles. Improvements in the model are currently being developed which should permit inclusion of the polydispersity of the system.

In collaboration with ANL staff, small-angle neutron scattering experiments (SANS) have been initiated on Pu(IV) polymer suspensions in nitric acid solutions. These experiments are being performed on the Intense Pulsed Neutron Source (IPNS) at ANL. At this stage of the analysis, the polymers appear to be long, thin rods of 14-Å diameter. If the polymer is grown in the presence of UO_2^{2+} where U/Pu = 5, the length of the rod is considerably shortened. Extraction of the polymer into a variety of organic extractants appears to be accompanied by some depolymerization.

Spectroscopic Studies of Matrix-Isolated Actinide Compounds (S. A. Sherrow)

The focus of our low-temperature studies of matrix-isolated actinides has been production of a uranyl species, which could subsequently be photoreduced, in the inert gas matrix. Although the technique for producing matrix-isolated uranyl has not been perfected, two sets of experiments have yielded very promising results. In both procedures, gas samples were condensed on an infrared transmitting cold window as shown schematically in Fig. 1. Reactions were monitored spectroscopically.

During the first group of experiments pure UF_6 and H_2O were deposited on the cold window, which was then warmed to effect hydrolysis of UF_6 to uranyl fluoride (UO_2F_2). In addition to reactants and products, at least two distinct species were observed. The

Fig. 1.

first species was formed in substantial quantity during the deposition, and was characterized by a strong absorption at 550 cm^{-1} . Because the peak position did not shift upon isotopic substitution (^{18}O labeled H_2O), we attributed the absorption to a $\text{UF}_6\text{-H}_2\text{O}$ adduct. A small amount of the second species was also formed during deposition. This species was characterized by a strong absorption at 850 cm^{-1} , which shifted to 800 cm^{-1} upon ^{18}O substitution. The frequency and isotopic shift indicated that this peak was the U-O stretching vibration of a hydrolysis intermediate. As the sample temperature was increased, the absorption due to the adduct decreased in intensity while that due to the intermediate increased. Most of the adduct had reacted to form the intermediate before the temperature reached 100 K . A small amount of UO_2F_2 was also detected below 100 K . These experiments indicated that the formation of uranyl by hydrolysis is thermodynamically possible at low temperatures.

During the second group of experiments UF_6 and H_2O were codeposited with an excess of Ar matrix gas, as indicated in Fig. 1. Spectra obtained during these experiments exhibited the sharpness and intensity characteristic of matrix-isolated species. Again, we observed a band which we attributed to an adduct. Warming to effect hydrolysis has been limited to 30 K (due to boiloff of the Ar), which has not been sufficient to induce reaction. Warming combined with 254-nm photolysis, however, produced the results shown in Fig. 2. A pair of bands, again assigned to a hydrolysis intermediate, appeared at $866, 855\text{ cm}^{-1}$. Isotopic substitution demonstrated that the species contains only one U-O bond. Also shown in the figure are the U-F stretching absorptions. Those at $600\text{-}620\text{ cm}^{-1}$ are due to UF_6 . The absorption at 589 cm^{-1} (greatly reduced after reaction) is due to the adduct. The bands which appear at 586 and 563 cm^{-1} are due to UF_6 (product of UF_6 photolysis), while the other U-F absorptions must be associated with the intermediate.

Fig. 2.

Because the earlier experiments indicated that hydrolysis to UO_2F_2 can occur without photolysis below 100 K, we are currently experimenting with matrix gases (Xe) which can be warmed to temperatures substantially above 30 K. In addition to producing matrix-isolated uranyl, we will attempt to establish the identities of the adduct and intermediate species.

CHEMICAL STUDIES (D. J. Pruett)

Synergistic Effects of Macrocycles on the Solvent Extraction of Actinides and Lanthanides

The goal of this task is the development and characterization of synergistic solvent extraction systems using macrocyclic ligands for the separation of lanthanides and actinides.

Initial studies of the mechanism of extraction of U(VI) and several trivalent actinide and lanthanide elements using thenoyltrifluoroacetone (TTA) in combination with a linear polyether, an aza-crown ether, or a crown ether (Fig. 3) were completed. Two papers describing these studies have been accepted for publication. The addition of K-5 or K22DD caused a significant synergistic effect on the extraction of UO_2^{2+} by TTA (Fig. 4). The extraction constants and the organic phase stability constants (β_{org}) for the formation of uranyl and several actinide and lanthanide synergistic complexes are reported in Table 1.

Fig. 3. Macrocycles used in synergistic studies.

Fig. 4. Effect of K-5 and K22DD on the extraction of U(VI) by TTA.

Table 1. Equilibrium values for the extraction of metal ions by synergistic mixtures (organic phase: chloroform; aqueous phase: 0.50 M NaNO₃, pH = 4.7 acetate buffer; 25°C)

Synergist	U(IV)	Ce(III)	Pm(III)	Eu(III)	Am(III)	Cm(III)
Log K						
TTA only	-3.00	-9.95	-9.28	-8.58	-9.10	-9.10
TTA + K22DD	-2.85	-4.70	-5.12	-5.03	-5.32	-4.00
TTA + K-5	-3.12					
Log B _{org}						
TTA + K22DD	3.47	4.93	4.54	4.61	5.06	4.97
TTA + K-5	3.64	4.15	3.97	3.62	4.35	4.21

The two nitrogen-containing synergists show similar values for B_{org} in the extraction of each metal, despite the different sizes, shapes, and complexing geometries in the ligands. The synergistic effect obtained using 15-C-5 was too small to measure under the conditions examined. These results suggest that the nitrogen atoms in the macrocycle are largely responsible for the synergistic effect. It can further be seen that the synergistic effect is largest for the ions with the greatest ionic radius, and decreases as the radius decreases. An excellent group separation could be achieved, but, there was no significant separations of the individual elements (Fig. 5).

This work is being carried out in collaboration with D. D. Ensor of Tennessee Technological University.

Coordination Chemistry of Actinides and Lanthanides in Nonaqueous Systems

Current studies emphasize actinide and lanthanide redox and coordination chemistry in concentrated electrolytes, low-melting fused salts, and other nonaqueous systems. The phosphoryl trichloride-tin(IV) chloride system, the aluminum chloride-n-butyl pyridinium chloride system, and aluminum chloride-1-ethyl-3-methyl-1H-imidazolium chloride system have been examined in the last year.

Attempts to measure acetate, sulfate, thiocyanate, and nitrate complexation of neodymium and uranium in POCl₃-SnCl₄ were unsuccessful. It was found that the solvent attacks all of these common anions very quickly, producing a variety of products. No further studies of this system are planned.

The aluminum chloride-n-butyl pyridinium chloride system (a salt mixture that melts at or slightly above room temperature) was also examined. The reagents were successfully synthesized and purified. However, the reagents were expensive and time-consuming to prepare. Furthermore, the resulting melts did not have sufficient optical purity to allow spectroscopic studies. The aluminum chloride-1-ethyl-3-methyl-1H-imidazolium chloride (AC-EMIC) system proved to be much less expensive to prepare, has better spectroscopic and electrochemical properties, and is not photosensitive. Hence, the pyridine system was

Fig. 5. Extraction of Cm(III), Am(III), and Ce(III) by K22DD-TTA mixtures.

abandoned and a graduate student spent two months at ORNL synthesizing approximately 2 kg of the AC-EMIC salts. Studies of $^{238}\text{Pu(III)}$ -U(IV) complexation and redox chemistry are just beginning.

These studies are a continuation of an ongoing collaboration with G. R. Choppin of Florida State University. One post-doctoral student and one undergraduate are supported by a \$48K subcontract.

Extraction Chemistry of Actinides and Lanthanides in Alkaline Solution

This task is aimed at exploring the separation chemistry of the transplutonium elements in alkaline media. Initial studies have focused on the chemistry of berkelium(IV) and californium(III) and their lanthanide analogs, cerium(IV) and europium(III).

Preliminary work showed that *t*-butylcatechol could be used to preferentially extract trivalent actinides/lanthanides from a mixture of trivalent and tetravalent ions (Fig. 6). However, the catechol was quite soluble in the aqueous phase, reducing its usefulness as a solvent extraction reagent.

Recent results have shown that 3,5-di-*t*-butylcatechol is equally effective at extracting the trivalent ions, and there is little or no loss of this reagent to the aqueous phase. However, the compound is easily oxidized, and the extractions must be carried out under

Fig. 6. Extraction of Ce(IV) and Eu(III) by t-butyl catechol from aqueous carbonate solution.

an inert atmosphere. In collaboration with J. R. Petersen of the University of Tennessee, efforts are now under way to find an extraction reagent that is water insoluble and stable to air.

Inorganic Ion Exchange Materials for Actinide and Fission Product Separations

Initial studies of inorganic ion exchangers made from heteropolyacids have been shown to have some selectivity for lanthanide and actinide elements, but the synthesis and properties of the materials are irreproducible. The use of sol-gel technology to produce these materials is being explored.

Chemistry of Actinides and Fission Products**Peer-Reviewed Publications in Press**

S. L. Blaha, C. J. Anderson, D. J. Pruett, and G. R. Choppin, "Evaluation of Phosphorous Oxychloride and Tin (IV) Tetrachloride as a Solvent for Complexation Studies," (manuscript in preparation).

D. J. Pruett, M. E. Nicks, and D. D. Ensor, "Synergistic Extraction of Trivalent Actinides and Lanthanides Using HTTA and an Aza-Crown Ether," *Sep. Sci. Technol.*

D. J. Pruett, M. E. Nicks, and D. D. Ensor, "Synergistic Extraction of Uranyl Ions Using HTTA and an Aza-Crown Ether," *Solvent Extraction and Ion Exchange*.

L. M. Toth and J. S. Lin, "SAXS Measurements of Th(IV) Hydrous Polymers," (manuscript in preparation).

**Interactions of Solvents, Solutes, and Surfaces:
Adsorption and Supercritical Extraction**

KC 03 02 02 0; FWP ERKCT07
H. D. Cochran, C. H. Byers, and C. D. Scott

Fundamental experimental and theoretical studies are focused on relating macroscopic properties of mixtures to intermolecular interactions and molecular correlation functions for the highly asymmetric systems characteristic of extraction by supercritical fluids and adsorption from supercritical fluids. Experimental studies of solubility of transition metal fluorides in supercritical CF_4 are under way. Complementary theoretical studies based on distribution function theories from statistical mechanics are continuing; these efforts have already led to new models for solubility and other equilibrium properties. A new technique for measuring adsorption rates from supercritical mixtures based on a surface acoustic wave transducer is being evaluated. Future experiments are under consideration for direct measurement of molecular correlation functions of supercritical mixtures using neutron scattering.

**Interactions of Solvents, Solutes, and Surfaces:
Adsorption and Supercritical Extraction**

KC 03 02 02 0; FWP ERKCT07

H. D. Cochran, C. H. Byers, and C. D. Scott

Fundamental experimental and theoretical studies focus on relating macroscopic properties of mixtures to intermolecular interactions and molecular correlation functions for the highly asymmetric systems characteristic of extraction by supercritical fluids and adsorption from supercritical fluids in order to improve understanding of the molecular interactions and their influence on basic phenomena important in practical separation processes.

Experimental studies of solubility of transition metal fluorides in supercritical CF_4 are under way. The choice of metal fluorides as solutes will substantially broaden the database for supercritical solubility because virtually all previous data are for large organic solutes. The current solute is MoF_6 , and future studies are planned for UF_6 and SF_6 . These solutes exhibit a range of volatility appropriate for our measurements, are considerably smaller in molecular size than previously studied solutes, and are of some importance in the nuclear energy programs of DOE. The molecular size should be of benefit in testing models because this parameter appears to be of primary importance, and the range of molecular size of previously studied solutes is rather narrow. CF_4 is an interesting solvent, not previously studied as a supercritical solvent, and, in its critical point properties, is appropriate for the chosen solutes.

Complementary theoretical studies based on distribution function theories from statistical mechanics are continuing; these efforts have already led to new models for solubility and other equilibrium properties. Through the formalism of Kirkwood-Buff theory, bulk equilibrium properties are related via the Kirkwood fluctuation integral to the molecular distribution functions. One approach to modeling, applicable to dilute supercritical solutions, relates the solute-solvent fluctuation integral to that for the pure solvent through molecular solution approximations. The formalism for dealing with solute-solute interactions is available so that models for more concentrated solutions may be developed. This approach is also suitable for treating the effects of added co-solvent or entrainer as may be used in practical separations. Other routes to relate molecular interactions to bulk properties which are being explored include scaled particle theory (particularly well suited to modeling the effects of solute size and shape), integral equation theories (accurate integral equation theories for mixtures have recently been developed), and molecular simulations (a grand canonical Monte Carlo code is being adapted for this application).

A new technique for measuring adsorption rates from supercritical mixtures based on a surface acoustic wave transducer is being evaluated. It has been shown that the frequency of surface acoustic waves on a piezoelectric substrate can be used as an extremely sensitive monitor for the mass adsorbed on the surface (100-1000X as sensitive as bulk wave devices). This suggests a technique for measuring the mass adsorbed that may be amenable to operation at elevated pressures (in contrast to almost all other surface physics techniques which operate only at vacuum conditions) and which may be

used to measure rates of adsorption/desorption. Experiments are under way to test the feasibility of this experimental approach because of the opportunities for research that such a technique could open.

Future experiments are under consideration for direct measurement of molecular correlation functions of supercritical mixtures using neutron scattering.

Ongoing interactions with Professor L. L. Lee and his student, D. M. Pfund, from the University of Oklahoma focus on theory of supercritical solutions, and similar interactions with Professor P. R. Bienkowski and his student, V. P. Gilbert, from the University of Tennessee focus on experimental research with dense fluids.

During the past year, significant developments were made in both theoretical and experimental studies, and a few highlights are listed below.

Further theoretical developments from our Kirkwood-Buff approach to understanding molecular interactions in supercritical solutions have been successfully tested. This work has produced practical models which can predict the solubility and partial molar volume of solutes in supercritical fluids from fundamental molecular theory (see, for example, Fig. 7). The theory provides the basis for planned models explaining the effect of increased solute concentration and solute-solute interactions which are also important in systems with added entrainers or co-solvents.

Fig. 7. Partial molar volume of naphthalene in supercritical carbon dioxide predicted by model.

Related distribution function theory has been developed to better describe the effects of solute size and shape. This work employs scaled particle theory to determine reference state chemical potentials and then uses a Kirkwood coupling parameter technique. Distribution functions have been obtained from the accurate HMSA integral equation theory which has been applied for the first time to supercritical solutions (see, for example, Fig. 8). The robust and efficient algorithm of Labik has been adapted to make these theoretical calculations possible.

Fig. 8. Pair correlation functions of naphthalene in supercritical carbon dioxide calculated by HMSA integral equation using Labik algorithm.

The experimental effort with supercritical fluids is helping to relieve the need for reliable data over a wide range of characteristic molecular parameters. Solubility of molybdenum hexafluoride in supercritical carbon tetrafluoride has been measured. This system provides information of an unusually dense solute with appropriate volatility. Measurements (see Fig. 9) have been made over a range of pressures from well below the critical point to pressures well above the critical point. Temperature has been varied over a more limited range of approximately 20°C. The experimental apparatus has been substantially improved during the past year to ensure that maximum solute purity is maintained (see Fig. 10). All of the surfaces which could contact MoF₆ are treated with fluorine gas prior to experimentation. This effectively removes all water, hydrocarbons, and oxygen from the surfaces preventing reaction and contamination of the MoF₆. The solute is transferred as a gas to a cooled extraction cell where it is deposited as a high surface area solid. The extraction cell is contained in an air bath with accurate temperature control. The supercritical CF₄ solvent passes through the extraction cell at the desired temperature, pressure, and flow rate. The solution is then flashed to atmospheric pressure, heated, and analyzed for its Mo content. A new mass spectrometer has been installed for efficient and accurate on-line analysis.

Fig. 9. Solubility of MoF₆ in supercritical CF₄ at 243 K.

Fig. 10. Schematic drawing of supercritical solubility apparatus.

Experimental studies of interactions with adsorbed molecules have concentrated upon testing the feasibility of a new and powerful experimental technique for direct, dynamic measurement of the mass of adsorbed gas on a surface. After demonstrating that piezoelectric silica crystals could detect even small changes in the mass of adsorbed molecules by measuring the change in frequency of acoustic waves across the surface, we have designed a research apparatus (Fig. 11) suitable for quantitative measurement of adsorption phenomena. This has involved design of new electronic circuitry as well as an improved experimental adsorption cell with associated flow systems. The initial goal of this improved apparatus is to demonstrate that quantitative and reproducible static adsorption-desorption results can be obtained first in vacuum conditions then at high pressure including necessary calibration factors for pressure and temperature effects. The second goal is to determine the capability of the approach to make dynamic measurements; transient measurements of period less than one second appear attainable and one millisecond may be achieved. If this apparatus realizes its potential, it should be very useful for measuring diffusion and mass transfer in supercritical solutions and as a detector for supercritical fluid chromatography.

Fig. 11. Schematic drawing of SAW apparatus for adsorption dynamics.

**Interactions of Solvents, Solutes, and Surfaces:
Adsorption and Supercritical Extraction**

Peer-Reviewed Publications

H. D. Cochran, L. L. Lee, and D. M. Pfund, "Application of the Kirkwood-Buff Theory of Solutions to Dilute Supercritical Mixtures," *Fluid Phase Equilib.* 34, 219-34 (1987).

D. M. Pfund, L. L. Lee, and H. D. Cochran, "Application of the Kirkwood-Buff Theory of Solutions to Dilute Supercritical Mixtures, II. The Excluded Volume and Local Composition Models," *Fluid Phase Equilib.* 39, 161-92 (1988).

H. D. Cochran and L. L. Lee, "General Behavior of Dilute Binary Solutions," *AIChE J.* 33, 1391-93 (1987); 34, 170 (1988).

M. Tanase and P. W. Fisher, "Tritium Release from Yttrium and Its Alloys in a Gas Stream," *J. Nucl. Mats.* 144, 151-56 (1987).

Peer-Reviewed Publications in Press

H. D. Cochran, D. M. Pfund, and L. L. Lee, "Theoretical Models of Thermodynamic Properties of Supercritical Solutions," *Sep. Sci. and Tech.* (accepted).

V. P. Gilbert, P. R. Bienkowski, and H. D. Cochran, "Technique for Surface Dynamics Measurements at High Pressures," *Sep. Sci. and Tech.* (submitted).

D. M. Pfund, L. L. Lee, and H. D. Cochran, "Application of the Scaled Particle Theory to Supercritical Mixtures," *Int. J. Thermophysics* (to be submitted).

Chemical and Physical Principles in Multiphase Separations

**KC 03 02 02 0; WFP ERKCTO6
C. H. Byers, T. C. Scott, and O. A. Basaran**

This program is comprised of several fundamental studies which address the issue of the use of electromagnetic fields to enhance the efficiency of multiphase separation processes. The primary focus of the program is upon improving mass transfer performance in liquid-liquid solvent extraction by utilizing theoretical insight gained from an in-depth analysis of electric field effects in dispersed liquid systems. A secondary thrust has been initiated to pursue investigation of potential applications of magnetic field interactions in macromolecular separation schemes.

A brief overview of recent progress in this program is presented in terms of the following specific areas:

- 1. Droplet Formation in Electric Fields
(O. A. Basaran, C. H. Byers, and J. J. Perona)**
- 2. Mass Transfer Enhancement by External Electric Fields
(T. C. Scott and R. M. Wham)**
- 3. Phase Stability and Coalescence in External Fields
(T. C. Scott and O. A. Basaran)**
- 4. High Gradient Magnetic Field Separations
(T. C. Scott)**

Chemical and Physical Principles in Multiphase Separations

KC 03 02 02 0; WFP ERKCTO6
C. H. Byers, T. C. Scott, and O. A. Basaran

DROPLET FORMATION IN ELECTRIC FIELDS

The use of an electric field to control the formation of small drops at an orifice in a circular disk is under investigation. During the past year, water drops were formed in a pure cyclohexane continuous phase in the pre-jetting regime using four different orifice diameters. Because of the application of high potential gradients (up to 1000 V/cm) and because the orifice plate produced a nonuniform field, drop volumes varied to as little as 20 times smaller than the drop volume for a zero-field case. The drops were virtually ellipsoidal in shape, and droplet eccentricity increased dramatically with field intensity.

An approximate mathematical model was developed, based on the potential field between a disk (the orifice plate) and an infinite plate (the grounded screen). The electric force on the drop was calculated from the field intensity at discrete points around the periphery. An empirical correlation for the electrical force for this particular plate diameter, spacing and organic fluid is

$$F_e = 9.80 \times 10^{-5} (V/1000)^2 v^{0.54}$$

where V is the applied voltage, and v is the drop volume. Values for predicted drop volumes using this model and those for experimental drop volumes agreed well up to voltages of about 2000 to 2500 volts, as shown in Fig. 12. The role of organic fluid properties is now under investigation.

The shapes of electrified drops formed at an orifice or that are pendant/sessile on a surface can be calculated exactly by finite element analysis. Figure 13 shows the effect of increasing electric field on a sessile drop of fixed volume that is neutrally buoyant in the surrounding fluid.

MASS TRANSFER ENHANCEMENT BY EXTERNAL ELECTRIC FIELDS

A general computer model based on finite element methods has been developed to simulate both numerically and graphically the flow of fluids in laminar channel flow. Special features of the computer code include capability to compute velocity profiles for any axisymmetric geometry and to place obstructions such as spheroids in the flowing fluid stream. This development will allow precise simulation of the velocity profiles in electric-field-distorted droplet/continuum flow, and thus allow explicit modeling of mass transfer phenomena observed in stretched water droplets suspended in flowing 2-ethyl-1-hexanol.

The finite difference method previously used to model circulating and oscillating-circulating droplet mass transfer has been extended to include stagnant and oscillating-stagnant droplets. A preliminary comparison of results for circulating and stagnant droplets reveals that the rate of mass transfer is a complex function of the hydrodynamic

Fig. 12.

Fig. 13. Effect of increasing electric field, (a) - (d), on the shape of a sessile drop that makes a fixed contact angle of 90° with a face of a parallel-plate capacitor. The arrows represent electric field vectors and the curves represent lines of constant electrostatic potential.

state of the system as well as the interfacial distribution properties of the transporting chemical species. The results suggest that with certain combinations of distribution coefficients that the transient separation factor between two chemical species may be enhanced by utilizing a stagnant droplet rather than a droplet which undergoes internal circulation.

Improvement on and continued use of the fluorescent dye technique has provided a large set of precise, single-component mass transfer data for circulating, oscillating-circulating, stagnant, and oscillating-stagnant droplets. Use of the fluorescence technique along with the video camera system allows accurate determination of values of the flux rate below $3 \times 10^{-11} \text{ g cm}^{-2} \text{ sec}^{-1}$ (Fig. 14). Figure 15 contains a plot of a portion of the mass transfer results for circulating and oscillating-circulating droplets. For the circulating case, a plot of dye flux vs continuous phase concentration yields a straight line which is indicative of the presence of an overall mass transfer coefficient relationship. Additional data on the graph indicate increases in the rate of mass transfer due to droplet oscillation at oscillation amplitudes of 5 and 10% of the droplet radius. The magnitude of the increase is a function of amplitude of oscillation as well as concentration of dye in the continuous phase with higher oscillation amplitudes and continuous phase concentrations resulting in the greatest increases. Enhancement ranges from a 10% increase, where the amplitude is 5% of the droplet radius, and the continuous phase concentration is 0.05 mg/L dye, up to approximately a 50% increase for a droplet with 10% amplitude and a 0.35 mg/L concentration.

Through an understanding of the basic principles of droplet behavior in steady and pulsed electric fields, a concept for a new type of solvent extraction apparatus had previously been introduced -- the emulsion-phase contactor (EPC). During the last reporting period, benchmark mass transfer runs were carried out on the conceptual device by measuring the ability of the system to transfer acetic acid from water into methyl-isobutyl-ketone (MIBK). The EPC outperformed conventional solvent extraction equipment by more than a factor of 10 in mass transfer efficiency, while requiring only a fraction of the energy necessary to create interfacial surface area. A proposal for a new program involving further research and development of the EPC has been prepared and submitted to the Advanced Energy Projects Division of BES. Any further development work on this item will be carried out separately in order to avoid possible dilution of the fundamental nature of the separations program.

PHASE STABILITY AND COALESCENCE IN EXTERNAL FIELDS

1. Dispersion: Drop Oscillations, Stability, and Break-up

The oscillations of drops play a central role in areas as diverse as mass transfer and separations and meteorology. Mathematical analysis of this problem leads to a dispersion equation that governs the frequency, B_I , and the rate of damping (or decay factor), B_R , of oscillations of a drop of one viscous fluid immersed in another. The dispersion equation is expressed by the vanishing of the determinant of a 7×7 matrix, solutions to which were heretofore known only in limiting cases -- for example, when both fluids are inviscid, when a drop of a viscous fluid is oscillating in a vacuum or a low density gas, when the viscosities of both fluids are "low," etc.

Fig 20 68 10-01

Fig. 15. Mass transfer results for circulating and oscillating-circulating droplets.

The original determinant has first been reduced to a 3×3 determinant: Fig. 16. The resulting nonlinear equation has been solved numerically in the complex plane to determine for the first time the exact character of drop oscillations for arbitrary values of drop size, physical properties of the two fluids, and interfacial tension. New experiments have been performed with drops that are much smaller than in previous studies and for values of the physical properties that are typical in solvent extraction. Preliminary theoretical results that have been obtained are found to agree well with experiments and also determine the range of validity of the previous approximate theories. By way of example, the theoretical results show that the low-viscosity approximation overestimates both B_R and B_I . The predictions of the low-viscosity approximation have been found to deteriorate as the drop radius decreases, the difference between the kinematic viscosities of the two fluids increases, and interfacial tension decreases.

A systematic study of the solutions of the dispersion equation is now under way. The theoretical results play a big role in providing guidance on future experiments that need to be performed.

2. Drop Coalescence in an Electric Field

In the absence of an externally applied electric field, two drops that are neutrally buoyant in the surrounding fluid can remain stationary if neither drop carries a net charge. Application of an external electric field, no matter how small, induces charges of the opposite sign on the sides of the two drops closest to one another and causes the drops to be attracted to each other. This is the basis of a new experiment that has been

$$\Delta = \left| \begin{array}{ccc} \omega, RQ^I & -1 - 2l & C \\ \frac{2\mu_i \omega_i Q^I}{R} - \frac{\beta \rho_i}{l} & \frac{\beta \Gamma}{l(l+1)} - \frac{2}{R^2} \left[\mu_i (l-1) + \mu_o (l+2) \right] + \frac{\beta \omega^2 \Gamma}{\beta l(l+1)} & - \frac{\beta \rho_o}{l+1} + \frac{2\mu_o C}{R^2} \\ \mu_i G & 2 \left[\mu_i (l^2 - 1) - \mu_o l(l+2) \right] & \mu_o F \end{array} \right| = 0$$

Fig. 16. Dispersion equation for small - amplitude oscillations of a drop of one viscous fluid immersed in another.

conceived to carry out a fundamental study of coalescence. The experimental setup will allow study of interactions between two charged/uncharged drops that are either (a) initially stationary or (b) falling in the surrounding fluid or (c) hurled at each other at an arbitrary angle.

3. Computer-Aided Finite Element Analysis

Powerful finite element methods are being used to determine theoretically, without any assumptions, static and dynamic shapes of electrified drops. Figure 17 shows the predicted profiles of a charged drop levitated by an externally applied dc electric field. Figure 18 shows the sequence of dynamic shapes that results as an initially spherical charged free drop is given a large amplitude impulse. As the drop oscillates, it goes through prolate and oblate configurations, and the oscillations also display coupling between the second and fourth harmonics.

The effect of externally applied electric fields, especially time-varying ones, is under investigation. Theoretical predictions of fissioning, jetting, and coalescence are some of the goals of this work.

HIGH GRADIENT MAGNETIC FIELD SEPARATIONS

Experimental results have been obtained using the 6-tesla superconducting magnet system shown in Fig. 19. Latex beads which are 0.1 microns in diameter have been captured by high-intensity, high-gradient magnetic fields located in a column packed with ferromagnetic spheres. In order to initiate capture, it was necessary to use a carrier solution containing $MnCl_2$ to increase the magnetic susceptibility of the beads in solution. Theoretical treatment of the magnetic field interactions with electrically charged molecules has been initiated to assess the possibility of using HGMS for protein separations.

Fig. 17. Effect of increasing electric field, (a) - (d), on the shape of a charged, levitated drop. The arrows represent electric field vectors and the curves lines of constant electrostatic potential.

Fig. 18. Sequence of predicted drop shapes: slightly charged drop subjected to a large amplitude disturbance.

Chemical and Physical Principles in Multiphase Separations

Peer-Reviewed Publications

- J. J. Perona and C. H. Byers, "Electrostatic Forces on Conducting Fluid Spheroids in a Parallel Field," *Chem. Engr. Science*, 42(11), 507 (1987).
- T. C. Scott, "Visualization of Flow Fields and Interfacial Phenomena in Liquid-Liquid Solvent Extraction," *Separation Science and Technology*, 22(2,3), 503 (1987).
- T. C. Scott, "Surface Area Generation and Droplet Size Control Utilizing Pulsed Electric Fields," *AIChE Journal*, 33(9), 1557 (1987).
- J. S. Watson, C. H. Byers, and D. R. Reinholt, "Electrically Stabilized Expanded Beds for Sorption Separations," *Separation Science and Technology*, 22(2,3), 949 (1987).
- R. M. Wham and C. H. Byers, "Mass Transport from Single Droplets in Imposed Electric Fields," *Separation Science and Technology*, 22(2,3), 447 (1987).

Papers Submitted, Reviewed, Accepted

- C. H. Byers and T. C. Scott, "An Electric Field Induced Dispersion and Coalescence Technique in Multiphase Liquid Systems," accepted for publication in *Proceedings of NATO ASI Meeting on the Liquid State and Its Electrical Properties*, Sinto, Fortugal, (1987).
- C. H. Byers, J. S. Watson, and W. G. Sisson, "Effects of Particle Shape and Size Distribution on Sorption and Flow Performance in Electrically Stabilized Expanded Beds," submitted to *Proceedings of the Fifth Symposium on Separation Science and Technology for Energy Applications*, Knoxville, Tennessee (1987).
- T. C. Scott and W. G. Sisson, "Droplet Size Characteristics and Energy Input Requirements of Emulsions Formed Using High-Intensity-Pulsed Electric Fields," accepted for publication in the *Proceedings of the Fifth Symposium on Separation Science and Technology for Energy Applications*, Knoxville, Tennessee (1987).
- T. C. Scott and T. L. Brumfield, "Use of High-Gradient Magnetic Fields for the Separation of Macromolecules," submitted to *Proceedings of the Fifth Symposium on Separation Science and Technology for Energy Applications*, Knoxville, Tennessee (1987).
- T. C. Scott and C. H. Byers, "A Model for Mass Transfer in Oscillating-Circulating Liquid Drops," submitted to *Chemical Engineering Communications*, December 1987.
- T. C. Scott and R. M. Wham, "An Electrically Driven Multistage Countercurrent Solvent Extraction Device: The Emulsion-Phase Contactor," submitted to *Industrial and Engineering Chemistry Research*, March 1988.
- C. H. Byers and J. J. Perona, "Drop Formation From an Orifice in an Electric Field," submitted to *AIChE Journal*, September 1987.

Chemical Kinetics of Enzyme Catalyzed Reactions

KC 03 02 01 0; FWP ERKCTO4

E. Greenbaum and J. Woodward

The project on Chemical Kinetics of Enzyme Catalyzed Reactions is focused on four research areas: (1) kinetic studies; (2) fundamentals of light energy conversion; (3) electron transfer reactions at metal-membrane interfaces; and (4) fundamentals of immobilization and chemical modification of cellular organelles and enzymes.

Chemical Kinetics of Enzyme Catalyzed Reactions

KC 03 02 01 0; FWP ERKCTO4

E. Greenbaum and J. Woodward

This research project is focused on quantum processes and enzyme catalysis for basic studies on the chemical and physical principles of renewable energy production by photosynthesis. Key areas of investigation during the current reporting period were: (1) the nature and location of the light reactions in photosynthetic membranes; (2) chemistry and physics of photosynthetic photoelectrochemical cells; (3) electron transfer reactions at metal-membrane interfaces; and (4) an investigation of synergism among cellulase components.

Oriented Photocurrents by Entrapped Platinized Chloroplast Membranes

According to the presently accepted molecular model of green plant photosynthesis, the conversion of light energy into chemical free energy occurs by vectorial photochemistry. As illustrated in Fig. 20, the vectorial nature of the photochemical reactions of photosynthesis takes place in specialized reaction centers that are embedded in the photosynthetic membranes. The membranes themselves are flattened sack-like structures that are topologically equivalent to spheres. The orientation of the primary electron transfer process in the reaction centers is such that movement of electrons takes place from the inner surface of the membrane to the outer surface. Based on this molecular model of photosynthesis it follows that upon illumination the electric potential of the external surface of the photosynthetic membrane swings negative with respect to the internal surface.

Fig. 20. Schematic illustration of platinized photosynthetic membrane.

It has recently been discovered in the Chemical Technology Division that appropriate surface chemical modification of photosynthetic membranes allows electrical contact with the reducing end of the Photosystem I reaction center. This contact has been experimentally verified by measuring the hydrogen that is photocatalytically evolved from the platinized chloroplasts. As illustrated in Fig. 21, oriented photocurrents have also been observed from platinized chloroplasts by placing them in an electrochemical cell assembly. The vectorial model of photosynthesis predicts the sign of the photovoltage and direction of flow of photocurrent. The observed photocurrents are consistent with this prevailing model and provide a macroscopic verification of the model. Control experiments (Fig. 22) indicated that the oriented nature of the observed photocurrents could not be attributed to inherent asymmetries associated with the construction of the cell or light gradients created by the attenuation of light by chlorophyll pigments.

Comparative Study of the Photochemistry of Chloroplast Membranes and Photosystem II Particles

A comparative study of the photoreducing potentials of spinach thylakoid membranes and spinach photosystem II particles has been made. The study is based on energetic requirements for the evolution of molecular hydrogen. Hexachloroplatinate ions have been used as electron acceptors in a Hill-like assay for oxygen evolution measurements with both thylakoid membranes and photosystem II particles. However, unlike other Hill acceptors, such as ferricyanide, hexachloroplatinate can be fully reduced to metallic

Fig. 21. Photocurrent vs incident-light intensity-Pt/Ag electrode assembly.

Fig. 23. Scatchard plots for the purified cellulase components from *T. reesei*.

Synergism between EG I and CBH I was observed at both saturating and non-saturating concentrations over a 24-h period. However, the greatest synergistic effect was observed with non-saturating concentrations of EG I and CBH I (Fig. 24). A similar result was obtained with CBH I and CBH II (data not shown). The relationship between the level of saturation of Avicel with cellulase components and the synergistic effect was seen emphatically when Avicel was hydrolyzed by a mixture of EG I, or EG II with CBH I and CBH II (Table 2). Further studies indicated that there was a distinct relationship between the concentration of the cellulase components and the degree of synergism among them (Fig. 25). At the highest concentration of cellulase used, 360 micrograms/mL (160 micrograms/mL EG II, 100 micrograms/mL CBH I, and 100 micrograms/mL CBH II), little synergism was observed. However, as the concentration of each component decreased, the degree of synergism increased reaching a maximum at a cellulase concentration of 20 micrograms/mL (5 micrograms/mL EG II, 10 micrograms/mL CBH I, and 5 micrograms/mL CBH II). At lower concentrations than these the degree of synergism declined, suggesting that an optimum concentration of cellulase components exists for maximum synergistic effect on Avicel.

Fig. 24.

Table 2. Hydrolysis of Avicel by a mixture of EG I, CBH I, and CBH II by saturating and non-saturating concentrations of each enzyme

TIME OF REACTION (h)	GLUCOSE CONCENTRATION (mg)					
	NON-SATURATING			SATURATING		
	THEOR. (A)	MEAS. (B)	B/A (%)	THEOR. (A)	MEAS. (B)	B/A (%)
1	3.6	5.6	155	7.4	7.6	103
2	5.0	10.3	206	10.6	12.6	119
3	6.0	10.9	182	13.5	16.3	121
4	7.3	13.9	190	16.0	16.4	115
5	7.6	15.4	203	17.5	20.6	118
6	6.1	17.5	216	19.3	23.5	122
7	8.8	19.3	219	20.3	24.4	120
24	18.4	31.6	173	41.2	43.4	105

AVICEL (10 mg/mL) WAS INCUBATED WITH EG I (20 μ g/mL), CBH I (20 μ g/mL), AND CBH II (10 μ g/mL) UNDER NON-SATURATING CONDITIONS AND WITH EG I (100 μ g/mL), CBH I (80 μ g/mL), AND CBH II (87 μ g/mL) UNDER SATURATING CONDITIONS. FOR OTHER DETAILS SEE EXPERIMENTAL PROTOCOL.

ABBREVIATIONS: MEAS. - MEASURED
THEOR. - THEORETICAL

Fig. 25.

Table 3 shows the relationship between the amount of glucose formed by the action of EG II, CBH I, and CBH II on Avicel as a function of the percentage of the highest concentration of these components used (360 micrograms/mL). This concentration of cellulase resulted in the greatest glucose production in 7 h (~51 mg). Approximately 75% (~38.3 mg) of this amount of glucose was produced by 40 micrograms/mL of cellulase, or 11% of the maximum enzyme concentration. The enzymatic hydrolysis of cellulose should become a more efficient and cheaper process if the phenomenon of synergism between cellulase components is utilized effectively, so that the enzyme requirement to generate glucose is dramatically reduced. This would be possible when supplies of cellulase components are readily available and cheap through the application of genetic engineering techniques. The genes for CBH I and EG I have already been cloned.

Table 3. Hydrolysis of Avicel as a function of the percentage of maximum enzyme concentration

Percentage of Maximum Enzyme Concentration	Glucose Production*			
	Theoretical**		Measured	
	mg	% of max.†	mg	% of max.†
1.1	5.8	12	9.3	18
2.8	9.8	20	14.6	28
5.6	10.4	21	21.1	41
11.1	22.1	45	38.3	74
25	23.0	47	39.1	76
40	30.7	63	42.1	82
50	28.1	58	34.8	68
75	38.5	79	46.2	90
100	48.6	100	51.5	100

*The amount of glucose produced is that after 7h. Maximum enzyme concentration equals 360 g/L (160 g/L EG II, 100 g/L CBH I and 100 g/L CBH II).

** Summation of glucose produced by components acting alone.

†Percentage of glucose produced by maximum enzyme concentration.

Chemical Kinetics of Enzyme Catalyzed Reactions

Peer-Reviewed Publications

E. Greenbaum and M. Reeves, "Photosynthetic Water Splitting: A Biotechnological Approach to Gaseous Fuel Synthesis," pp. 49-54 in Vol. IV of *Proceedings of the 1986 International Gas Research Conference, Sept. 8-11, 1986, Toronto, Canada*, pp. 49-54.

J. Woodward, H. J. Marquess, and C. P. Picker, "Affinity Chromatography of β -Glucosidase and Endo- β -Glucanase from *Aspergillus niger* on Concanavalin A-Sepharose: Implications for Cellulase Component Purification and Immobilization," *Preparative Biochemistry* 16, 337-52 (1986).

Peer-Reviewed Publications in Press

J. Woodward, M. K. Hayes, and N. E. Lee, Hydrolysis of Cellulose by Saturating and Non-Saturating Concentrations of Cellulase: Implications for Synergism," *BIO/TECHNOLOGY* 6 (1988).

E. Greenbaum, "Hydrogen Production by Algal Water Splitting," to be published as a chapter in Algae and Human Affairs, C. A. Lembi and J. R. Waaland (ed.), Cambridge University Press (1987).

E. Greenbaum, "Electrical Contact of Molecular Components in a Submicron Biological Structure," in Proceedings of the Third International Symposium on Molecular Electronic Devices, F. L. Carter, ed. (1987).

J. Woodward, M. Reeves, D. Allison, and E. Greenbaum, "Effect of Exogenously Added Manganese Chloride on the Operational Stability of the Chloroplast-Ferredoxin-Hydrogenase System," *Enzyme Microbial Technology* 10 (1988).

J. Woodward and J. C. Bales, "The Adsorption of *Trichoderma reesei* C30 Cellulase Protein to Protein Adsorbents: Application to Cellulose Recovery and Reuse," Advances in Biochemical Engineering.

Non-Peer-Reviewed Publications

J. Woodward, "Utilization of Cellulose as a Fermentation Substrate: Problems and Potential," in Carbon Substrates in Biotechnology, J. D. Stowell, A. J. Beardsmore, C. W. Keevil, and J. R. Woodward, Eds. IRL Press, Oxford, pp. 45-65 (1987).

E. Greenbaum, "Platinized Chloroplasts," *ORNL Review* 19(3), 161 (1986).

J. Woodward, "Methods of Immobilization of Microbial Cells," *J. Microbiological Methods* (1988) - in press.

Biographical Sketches

Osman A. Basaran

Osman Basaran received his degrees in chemical engineering from the Massachusetts Institute of Technology (B.S.) and the University of Minnesota (Ph.D.). He spent 3-1/2 years at Air Products and Chemicals and then joined the Oak Ridge National Laboratory in January 1988. His current and recent research interests include: electrohydrodynamics of drops and bubbles, ferrohydrodynamics, numerical (esp. finite element) analysis, fluid mechanics, membranes and facilitated transport, reactive distillation, landfill gas generation and kinetic theory of polymeric fluids. He has published 5 papers and has 2 papers accepted for publication in refereed journals, has 10 publications of work presented orally or by poster, and has published (with R. E. Rosensweig) a set of lecture notes on ferrohydrodynamics. He is a member of the AIChE, APS, and SIAM.

Jimmy T. Bell

Jimmy Bell (B.S., 1960 Berry College; Ph.D., 1963, Physical Chemistry, University of Mississippi) is a member of the Chemical Technology Division of the Oak Ridge National Laboratory. He has been with ORNL for approximately 24 years. His research has been associated principally with separation science and technology related to fission, fusion, and other energy systems. He has published approximately 80 papers and reports, 40 of which are in refereed journals.

Paul R. Bienkowski

Paul Bienkowski received the B.S. degree in chemical engineering from Newark College of Engineering in 1970 and the M.S. and Ph.D. degrees, also in chemical engineering, from Purdue University in 1972 and 1975. He spent 7 years working as a research engineer for Amoco Chemicals R&D in Naperville, Illinois, followed by 4 years at Purdue University as an instructor in chemical engineering and a research engineer at the Laboratory of Renewable Resources Engineering. For the last 3 years he has held a position as an Associate Professor of Chemical Engineering at the University of Tennessee with research interests concentrated in thermodynamics, biotechnology, and environmental engineering. He has published 18 articles in refereed journals.

Charles H. Byers

Charlie Byers holds chemical engineering degrees from McGill University (B.S.) and the University of California at Berkeley (Ph.D.). His professional experience includes industrial research and research management with the Merichem Company and Polaroid Corporation. He has held teaching positions at the University of Rochester and Massachusetts Institute of Technology. In addition to his position as group leader of the Engineering Research Group, he holds a part-time professorship at the University of Tennessee. Among his areas of interest are crystallization and transport properties using laser-light scattering methods, interfacial phenomena in separation processes, thermodynamics, and process simulation. He has recently taught graduate chemical engineering courses in transport phenomena, thermodynamics, reactor design, and applied mathematics as well as directing graduate research. He has more than 25 publications to his credit, holds memberships in the AIChE and ACS, and is a professional engineer.

Henry D. Cochran

Hank Cochran received the B.S. degree in chemical engineering from Princeton University in 1965 and the M.S. and Ph.D. degrees also in chemical engineering from MIT in 1967 and 1973. After one year on the faculty of the MIT Department of Chemical Engineering, he has spent 17 years in the Chemical Technology Division at ORNL, including 7 years as an R&D program manager. In addition, he is an adjunct professor in the Department of Chemical Engineering at the University of Tennessee. He has published 27 articles in refereed journals (plus more than 100 non-refereed publications) in the following fields: supercritical solubility, vapor-liquid equilibrium, statistical mechanics, a gas absorption-stripping process, coal liquefaction and gasification, fluid dynamics of open bubble columns, a molten salt reductive extraction process, reverse osmosis, and heterogeneous catalysis.

Elias Greenbaum

Eli Greenbaum is a group leader in the Chemical Technology Division. His primary responsibilities are fundamental research in the chemical and physical principles of conversion of light energy into chemical energy and surface chemical modification of photosynthetic membranes for the study of new composite bioelectronic material structures. During the past year, Greenbaum was selected by the National Academy of Sciences to participate in the Visiting Scholar's Exchange Program with the People's Republic of China and will be a plenary speaker at the Seventh International Conference on Photochemical Conversion and Storage of Solar Energy. He holds a Ph.D. degree from Columbia University and is the author of 35 publications, 33 of which have appeared in peer-reviewed scientific journals. Greenbaum has been at ORNL 9 years.

J. Robert Hightower

Bob Hightower received the B.S., M.S. and Ph.D. degrees in chemical engineering at the University of Mississippi and Tulane University. He joined the staff of the Chemical Technology Division at the Oak Ridge National Laboratory in 1964. Dr. Hightower has held a series of research and development positions in Chem Tech and is at present Head of the Chemical Development Section. His current primary research interests are in the fields of nuclear fuel reprocessing and fission product transport in nuclear reactor accidents. He also serves as an adjunct professor of chemical engineering at the University of Tennessee, Knoxville. He has more than 25 publications to his credit, is a Fellow of the American Institute of Chemical Engineers, is chairman of the Advisory Committee for the Chemical Technology Program at State Technical Institute in Knoxville, and is a registered professional engineer in Tennessee.

Joseph J. Perona

Joe Perona studied chemical engineering at Rose Polytechnic Institute (B.S., 1952) and Northwestern University (Ph.D., 1956). He is currently professor and Head of the Department of Chemical Engineering at the University of Tennessee and a part-time member of the research staff of ORNL. His research interests center on transport of mass and heat with reaction in multiphase systems. He is a Fellow of the American Institute of Chemical Engineers and a registered professional engineer in Tennessee.

David J. Pruett

Dave Pruett (B.S. and M.S. in Chemistry, Michigan Technological University, 1974 and 1975, respectively; Ph.D. in Chemistry, Michigan State University, 1978) has been with the Chemical Technology Division since 1978. His research has covered the chemistry of actinides and fission products. He has 2 patents and over 20 published papers, 13 of them in refereed journals. He also has a book chapter in press and is a member of the National Research Council's Committee on Nuclear and Radiochemistry.

Charles D. Scott

Chuck Scott received the B.S., M.S., and Ph.D. degrees in chemical engineering at the University of Missouri and the University of Tennessee. He joined the staff at the Oak Ridge National Laboratory in 1957 where he has been a member of the Chemical Technology Division. Dr. Scott has held a series of research and development positions in that division and at present is a Senior Research Fellow and Head of the Energy Research Section. His primary research interests are with heterogeneous interactions with an emphasis in separations science and technology and bioprocessing research. He also serves as an adjunct professor of chemical engineering at the University of Tennessee, Knoxville. Dr. Scott has over 100 open-literature publications, many technical reports, and 11 patents. He has received a number of national awards and honors for his work, including membership in the National Academy of Engineering. He also regulatory serves on various committees of the National Research Council and the National Science Foundation.

Timothy C. Scott

Tim Scott received the B.S. degree in chemical engineering from the University of Tennessee, Knoxville, in 1980 and the Ph.D. in chemical engineering from the University of Wisconsin, Madison, in 1985. He has spent the last 3 years in the Energy Research Section of the Chemical Technology Division of Oak Ridge National Laboratory as a principal investigator in the area of multiphase separation science research. In addition, he is an Adjunct Associate Professor in the Department of Chemical Engineering at UTK with both teaching and graduate research responsibilities. He has published 9 articles in refereed journals, has 5 articles currently submitted for publication in refereed journals and 2 non-refereed publications. Publications are relevant to the following fields: biotechnology, nuclear fuel reprocessing, reaction engineering, and separation science and technology.

Susan A. Sherrow

Susan Sherrow (B.S. in Chemistry, North Carolina State University, 1978; Ph.D. in Physical Chemistry, University of California, Berkeley, 1983) has been in the Chemical Technology Division since 1984 working principally on spectroscopy. Her major fields of interest are molecular spectroscopy and molecular beams. She has authored 3 publications.

Louis "Mac" Toth

Mac Toth (B.S. in Chemistry and Physics, Louisiana State University, 1963; Ph.D. in Chemistry, University of California, Berkeley, 1967) has been with the Chemical Technology Division since 1967 and is currently a research group leader. His interests are in spectroscopy, photochemistry, structural characteristics of polymers, kinetics, and equilibria of molecules related to nuclear fuels. He has authored more than 50 publications.

Jonathan Woodward

Jonathan Woodward obtained his B.Sc. (Hons) and Ph.D. in biochemistry from the University of Surrey, England. He was a post-doctoral research associate at Vanderbilt University, Nashville, prior to obtaining his present position as staff scientist in March 1980. He has 20 publications in peer-reviewed journals, 6 book chapters and/or review articles, 1 edited book, and 12 publications of work presented orally or by poster.