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Period Ending March 31, 1977

OAK RIDGE NATIONAL LABORATORY

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for Period Ending March 31, 1977

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Abstract

This report contains a description of the work of the Chemistry Division covering the period from Nov. 1, 1975, to Mar. 15, 1977, in the various fundamental and applied research areas of chemical interest in energy research. These synoptic reports, in order to be current, include unpublished as well as published work.

1. Coal-Related Research, Catalysis, and Organic Chemistry

1.1 COAL-RELATED RESEARCH

1.1.1 Analytical Method for Determining Alkenic Unsaturation in Coal and in Coal-Derived Products

G. W. Kabalka¹
V. F. Raaen

W. H. Roark
C. J. Collins

The molecular rearrangements in coal liquefaction processes are not completely understood, but it is assumed that liquefaction involves the cleavage of certain labile (scissile) bonds in the coal structure. Numerous candidates for the scissile bond category exist; methylene groups and ether linkages are often-discussed possibilities.

Because the possibility of the alkene linkage (i.e., carbon-carbon double bond) as a potential scissile bond had been overlooked, we decided to investigate alkene linkages in coal and to attempt to cleave these linkages under liquefaction conditions. At the onset of our study, no reliable method was available for determining the number of alkene linkages in coal structures. We felt that such determinations were possible via the hydroboration-carbonylation sequence and isotopic labeling experiments.

Our procedure for the determination of the number of double bonds in coal is based on certain facts: (1) trialkylboranes are readily formed via the reaction of borane (BH₃) with carbon-carbon double bonds, (2) trialkylboranes react with carbon monoxide to form new carbon-carbon bonds, and (3) carbon monoxide containing ¹⁴C is readily synthesized.

We planned to hydroborate all of the double bonds in coal, convert the resultant organoborane into trialkylboranes by reaction with a simple alkene (ethylene), and carbonylate the trialkylboranes with labeled carbon monoxide. The number of double bonds in a coal sample can be determined by ¹⁴C

assay. The reaction sequence is outlined in Scheme I (where ~C=C~ is a schematic representation of coal containing a carbon-carbon double bond):

Application of the technique to coal and coal-derived products would determine the number of double bonds in the samples before and after liquefaction.

Scheme I represents an oversimplification of the problem. Although coal contains numerous functional groups that react with borane, only reactions of carbon-carbon double bonds lead to formation of trialkylboranes. We demonstrated that only trialkylboranes react with carbon monoxide under our test conditions. To ensure the desired reaction, we added excess hydride and removed the volatile triethylborane (formed by reaction of excess BH₃ with CH₂=CH₂) before adding carbon monoxide.

As a double check on our data, a series of reactions was also carried out in which labeled cyanide ion was added to the hydroborated coal. The cyanide reaction parallels the carbon monoxide reaction. Results, summarized in Table 1.1, demonstrate that our newly developed technique does differentiate between the number of double bonds in coal samples.

Control experiments show that pyridine-soluble vitrinite does not incorporate labeled carbon monoxide unless subjected to the borane treatment. The apparent molecular weight in these control experiments is 61,000 g for each fraction containing a carbon monoxide unit. Other control experiments indicate that partially alkylated boranes (boronic esters, etc.) do not react with carbon monoxide.

Table 1.1. Results of determination of alkenic bonds in coal fractions

Sample	MW ^{a,b}	Double bonds ^c (%)
Pyridine-soluble vitrinite ^d	1500	1.7
Vitrinite	7300	0.2

^aMW is the apparent molecular weight of the sample containing one ¹⁴C (and hence, originally, one double bond) after the treatment outlined above.

^bAverage of two or more experiments.

^cPercent by weight of carbons involved in double bonding.

^dPyridine-soluble fraction obtained by extracting vitrinite with pyridine. This fraction comprises approximately 20% of the mass of vitrinite itself.

The experiment with labeled cyanide shows that pyridine-soluble vitrinite has an apparent molecular weight per double bond of 1400 g—a close agreement with the carbon-¹⁴C monoxide experiment.

A new experimental technique that measures the number of double bonds in coal has been developed. The technique has been applied to Illinois No. 6 vitrinite and to the pyridine extractables derived from it. The method appears to offer reproducible results and is being applied to coal samples that have been subjected to liquefaction. If dichlorocarbene reacts only with alkenic unsaturation (i.e., double bonds), the results of the present study are in remarkable agreement with the hydroboration-carbonylation method for determining double bonds in coal developed by Kabalka.

1. Research participant, Department of Chemistry, University of Tennessee, Knoxville, June through August 1976.

1.1.2 Thermal Cleavage of Chemical Bonds in Selected Coallike Structures

B. M. Benjamin	W. H. Roark
V. F. Raaen	L. Brown
P. H. Maupin	C. J. Collins

Experimental results suggest that ether and hydrogen-bonded structures are ruptured during conversion of coal to pyridine-soluble material (i.e., when coal is heated to 400°C with or without a hydrogen-donor solvent).¹ We showed recently that carbon-carbon cleavage of certain alkanes occurs under similar conditions, and that Illinois No. 6 vitrinite is a better catalyst for some of these reactions than is tetralin.² We now report the chemical effects

of thermolysis and hydrogenolysis on a large number of compounds containing a variety of structural features and functional groups. These compounds were chosen on the basis of models³⁻⁵ proposed to represent coal structures.

Experiments were conducted in two ways. Small samples, 100 mg, were placed in thick-walled glass tubing with 200 mg of tetralin. After flushing with argon, the tube was sealed and heated to 400°C in a furnace. Larger quantities, 1 to 2 g, were allowed to react in 6-in.-long, 3/8-in.-OD, 1/16-in.-wall stainless steel tubing sealed at both ends by Swagelok fittings. Air was not removed, since no product differences could be detected when air was replaced by argon.

Gases were collected by vacuum line techniques and were characterized by gas chromatography (GC) or by conversion to suitable derivatives for identification. Liquid and solid products were separated by preparative GC or by fractional distillation and crystallization. These products were identified by GC retention times, NMR, and mass spectral analyses.

When reactions were conducted for short times, the tubes were placed in a preheated oven. The tubes were cooled in air after removal from the oven. No attempts were made to correct for heatup and cooldown times.

The following compounds were stable in tetralin at 400°C for 18 hr: toluene, hexamethylbenzene, triphenylmethane, tri(*p*-tolyl)-methane, diphenylmethane, ethylbenzene, propylbenzene, amylbenzene, phenanthrene, 9-10-benzophenanthrene, *o,m,p*-cresols, β -naphthol, 5-hydroxyindane, dibenzofurane, dibenzothiophene, carbazole, diphenylsulfide, and POPOP.

In contrast to the above-mentioned results, structures containing two-carbon bridges between aromatic residues are cleaved with varying degrees of ease, depending, in part, on the number of attached aryl groups. Thus, a series of diaryl- and triarylethanes are cleaved between the two central carbons. For example, 1,2-diphenyl-1-*p*-tolylethane yields equimolar quantities of toluene and *p*-tolylphenylmethane. The latter reactant cleaves more readily than 1,1,2-triphenylethane, which, in turn, is more reactive than the diarylethanes. 1,1,2,2-Tetraphenylethane is the most reactive of the substituted ethanes investigated.

Although diaryl ethers do not cleave readily,⁶ we found that aryl alkyl ethers containing at least two alkanic carbons cleave with about the same ease as benzyl ethers, yielding water as one of the products. Water is produced also as a result of the breakdown

of certain other compounds, such as 2,2'-dihydroxy-di(1-naphthyl)-ethane, which decomposes to produce, in addition to water, dinaphtho[*a*]-furane, methane, β -naphthol, α -methyl- β -naphthol, and a dark residue. These cleavage and condensation reactions undoubtedly contribute to the formation of water during solvent refining of coal.

A number of diverse compounds were found as a consequence of heating phenetol (phenyl ethyl ether) with tetralin at 400°C. The major products are ethane, ethylene, benzene, phenol, toluene, ethyl benzene, and water. Small yields of many other compounds were found; we identified the following using gas chromatography-mass spectrometry: propylbenzene, butylbenzene, indane, methylindane, *p*-ethylphenol, ethylindane, 1-ethyl-tetralin, 6-ethyltetralin, methyl-naphthalene, and ethyl-naphthalene. We proved that some of the compounds are derived from the starting tetralin by carrying out separate reactions with the ¹⁴C-labeled starting materials, phenylethyl-1-¹⁴C-ether and tetralin-1-¹⁴C.

Nitrogen and sulfur compounds are also components of coal, and their presence is of economic importance in producing clean fuel from coal. During solvent refining of coal, the sulfur content of the product is reduced. Some of the sulfur is removed as H₂S and probably is derived from thiophenol-like constituents. We found that thiophenol is converted under experimental conditions to diphenyl sulfide, H₂S, and a trace of benzene. Similar results were obtained with methylphenylsulfide—methane and thiophenyl were produced. Thianthrene yielded H₂S and 9-thiafluorene.

The fate of nitrogen-containing structures remains obscure. In our experiments some of the small

nitrogen-containing model heterocyclic structures polymerize when heated with tetralin. Carbazole, aniline, and methyl aniline are structural types that are stable.

Two classes of compounds are frequently mentioned as constituents of coal: (1) condensed polynuclear aromatic hydrocarbons and (2) quinones. The presence of these classes has not been satisfactorily demonstrated in significant quantities. Our evidence suggests that many polynuclear aromatic hydrocarbons are stable with tetralin at 400°C. Several different quinones were studied. Thus, *o*-phenanthraquinone quantitatively yields 9-phenanthrol; anthraquinone yields anthracene and 9,10-dihydro-anthracene. 1,4-Naphthoquinone is converted to an intractable oil.

Two important observations should be mentioned here. Many of the compounds subjected to hydrogenolysis with tetralin at 400°C react slowly enough to suggest that cleavage of the structures they represent cannot be important in coal conversion:

1. Reactivities differ between parent compounds such as 1,1,2-triphenylethane and their derivatives, which have an additional alkyl or hydroxyl group. For example, 1,2-diphenyl-1-*p*-tolylethane decomposes much more rapidly than does 1,1,2-triphenylethane. *o*-Hydroxydiphenylmethane undergoes partial cleavage in 1 hr, whereas diphenylmethane is stable for 18 hr.

2. Decomposition and cleavage at 400°C of many of the arylalkyl compounds studied take place much faster in the presence of vitrinite alone than in the presence of tetralin. Illinois No. 6 vitrinite is a better hydrogen donor than is tetralin. This fact is illustrated by the results listed in Table 1.2. The data for the hydrogenolysis of benzophenone in the

Table 1.2. Comparison of cleavage of 1,3-diphenylpropane and benzophenone with tetralin and vitrinite as hydrogen donors

Reactants	Time	Temperature (°C)	Decomposition (%)
1,3-Diphenylpropane, tetralin ^a	30 min	400	23
1,3-Diphenylpropane, tetralin, vitrinite ^a	30 min	400	43
1,3-Diphenylpropane, vitrinite ^a	30 min	400	65
Benzophenone, tetralin ^b	1 hr	400	12
Benzophenone, vitrinite ^b	1 hr	400	30

^aAn excess of tetralin and/or vitrinite was noted. The products were essentially the same in each case.

^bTetralin or vitrinite was in excess. Different ratios of vitrinite were used. The product was mostly diphenylmethane, with traces of toluene and water.

presence of vitrinite are particularly important, since they rule out disproportionation of the reactant and require that hydrogen for the formation of diphenylmethane and toluene must come from the vitrinite.

Finally, we investigated the mechanism of the formation of a mixture of α - and β -methyl-naphthalenes from Wyodak coal and tetralin- ^{14}C at 400°C (see Sect. 1.1.4). Using 1,3-diphenyl-propane-2- ^{14}C as a partial model for coal structure, we demonstrated the formation of α - and β -methyl- ^{14}C -naphthalenes. Thus the methyl groups in the α - and β -methyl-naphthalenes come from the center carbon in 1,3-diphenyl-propane. We have proposed free-radical mechanisms for these reactions.

1. H. W. Sternberg, "Storch Award Address," *Proc. Div. Fuel Chem.*, 172d National Meeting of the American Chemical Society, San Francisco, Aug. 31, 1976.

2. C. J. Collins, V. F. Raaen, B. M. Benjamin, and G. W. Kabalka, *Fuel* 56, 107 (1977).

3. P. N. Givens, *Fuel* 39, 147 (1960).

4. G. R. Hill and L. B. Lyon, *Ind. Eng. Chem.* 54, 36 (1962).

5. W. Wiser, *Prepr. Pap. 169th Nat. Meet. Div. Fuel Chem. Am. Chem. Soc.*, Philadelphia, Pa., April 6-11, 1975, 20(2), 122 (1975).

6. G. Kölling and D. Hausigk, *Brennst.-Chemie* 50, 1 (1969); R. Brucker and G. Kölling, *ibid.* 46, 41 (1965).

1.1.3 Phase Transfer Catalysis Reactions of Dichlorocarbene- ^{14}C with Illinois No. 6 Vitrinite and with Wyodak Coal

V. F. Raaen C. Hilborn¹

The product obtained by heating Illinois No. 6 vitrinite for 1 hr at 400°C with tetralin was extracted with pyridine, the unbound pyridine was removed, and the residue was subjected to treatment at ambient temperature with dichlorocarbene- ^{14}C , which was generated from $^{14}\text{CHCl}_3$ through phase transfer catalysis [see, for example, C. M. Starks, *J. Am. Chem. Soc.* 93, 195 (1971)]. Triethylbenzylammonium chloride was used as the catalyst. The product was continuously extracted with pentane, and the residue was extracted continuously with benzene, yielding as a benzene-insoluble fraction the major portion of the total sample. Radioactivity assay demonstrated 5.4% reaction of the dichlorocarbene- ^{14}C .

A similar experiment in which dichlorocarbene- ^{14}C was allowed to react with pyridine extractables from vitrinite demonstrated 6% reaction, whereas crushed vitrinite alone reacted to the extent of 5%.

Chloroform- ^{14}C will react with vitrinite, but even at 300°C its reactivity is much less than any of the reactivities reported above. Blank experiments with chloroform- ^{14}C at ambient temperatures show a maximum of 1.6% retention. Dried Wyodak coal, when subjected to reaction with dichlorocarbene- ^{14}C under conditions similar to those reported above, exhibited an amazing 14% uptake of $^{14}\text{CCl}_2$.

Dichlorocarbene reacts with alkenes and with alkanols; it is not reactive toward phenols or toward aromatic unsaturation. Final interpretation of the results must await confirmatory as well as blank experiments in order to rule out interfering reactions.

1. Student from Centenary College during an Oak Ridge semester under Southern Colleges and Universities Union sponsorship.

1.1.4 Reactions of Vitrinite (Illinois No. 6) and Wyodak Coal with Tetralin- ^{14}C

V. F. Raaen C. Hilborn¹

In a typical preliminary experiment with Wyodak coal (a subbituminous noncaking coal obtained from Wyodak Resources Development Co., Gillette, Wyoming), a sample was heated with tetralin- ^{14}C for 1 hr at 400°C . The product was extracted with pyridine. After removal of pyridine from the extract, the solid residue was continuously extracted with benzene. On ^{14}C assay the solid residue contained 4.6% tetralin equivalent. This solid material was heated again to 400°C with nonradioactive tetralin for 1 hr; the tetralin isolated contained no radioactive tetralin nor naphthalene. Gas chromatography, however, revealed two peaks that were radioactive and whose retention times corresponded to methyl- and ethylnaphthalenes. Our preliminary conclusion is that the tetralin is more than a hydrogen donor; it actually reacts chemically with the pyridine-soluble benzene-insoluble fraction.

Similar experiments with vitrinite from Illinois No. 6 coal were inconclusive because the samples contained larger fractions of asphaltenes and oils, which could not be separated completely from the tetralin- ^{14}C and naphthalene- ^{14}C . Experiments that should circumvent these problems are now under way.

1. Student from Centenary College during an Oak Ridge semester under Southern Colleges and Universities Union sponsorship.

1.1.5 Reaction of Coal Fractions with ^{14}C -Labeled Amines

E. W. Hagaman V. F. Raaen

Preasphaltenes, asphaltenes, and oils are all soluble in pyridine. Vitrinites are also partially soluble in this solvent. Enhanced pyridine solubility indicates that certain chemical bonds in the coal have been broken or otherwise modified. Present work has demonstrated that the solubilizing actions of pyridine for asphaltenes and related coal fractions can be classified into three types: (1) physical solution processes; (2) weak chemical processes in which the bound pyridine can be displaced, probably acid-base complexation through hydrogen bonding; and (3) stronger processes in which the bound pyridine probably reacts chemically with the coal.

Chemically pure pyridine- ^{14}C was synthesized and used for the continuous extraction of a sample of Illinois No. 6 vitrinite. The labeled solvent was subsequently removed from the solution under high vacuum (10^{-6} torr) by distillation into a trap surrounded with liquid nitrogen. After being pumped for several days, the percentage pyridine- ^{14}C still bound to the sample was determined by radioactivity assay: $19.7\% \pm 0.3\%$ of the solid residue was pyridine or pyridine equivalent.

In a separate experiment another sample of vitrinite was heated to 400°C for 1 hr in the presence of tetralin, and the asphaltene fraction obtained (soluble in benzene, insoluble in pentane) was isolated and dissolved in pyridine- ^{14}C . The pyridine- ^{14}C solution was treated as described in the preceding paragraph, leaving a solid residue from which no more solvent could be removed under high vacuum. Radioactivity assay indicated that 14% of the solid material was pyridine or pyridine equivalent.

The vitrinite-pyridine- ^{14}C sample ($19.7\% \pm 0.3\%$ pyridine- ^{14}C content) was exchanged with normal pyridine, but only 65% of the total pyridine- ^{14}C content could be removed; that is, the total pyridine- ^{14}C content of 19.7% could be reduced no lower than 6.9%. Similar experiments with benzene- ^{14}C showed that less than 1% of the benzene was retained by an asphaltene fraction.

α -Phenylethyl- ^{14}C -amine, which is a stronger base than pyridine, was substituted for pyridine in a repeat of the above-mentioned experiments. Although the amine-insoluble and -soluble fractions retained more α -phenylethyl- ^{14}C -amine on a weight basis, the uptakes per mole of each amine were roughly parallel. Thus, little difference exists in reactivities of pyridine- ^{14}C and of α -phenylethyl- ^{14}C -amine toward vitrinite fractions of Illinois No. 6 coal.

1.1.6 NMR Identification of Coal-Related Oxidation Products

B. M. Benjamin E. W. Hagaman
V. F. Raaen

Heating a dispersion of finely ground coal with a solution of potassium permanganate results in its ultimate breakdown to oxidation-resistant aromatic acids. In order to isolate more meaningful acid fragments, Raaen developed a novel oxidation procedure.¹ Permanganate solution was passed through a column containing ground coal dispersed on a Celite support. Numerous acids found in the basic effluent were isolated and identified. In an effort to better understand the course of the oxidation process, we subjected the simpler, pure compound, 2,6-di-*t*-butyl-4-methylphenol, to the same conditions. In addition to the expected mixture of acidic products, we isolated a neutral fraction. One compound was separated from this fraction by vacuum distillation at room temperature, and six more compounds were separated by column chromatography on alumina. Six of the compounds were identified using proton and ^{13}C nuclear magnetic resonance spectroscopy. The remaining compound, which surprisingly was obtained as one large, single crystal, was identified by Phyllis Rafferty² et al. by x-ray structure analysis. The compounds are shown in Fig. 1.1; their names and structures follow:

1. 3,3-dimethyl-1-hydroxy-2-butanone
2. 3-oxo-2-hydroxy-5-acetyl-2,4-di-*t*-butyltetrahydrofuran
3. 4,5-dihydroxy-4-methyl-2,5-di-*t*-butyl-2-cyclopentene-1-one
4. 4,5-oxa-2,6-dihydroxy-6-methyl-2,4-di-*t*-butylcyclohexane-1,3-dione
5. 2,3,4,5,6-pentahydroxy-4-methyl-2,6-di-*t*-butylcyclohexane-1-one
6. 3,5,6-trihydroxy-5-methyl-1,3-di-*t*-butyl-7-oxa-bicyclo[2.2.1]-heptane-2-one
7. 4,5,6-trihydroxy-4-methyl-2,6-di-*t*-butyl-2-cyclohexene-1-one

A complex network of reactions occurs, including oxidations, hydroxylations, rearrangements, protonations, and degradations. Any interpretation of coal structure based on oxidation studies must

ORNL-DWG. 77-8537

Fig. 1.1. Coal-related oxidation products identified by NMR.

take into account, in part, these complicated chemical transformations.

1. V. F. Raaen et al., unpublished results.
2. Student from Centre College of Kentucky, Danville, during an Oak Ridge semester under Southern Colleges and Universities Union sponsorship.

1.1.7 Thermodynamic Investigation into Steam-Methane Reforming and the Synthesis of Methane from Carbon Monoxide and Hydrogen¹

Li-hua Wu M. H. Lietzke

The steam-methane equilibrium reaction has been investigated by considering both methane synthesis from hydrogen and carbon monoxide and steam-methane reforming from methane and steam. A FORTRAN computer program was written to carry out the calculations over a wide range of temperature, pressure, and initial composition. The products of each process as a function of pressure, temperature, and starting ratio of reactant gases were calculated, as well as the heats involved. In both processes the minimum ratios above which no carbon precipitates were determined as a function of temperature and pressure. A complete description of the mathematical model, a listing of the computer program, and the results of the calculations have been published.

1. This work is based on a thesis by Li-hua Wu presented to the Department of Chemistry of the University of Tennessee in partial fulfillment of the requirements for the M.S. degree, August 1976.
2. M. H. Lietzke and Li-hua Wu, *A Thermodynamic Investigation into Steam-Methane Reforming and the Synthesis of Methane from Carbon Monoxide and Hydrogen*, ORNL-5225 (November 1976).

1.2 CATALYSIS

1.2.1 Chemistry of Polycyclic Aromatic Hydrocarbons in Molten Antimony Trichloride

M. L. Poutsma¹ A. S. Dworkin
J. Brynestad G. P. Smith
R. Livingston

We have found that anthracene readily undergoes transfer hydrogenation and condensation-dehydrogenation reactions in solution with neat molten antimony trichloride at temperatures as low

as 100°C. The formation of hydrogenated products was observed in situ by proton NMR. The dehydrogenated products could not be observed by this method but were studied by quench and workup procedures. The following equations summarize our principal findings:

The condensation products may include more than one of the asymmetric bianthryl isomers and more than one of the anthraaceanthrylenes. The symmetrical bianthryl isomers tentatively have been ruled out and 9,9'-bianthryl definitely has been ruled out.

The rates of the autotransfer hydrogenation reactions are substantially reduced by relatively small additions of the Lewis bases potassium chloride and tetramethylammonium chloride. Therefore, aluminum trichloride was added to increase the Lewis acidity and the rate of transfer hydrogenation. However, the reaction formed a stable solution of the 9-anthracenium ion and the anthracene radical cation. The formation of the latter was determined by ESR; the electron abstracting agent was the Sb(III)/Sb(0) couple.²

We are extending these studies to other polycyclic aromatic hydrocarbons. Naphthalene, chrysene, and pyrene, which have lower proton basicities and higher oxidation potentials than anthracene, form stable solutions in molten antimony trichloride both with and without additions of tetramethylammonium chloride and show no sign of hydrogenation redistribution chemistry after extended periods at 125°C. Perylene and naphthacene, which have higher proton basicities and lower oxidation potentials than anthracene, are oxidized to their radical cations by the Sb³⁺/Sb couple under the same conditions. Naphthacene shows hydrogen redistribution

chemistry with the formation of 5,12-dihydronaphthacene. When aluminum trichloride is added to these melts, radical cations are formed in substantial steady-state concentrations.

Research on radical cations in molten antimony trichloride utilized ESR techniques and is described in Sect. 11.3.2. We found that when naphthalene is dissolved in antimony trichloride containing aluminum trichloride, the perylene radical cation is formed. Because the naphthalene radical cation is very unstable (it has never been observed), the oxidation of naphthalene normally yields the naphthalene dimer radical cation. The latter could, in principle, be converted to the perylene radical cation by hydrogen abstraction, and our experiments have shown that hydrogen abstraction reactions proceed very well in molten antimony trichloride.

1. Visiting scientist, Union Carbide Corporation, Tarrytown, N.Y.

2. D. Bauer, J. P. Beck, and P. Lexier, *Collect. Czechoslov. Chem. Commun.* 36, 940 (1971); P. Lexier, *Bull. Soc. Chim. France*, 4716 (1968); D. Bauer, J. P. Beck, and P. Lexier, *C. R. Acad. Sci. Ser. C* 266, 1335 (1968).

1.2.2 Chemistry of Heteroatom Removal from Coal

R. A. Strehlow P. A. Agron

Two kinds of catalysts are being studied in this program. Experiments suggesting that the inorganic constituents of coal may have catalytic value in the hydrogenolysis of coal to form liquid products have prompted additional studies. Catalysts using MoO₃·Al₂O₃ promote a large number of reaction types including hydrocarbon reformation, dehydrocyclization of normal paraffins, dehydrogenation H₂-D₂ exchange, hydrodesulfurization, and disproportionation of olefins. Since some of these reactions, especially hydrodesulfurization, are needed in coal liquefaction, catalysts of this type are being studied in this program.

Although many of the inorganic constituents in coal may have catalytic value for some of the reactions needed in coal liquefaction, our attention was first drawn to the possible role of FeS, which was an expected product of the reduction of pyrite. This material, were it to react rapidly enough to form FeS of a sufficiently large surface area, could contribute significantly to the hydrodesulfurization of coal or coal degradation products.

A series of experiments was conducted over a range of temperatures from 300 to 525° C. Reduction of the pyrite, FeS_2 , in a quartz reactor was monitored using a gas chromatograph (GC) to detect and measure the H_2S concentrations. The GC detection of H_2S has been calibrated with photometric measurements by the Analytical Chemistry Division. Iron(II) sulfide that formed at temperatures above 425° C appeared to possess some catalytic activity for reduction of butadiene, but materials formed and studied at lower temperatures did not appear to possess this catalytic value. Samples taken and submitted for surface area measurement showed no significant increase in surface area. This implies that the usefulness of reduced pyrite as a catalyst in coal liquefaction is contingent on the presence of very finely divided pyrite in the original coal.

Since mixed sulfides occur in coal, additional studies were conducted using a sulfided iron-titanium alloy as well as the reduced pyrite. In the reduction of 1,3-butadiene to 1-butene and butane, butane was produced in very small yields in all cases. This corresponded to our earlier work on cobalt-molybdenum sulfided catalysts for all conditions except those in which the gas phase sulfur activity was extremely low. It appears that the phenomena observed earlier are more general than we originally supposed. Using reduced pyrite as a catalyst, a conversion of 1,3-butadiene to 1-butene ranging from about 6 to 14% occurred at 420 to 480° C, with the larger yields being reached at the higher temperatures. Using the iron-titanium alloy in sulfided form, a conversion of more than 30% was observed at all temperatures from 400 to 440° C.

The role of alloying constituents in sulfided transition-metal catalysts is not understood. It may be analogous to the roles of cobalt in the cobalt-molybdenum catalysts or nickel in the nickel-tungsten catalysts, which are also not understood. We plan to determine the relationships between the transition metals as alloying constituents for iron and other materials when used as catalysts in the sulfided form.

A paper that reviewed the role of catalysis in new or unconventional energy systems was prepared and presented.^{1,2} Although the role of catalysis in new energy systems centers on the possible use of catalysts in conversion of coal to oil or gas, many areas exist in which catalytic processes may be important. Heterogeneous catalytic processes, reactions that occur at higher rates in the presence of a solid surface, were described in terms of the fundamental processes

of diffusion of reactants to the surface, diffusion and reaction of the surface, and diffusion of products away from the reaction site. Catalytic materials discussed include metals, oxides, and sulfides that are often dispersed on substrate oxides. Various catalytic applications in unconventional energy systems were discussed in terms of properties that are important in selection and application of materials. A section on the electronic properties of surfaces as they relate to catalytic reactions and to physical changes of catalysts was included. Work is continuing on the identification and study of catalytic reactions relevant to coal utilization.

1. TMS-AIME-ASM Fall Meeting, Niagara Falls, Sept. 20-23, 1976.

2. R. A. Strehlow, submitted for publication to *Metal. Trans.*

1.2.3 Chemical and Physical Characterization of Cobalt Molybdate Catalyst by Microgravimetric Analyses

E. L. Fuller, Jr.

The surface properties and reactions of a commercial cobalt molybdate catalyst have been studied over a wide range of temperature (77 to 130 K.) and pressure (10^{-7} to 10^3 torr). Hydration-dehydration, oxidation-reduction, and thermal treatments markedly affect the catalyst and its interplay with the γ -alumina support. Initial heating in vacuo to 500° C involves progressively greater amounts of surface dehydration (about 15 wt % in total) and a concurrent increase in apparent area (N_2 adsorption) from about 150 to 230 m^2/g (catalyst). Rehydration occurs to reverse this trend if the dehydrated sample is not exposed to > 50% relative humidity. Exposure to higher humidity leads to capillary condensation in the intrapellet voids so that the matrix is irreversibly flexed. Water uptake is greater, and subsequently the enhanced nitrogen and water adsorption capacity persists. Sintering is marked for exposures to temperatures in excess of about 600° C. These physical changes are of interest for optimum use of the catalyst. However, the general surface chemistry is even more important. The concentration of surface hydration entities controls the number of active sites for hydrogenation processes. The reduction of the catalyst (normal "activation" process) in hydrogen at 400° C is a complex, third-order reaction with the cobalt entity. This reduced form then is available for

its synergetic action with the surface molybdate. Reoxidation is a first-order process. Our analyses show that the contiguous monolayer of molybdenum oxide exists on the alumina and that hydrogen activation is required to produce the cobalt-molybdenum complex at the surface. This surface suprafacially catalyzes the hydrogenation of the activated (adsorbed) olefinic intermediates. Details of some of the experiments, interpretation, and relevance to catalytic processes are given in another report.¹

1. E. L. Fuller, Jr., and P. A. Agron, "Surface Properties and Reactions of a Cobalt Molybdate Hydrotreating Catalyst: Preliminary Results," ORNL-5168 (July 1976).

1.2.4 Calorimetric Characterization of the Surface of a Cobalt Molybdate Catalyst Supported on Alumina

E. L. Fuller, Jr.

Calorimetric measurements of the heats of immersion of the catalyst into liquid water were undertaken as a function of preimmersion coverage of sorbed water. This was accomplished by outgassing aliquots at various temperatures (25 to 500°C) while monitoring the evolved gases with a mass spectrometer residual gas analyzer. Only water vapor was seen to evolve as the samples were heated in vacuo; the slow evolution was followed continuously for over 16 hr. Return of both the background pressure (10^{-9} torr) and mass spectra to their original levels indicated steady states in about 6 to 8 hr. Calculation of the heat of adsorption (change in immersional heat per mole of preadsorbed water) is shown below; comparative results are given for γ - Al_2O_3 as noted in ref. 1:

	kcal/mole (H_2O)	
ΔH_a	Catalyst	γ - Al_2O_3
Low coverage	-17.0	-28.2
High coverage	-17.3	-15.5

The results favor the proposed structure of a complete, contiguous molybdate monolayer on the alumina

which does not accommodate surface hydroxyls as noted on alumina:

Apparently there is strong hydration (hydrogen bonding) to the molybdate structure and/or surface aluminol groups with evolution of only about 16 kcal/mole. No residual free aluminate units are detectable on the catalyst in terms of the greater exothermicity of rehydroxylation (about 30 kcal/mole). The detailed analyses of the kinetics and mechanisms have been presented in another report.²

1. D. S. MacIver, H. H. Tobin, and R. T. Barth, *J. Catal.* **2**, 485 (1963).

2. E. L. Fuller, Jr., and P. A. Agron, *Surface Properties and Reactions of a Cobalt Molybdate Hydrotreating Catalyst: Preliminary Results*, ORNL-5168 (July 1976).

1.2.5 Small-Angle X-Ray Scattering: Structure of Cobalt Molybdate Catalyst

E. L. Fuller, Jr. J. S. Lin¹
R. W. Hendricks¹

The recently developed ORNL 10-m, small-angle, x-ray scattering spectrometer² that utilizes a two-dimensional position-sensitive proportional counter was used to study structure and changes of a commercial cobalt molybdate catalyst. This spectrometer has a demonstrated data collection rate about two orders of magnitude faster than conventional devices with a single movable detector at equivalent angular resolution. Surface areas and pore volumes are calculated and compared with inert (N_2) vapor adsorption data. The results show that there is little conformational change (x-ray scattering) for thermal treatments below about 700°C for a cobalt molybdate catalyst. In contrast, the vapor adsorption of N_2 , CO , O_2 , Ar , and H_2O is greatly enhanced due to 15 wt % dehydration in the range 25 to 600°C. Both techniques reflect the loss of area due to sintering at 700 to 900°C. The x-ray technique elucidates the nature of the phase change of the support alumina that occurs at about 950°C and the corresponding intrapellet conformational changes.

The technique is a rapid, facile, nondestructive means of studying the nature of a catalyst and changes caused by chemical and thermal treatments similar to those encountered in production facilities.

1. Metals and Ceramics Division.

2. R. W. Hendricks, "The ORNL Ten-Meter Small-Angle X-Ray Scattering Camera," to be published in *J. Appl. Crystallogr.*

1.2.6 Spectroscopic and Micrographic Analyses of Cobalt Molybdate Hydrotreating Catalyst

E. L. Fuller, Jr. L. D. Hulett¹
J. M. Dale¹

Optical and electron microscopy of a commercial catalyst have shown that the pelleted material is a matrix of the primary crystallites (cobalt oxide and molybdenum oxide dispersed on alumina) in a laminar array perpendicular to the axial dimension of the cylindrical pellet. The shell of the pellet is dense, strong, and has rather large, irregular voids providing access to the interior. Spark emission spectroscopy and x-ray fluorescence are used for bulk analyses; quantitative results are obtained by comparison with pure materials and with neutron activation analyses. These results are compared with more surface-sensitive techniques. Photoelectron spectroscopy has shown that thermal treatments at 500 to 800°C deplete the surface concentration of cobalt and molybdenum due to diffusion into the alumina substrate. At about 950°C, formation of large crystallites is noted through use of scanning electron microscopy. Due to the transition of the support to α -alumina, neither the cobalt nor the molybdenum has any appreciable affinity for the bulk of the surface of this new alumina phase. The segregation is noted with optical microscopy as blue and red inclusions within the white alumina matrix. Elemental analyses using scanning electron microscopy show that the matrix is pure alumina, the red inclusions are relatively pure in cobalt and molybdenum, and the blue inclusions contain calcium, cobalt, and molybdenum. Details of trace

elemental and other analyses are given in another report² for this continuing program.

1. Analytical Chemistry Division.

2. L. D. Hulett and J. M. Dale, *Anal. Chem. Div. Annu. Prog. Rep.* Nov. 30, 1976, ORNL-5244, pp. 16-17.

1.2.7 Statistical Modeling of Surface Reactions on Heterogeneous Catalysts¹

E. L. Fuller, Jr. S. Ebey²
V. R. R. Uppuluri³

A three-faceted approach has been successful in modeling surface reactions involved in heterogeneous catalysis. The chemisorption reactions modeled as immobile binding involve adjacent sites on solid surfaces and form the "activated intermediate" which is the key step in most intrasurface or suprafacial catalytic processes. The kinetics and stoichiometry of these processes have been analyzed by a detailed comparison of experimental data, computer simulation, and mathematical analyses. Several unexplained calorimetric and gravimetric results are interpreted in terms of these models on a semiquantitative basis. Previously, qualitative explanations that embodied much of the logic of our models had been involved.

Our analyses have involved the strong interaction of a "dimer" (a mathematical analog of a diatomic molecule or equivalent, i.e., H₂, O₂, H₂O, etc.) with adjacent sites of idealized lattices of small to infinite dimensions. The lattice type controls the rate of reaction and the maximum degree of coverage achievable without migration or rearrangement due to isolation of single sites in the statistical process. For instance, a linear lattice, or chain, will saturate at 86.4%, whereas a square lattice (chess board) will achieve 90.3% of full capacity. These solutions are for very large (infinite) lattices and are of academic interest. However, results¹ for small crystal surfaces are much more relevant to applied catalysis where small crystallites (1 to 100 nm) are employed. The results differ (lesser coverage) due to the edge and corner effects altering the kinetics and stoichiometry. The details of the Monte Carlo simulations, mathematical analyses, and correlation with experimental results are given in another report.¹ The experimental examples listed below are of interest in

the field of catalysis and energy production and seem to relate to the statistical theories:

Experiment	Coverage (%)	Information reference
A. H ₂ on Ni	92.5	Experiment A ⁴
B. H ₂ on Ni	89.1	Experiment B ⁴
C. H ₂ on cobalt molybdate	85.5	Experiment ³
D. Dimer—linear	86.4	Statistical analyses ¹
E. Dimer—square	90.3	Statistical analyses ¹
F. Dimer—trigonal	91.4	Statistical analyses ⁶

1. E. L. Fuller, Jr., S. Ebey, and V. R. R. Uppuluri, *Statistical Modeling of Adsorption Processes on Catalyst Surface: Preliminary Report*, ORNL-5231 (December 1976).

2. Department of Mathematics, University of the South, Sewanee, Tennessee.

3. Mathematics and Statistical Research, Computer Sciences Division.

4. P. W. Selwood, *Chemisorption and Magnetism*, p. 89, Academic Press, New York, 1975.

5. E. L. Fuller, Jr., and P. A. Agron, *Surface Properties and Reactions of a Cobalt Molybdate Hydrotreating Catalyst: Preliminary Results*, ORNL-5168 (July 1976).

6. K. J. Vette, T. W. Orent, D. K. Hoffman, and R. S. Hansen, *J. Chem. Phys.* 60, 4854 (1974).

1.2.8 Ultraviolet-Photoemission Spectra of Adsorbed Molecular Surface Species on Single-Crystal Planes of Metals

P. A. Agron G. L. Nyberg²
W. B. Dress¹ T. A. Carlson¹

An ultrahigh vacuum assembly designed for x-ray photoelectric spectra, photon-induced Auger spectroscopy, and uv-photoelectron spectroscopic studies with polarized radiation was developed in the Physics Division.³ Because the electronic structure of adsorbed molecules on well-defined catalyst surfaces can be studied with this facility, a cooperative program is under way between the Physics and Chemistry groups. The interpretation of photoemission spectra will enhance our understanding of molecular interactions on catalyst surfaces. These techniques also complement other basic surface research.

Model compound stand-ins for carcinogenic materials emitted during conversion of coal to clean fuels will be studied on oriented faces of selected metal crystals.

The angular dependence of the photoemission spectra of adsorbed benzene thiol on the (110) and (111) faces of copper were recorded from a helium I resonance beam. Measurements with the incident 21.2-eV photon beam, as a function of polarization

direction, furnished additional data for analysis. Successful interpretation of this data should provide information on the geometry and electronic binding energy of adsorbed species.

1. Physics Division.
2. On leave of absence from La Trobe University, Melbourne, Australia.
3. W. B. Dress, F. H. Ward, and T. A. Carlson, *Phys. Div. Annu. Prog. Rep. Dec. 31, 1975*, ORNL-5137, p. 157.

1.2.9 Measurement of Forces Between a Metal Surface and Molecules Adsorbed on It

E. H. Taylor W. C. Waggener

About two years ago, a rereading of early speculations about geometrical factors in catalysis led us to explore the directionality of the forces holding an adsorbed molecule to a solid surface. A crude estimate suggested that it would be possible to measure the component of the adsorptive force parallel to the surface by confining the adsorption to one side of a thin metal foil and measuring the deflection that would occur as the tangential component was balanced by the elasticity of the foil. The one-sided adsorption could be achieved by coating one side of the foil with an inert, or at least differently adsorbing, material, or by supplying the adsorbate as a molecular beam, with the surface at a temperature allowing chemisorption but precluding migration.

We have concluded preliminary, very rudimentary experiments that, we believe, demonstrate that the tangential component of the adsorptive force for several gases on nickel is large enough to measure in this way. A 30-cm-long strip of 2.5- μ nickel about 6 mm wide was prepared by spot welding shorter lengths that had been vacuum coated with about 0.08 μ of gold on one side. The strip was hung vertically in a vacuum chamber and was surrounded coaxially (except for about 1 cm at the bottom) by an aluminum tube wound with fiberglass-insulated heating wire. The chamber was mounted on a vibration-absorbing base, and the gas connections were made of rubber tubing to provide mechanical isolation. This tubing and the neoprene gaskets limited the vacuum and the temperatures that could be used. The position of the ribbon was read on a scale mounted just below it with a telemicroscope. The latter contained a filar micrometer used for interpolation between the graduations on the scale. The smallest divisions on the micrometer were

equivalent to about $1.4\ \mu$ at the position of the ribbon, and the repeatability of settings was about $5\ \mu$. In most of the experiments the sample gas flowed through the vacuum chamber at atmospheric pressure, and the active gases were removed by flushing with helium rather than by evacuation. Vibration resulting from opening and closing the vacuum valves produced inconveniently large, irreversible offsets in the position of the ribbon.

Our principal findings are that the tangential forces between nickel and various molecules are large enough to measure in this way and that different molecules exhibit a variety of behavior—even the sign of the deflection varies. Hydrogen produces a deflection with the nickel side of the ribbon concave, but O_2 , H_2O , and NH_3 produce deflections in the opposite sense. Other details, particularly partial removal of the deflections by flushing with helium, indicates that we are indeed observing a consequence of adsorption. Some molecules give evidence for the occurrence of more than one process with different magnitudes or directions of adsorbate-surface force.

These preliminary results confirm that interesting information about adsorption and catalysis can be obtained in this way. We plan to repeat the experiment under definitive conditions—in ultrahigh vacuum and with well-characterized surfaces.

1.2.10 X-Ray Data for a Molybdenum-Sulfur Complex

C. Fritchie¹ P. Tsao²
H. A. Levy

Single-crystal x-ray diffraction data were collected for a molybdenum complex with the ligand $[S-(CH_2)_2-N(CH_3)-(CH_2)_2-S]^{2-}$, which was prepared at Tulane University as a structural model for the active site in xanthine oxidase, a water-soluble enzyme of molecular weight about 2×10^5 daltons which catalyzes the oxidation of xanthine to uric acid. Subsequent analysis at Tulane University disclosed that the complex is dimeric and has the following structural formula:

A crystallographic inversion center occurs at the central oxygen atom. Although the oxidation state of molybdenum is 5+, magnetic susceptibility measurements indicate that the ground state of the dimer is a singlet. The coordination about molybdenum is trigonal bipyramidal with axial N-Mo-O links. One of the two independent ethylene bridges is disordered, with two stable orientations occupied at random. Two crystallographically independent molecules have closely similar structures.

1. Visiting scientist, Chemistry Department, Tulane University, New Orleans, La.

2. Graduate student, Tulane University, New Orleans, La.

1.2.11 X-Ray Diffraction Data for an Iridium-Sulfur-Arsenic Ionic Complex

C. Fritchie¹ P. Tsao²
H. A. Levy

An iridium complex with the ligand $\phi_2\text{-As-CH=CH-As-}\phi_2$ has been prepared at Tulane University. The complex has the apparent composition $[\text{IrL}_2\text{S}_2]^+\text{Cl}^-$, where L represents the ligand. Three isomeric forms of the complex ion, all stable but interconvertible under proper conditions, are colored aqua, violet, and chocolate brown. To find the structural basis for the isomerism and to clarify the nature of the binding of Ir to S_2 , single-crystal x-ray data were collected from a crystal of the violet-colored isomer. Analysis of the data is in progress.

1. Visiting scientist, Chemistry Department, Tulane University, New Orleans, La.

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1.3 ORGANIC CHEMISTRY

1.3.1 Modification of Varian 100-MHz Spectrometer for Solid-State Analysis

E. W. Hagaman

Solid-state nuclear magnetic resonance spectroscopy can be successfully applied to the study of chemical bonding in coal and coal products. Conversion of our XL-100 spectrometer for solid-state work is in progress. A probe is being modified for spinning the samples at 2 to 3 kHz at the magic angle (54.7° C to the applied field), and high-power amplifiers will provide the rf pulses needed. High-

power pulses are required to provide sufficiently large rf fields at the sample to achieve ^{13}C - ^1H cross polarization and complete ^1H dipolar decoupling. The rf coils in the probe must be rugged enough to withstand the applied power levels.

Plans have been made to employ this technique to investigate several problems, including the aging process of so-called "liquid coal fractions." In related research, certain reagents used in coal extraction or coal liquefaction form chemical bonds with the coal. By utilizing ^{13}C -labeled reagents, the kinds of bonds formed will be investigated.

1.3.2 NMR Spectroscopy Performed for Other Groups and Other Divisions

B. M. Benjamin L. L. Brown
E. W. Hagaman

During the last eight months, we have conducted experiments in the NMR laboratory for other groups that involved the research of 29 people. Outlined below are a few subjects that were selected from the standpoint of interest or suitability for publication.

Certain organisms, such as *Sclerotium soffi* ATCC 15206 *Helotium* n.s.p. NRRL 3129 and *Sclerotium gluconicum* NRRL 3006, when fed glucose and nutrients in carbohydrate fermentation broth, produce glucose polymers (scleroglucans) with an average molecular weight in excess of 100,000. Carbon-13 NMR spectra of these polymers and their hydrolysates are recorded and compared with the spectra of smaller known compounds. The

purpose of the research is to identify the linkage sites and stereochemistry of the polymers. Chemically bound side groups and impurities are also identified. The research, conducted by Alicia Compere and William L. Griffith, Chemical Technology Division, is related to tertiary oil recovery.

In another project related to tertiary oil recovery conducted by Dwayne Smith, Chemistry Division, NMR chemical shift changes for the protons of selected aromatic compounds are measured in micellar solutions of different concentrations. Preliminary measurements in these solutions of proton spin-lattice relaxation times have also been made.

We determined and interpreted NMR spectra for G. P. Smith, A. S. Dworkin, and M. L. Poutsma, who studied the fates of polynuclear aromatic hydrocarbons heated in molten-salt catalyst systems.

Work with Jerry Braunstein et al., Chemistry Division, has produced several publications. Relaxation times of protons in hydrous melts have been determined as a function of temperature and concentration. The data were correlated with transport and diffusion phenomena in the same melts.

We have made progress in the identification of fragments from the hydrolysis of physiologically active lipids. This work was done for Claudia Moore and Merle Blank, ORAU Biomedical School.

M. H. Lietzke and M. Pastorcich used an NMR technique to study the kinetics of chloramine appearance and disappearance in aqueous solution. A portion of the project using dimethyl amine is near completion.

2. Aqueous Systems and Geothermal Energy

2.1 AQUEOUS SYSTEMS

2.1.1 Base Strength of Amines at High Temperatures; Ionization of Cyclohexylamine and Morpholine

R. E. Mesmer B. F. Hitch

Work completed earlier on the ionization of volatile amines was published.¹ A potentiometric technique using a hydrogen electrode concentration cell with flowing solutions was employed to measure the ionization equilibria of cyclohexylamine and morpholine over the temperature range 50 to 295°C in dilute KCl. Also, the isothermal pressure coefficients were determined to 250°C in the same media. Smoothing functions, which fit these and other selected data, and thermodynamic quantities for the ionization process were derived. Nearly linear variation of ΔH vs $T\Delta S$ was observed for this process as well as for other similar reactions, and the significance of the contribution of the thermodynamic quantities for the ionization of water is discussed. Differences in basicities of amines are found to decrease at elevated temperatures, and reversals in relative base strengths are seen.

1. R. E. Mesmer and B. F. Hitch, *J. Solution Chem.* 6, 251 (1977).

2.1.2 Oxide Solubilities and the Thermodynamics of Metal Ion Hydrolysis at High Temperatures

B. F. Hitch C. F. Baes, Jr.

Most metal cations form a series of mononuclear hydrolysis products

(where y usually does not exceed 4), each of which can be an important species over the appropriate range of pH, provided the concentration of the metal is low enough that polynuclear species $M_x(OH)_y^{(xz-y)+}$ are

not formed in appreciable amounts. Such mononuclear species therefore determine the chemistry of the metal valence—for example, its stability with respect to oxidation or reduction, the tendency to form other soluble complexes, and the solubility of the hydroxide $M(OH)_z$ —whenever the metal occurs at low concentration in aqueous systems. Such systems that are becoming increasingly important include the pressurized aqueous systems at elevated temperatures in LWRs, geothermal brines, natural waters, and the aqueous solutions in living systems.

The stability and other thermodynamic properties of the mononuclear hydrolysis products are often poorly known because polynuclear hydrolysis products interfere at the (higher) metal concentrations accessible to study by the usual methods. The most promising means to investigate mononuclear hydrolysis products is the measurement of the low concentration of the metal in solutions at equilibrium with the stable hydroxide or oxide phase. From such data, taken as a function of pH, the equilibrium constants for the reactions

can be determined, and by appropriate combination of these, the stability constants of the separate hydrolysis products can be derived. In such measurements it is essential that (1) equilibrium between the solid and aqueous phase is attained, (2) the solid phase is crystalline material of sufficiently large particle size that surface energy effects are negligible, and (3) the ionic strength is controlled to minimize

activity coefficient variation. Most previous efforts to employ this method have been compromised by failure to meet one (usually the second) or more of these requirements.

The object of the present program is to apply this method to selected M^{2+} -OH⁻ systems over a range of ionic strength and temperature. To facilitate the attainment of equilibrium, a column technique is being used. The solids will be crystalline and the particle size controlled. The results for a given M^{2+} -OH⁻ system, coupled with the known thermodynamic properties of the solid phase (e.g., $M(OH)_2$), should yield the thermodynamic properties of all the mononuclear hydrolysis products of the cation that are stable.

The first system selected for study is Al^{3+} -OH⁻ in NaCl solution. Commercially available¹ Gibbsite, γ - $Al(OH)_3$, has been sized by dry sieving to obtain the 10- to 38- μ m fraction. This material has been placed in a platinum-lined, thermostated column through which an NaCl-NaOH solution is passed. At room temperature, equilibrium in the effluent is apparently attained at flow rates less than 0.1 ml/hr per gram of $Al(OH)_3$. The base concentrations and ionic strength will be varied over the range 0.001 to 1 M, and the temperature will be increased to 90°C, near the upper limit of stability for Gibbsite. Subsequently, similar measurements in acid solution will be undertaken with the object of determining improved values for the stability and other thermodynamic properties of the species $Al(OH)_2^{2+}$, $Al(OH)_2^+$, $Al(OH)_3(aq)$, and $Al(OH)_4^-$.

Work has also begun on the Th^{4+} -OH⁻ system, the first objective being to produce a batch of ThO_2 of ≥ 10 - μ m crystallite size. While such material has been prepared previously by fusion techniques and by crystallization from molten salts,² our initial efforts are being directed at preparing such material by crystallization from an aqueous solution through the use of complexing agents to increase the solubility of ThO_2 and by elevated temperatures to increase the reaction rates.

2.1.3 Measurement of the Thermodynamics of Electrolyte Solutions at High Temperatures by the Isopiestic Method

H. F. Holmes C. F. Baes, Jr.
R. E. Mesmer

The high-temperature isopiestic facility at ORNL has been reactivated. The initial series of experiments was completed during this period. Accurate and reliable osmotic data for aqueous solutions of KCl, $MgCl_2$, $CaCl_2$, and three compositions of NaCl-KCl mixtures were obtained for the temperature range 110 to 200°C. (All of the data have NaCl solutions as standards.) Although the apparatus performed very well at concentrations up to those corresponding to saturated NaCl, three limitations were evident from the first series of experiments. First, the lower concentration limit was about 1 m NaCl due to an internal temperature gradient of a few hundredths of a degree. Second, the torsion balance¹ became inoperative above 200°C due to, as we later learned, the thermal expansion of a Teflon part. Third, the Stellite mirror became badly discolored and non-reflective above 200°C.

The apparatus has been modified to alleviate these limitations. Heaters for the air bath are now uniformly distributed on all six sides rather than concentrated in a circle at the bottom. A further reduction in temperature gradients should result from enclosing the isopiestic vessel in a cube constructed of 1/8-in. copper sheet. Circulation in the air bath has been improved by using larger fans in more favorable locations. The torsion balance was modified by substitution of insulated silver for the offending Teflon part, while the Stellite mirror was cleaned and coated with sputtered platinum.

These modifications of the apparatus are being tested in a second series of experiments using mixed electrolytes (NaCl-KCl and NaCl- $CaCl_2$) with NaCl as a standard. This second series will complete the high-concentration data for both of the NaCl-KCl and NaCl- $CaCl_2$ binary mixtures. Activity coefficients for all of the compositions studied in the first two series of experiments will be estimated from the osmotic data, using methods developed by Pitzer.²

Osmotic coefficients shown in Fig. 2.1 for KCl solutions are examples of the data obtained in the first series of experiments. All of the data are

1. Supplied by Aluminum Company of America.

2. C. E. Bamberger and C. F. Baes, Jr., *J. Nucl. Mater.* 35, 177 (1970).

Fig. 2.1. Osmotic coefficients (ϕ) of KCl solutions as a function of molality at the indicated temperatures ($^{\circ}\text{C}$). The 25° data were taken from R. A. Robinson and R. M. Stokes, *Electrolyte Solutions*, 2d ed., revised, Butterworths, London, 1965.

consistent to better than 0.002 in the osmotic coefficient. The absolute accuracy of the data depends, of course, on the reliability of the reference system, which in the present case is Pitzer's representation of the thermodynamic data for NaCl solutions.³ The present KCl data, when coupled with literature data, clearly indicate that the osmotic coefficient of KCl solutions, at any given concentration, has a maximum value at about 70°C . No such maximum is indicated for either MgCl_2 or CaCl_2 solutions. In most cases the present data agree reasonably well with extrapolations of existing low-temperature (below 100°C) values. Water activities of KCl solutions show very little temperature dependence. In contrast, the water activity of, for example, a 3 m solution of MgCl_2 or CaCl_2 increases by about 0.1 from 25 to 200°C . Data for the NaCl-KCl mixtures in the first series of experiments have not been analyzed in any detail yet since they represent only a part of the concentration range from pure NaCl to pure KCl.

1. The electromagnetic torsion balance is described in H. F. McDuffie and P. B. Bien, *Reactor Chem. Div. Annu. Prog. Rep. Dec. 31, 1967*, ORNL-4299, p. 102.

2. K. S. Pitzer, *J. Phys. Chem.* 77, 268 (1973). Also subsequent papers by Pitzer and his co-workers.

3. L. F. Silvester and K. S. Pitzer, *Thermodynamics of Geothermics of Geothermal Brines. I. Thermodynamic Properties of Vapor-Saturated NaCl(aq) Solutions from 0 to 300°C* , LBL-4456 (1976).

2.1.4 Ionization of Aqueous Ammonia to 300°C in KCl Media

B. F. Hitch R. E. Mesmer

Work completed earlier on the ionization of ammonia was published.⁽¹⁾ A potentiometric technique using a hydrogen electrode concentration cell with flowing solutions was employed to study the ionization of ammonia over the temperature range 50 to 295°C in KCl media from 0.04 to 3.3 m . The isothermal pressure coefficient of the ionization reaction was obtained at pressures up to 100 bars and temperatures to 250°C in these same media and was found to vary as the square root of the ionic strength within the experimental error. Smoothing functions have been derived which also fit selected published data on the ammonia ionization reaction with a standard error of fit of 1.8 times the assigned uncertainties. Thermodynamic parameters for the reaction have been tabulated at rounded temperatures and ionic strengths at the saturation vapor pressure. A limit is given for the association quotient of HCl at 300°C in 3 m KCl based on these data.

1. B. F. Hitch and R. E. Mesmer, *J. Solution Chem.* 5, 667 (1976).

2.1.5 Thermodynamic Properties of Deuterium Chloride-Sodium Chloride Mixtures in Heavy Water

M. H. Lietzke W. L. Salter

The activity coefficient of DCl in DCl-NaCl mixtures in D_2O has been measured from 20 to 75°C at total ionic strengths 0.5 and 1.0, using the emf technique. Values of the activity coefficient of NaCl in the mixtures have been calculated by using the parameters obtained in the fit of the emf data and parameters obtained by fitting osmotic coefficient data on solutions of pure NaCl in D_2O . It was found that the DCl in the mixtures obeyed Harned's rule, as does HCl in the corresponding protonated system. It was also demonstrated that a previously developed simple equation predicted very closely the activity coefficients of both the DCl and the NaCl in the mixtures. The results of the study have been incorporated into a paper which is now in press in the *Journal of Inorganic and Nuclear Chemistry*.

1. This paper is based on a thesis by W. L. Salter presented to the Department of Chemistry of the University of Tennessee, August 1976.

2.1.6 Thermodynamics of Silver Sulfate Solubilities in Aqueous Sulfuric Acid and Sodium Nitrate Solutions at 0 to 60°C¹

W. L. Marshall Ruth Slusher²

Application of an extended Debye-Hückel equation to the fitting of solubility data in aqueous systems at both low and high temperatures has proved to be very useful in previous studies at this laboratory. This approach has led to generalized predictions of solubility behavior, which is of wide current interest for geothermal energy and high-temperature aqueous geochemistry. In order to test further the adherence of solubility products of a 1-2 metal sulfate to an extended Debye-Hückel equation, solubilities of Ag_2SO_4 in $\text{NaNO}_3\text{-H}_2\text{O}$ and $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions were determined from 0 to 60°C. These data, agreeing with those at 25°C in the literature, were evaluated to obtain solubility products (Q_{sp}) at the several ionic strengths by use of second ionization constants of bisulfate ion (K_2) and an iterative process. Values of Q_{sp} fitted well to an extended Debye-Hückel equation, yielding solubility product constants (K_{sp}) at 0.4 to 60°C. These values agreed with those of Lietzke and Stoughton at 25 to 200°C when both sets were calculated using the same values of K_2 . Thermodynamic functions for the solubility product constant behavior of silver sulfate from 0 to 200°C were determined for comparison with the previously published values.

1. Summary of paper appearing in *J. Inorg. Nucl. Chem.* 38, 279 (1976).

2. Computer Sciences Division.

2.1.7 Solubility and Thermodynamic Functions for a 3-2 Salt, Samarium Sulfate, in Water and Sulfuric Acid Solutions at Temperatures to 350°C¹

W. L. Marshall Ruth Slusher²

Previously at ORNL, many solubility studies of 1-2 and 2-2 valence metal sulfate salts in aqueous solutions have been made at temperatures up to 350°C. With these studies and the application of an extended Debye-Hückel equation, generalized predictions of solubility behavior were made. The ability to predict high-temperature aqueous solution behavior is of current applied importance to geothermal energy studies, to the chemistry of power plant steam cycles, and to water desalination, among other disciplines.

To broaden the types of salts studies in these high-temperature systems, solubilities of 3-2 samarium

sulfate hydrates were determined in water (25 to 350°C) and in sulfuric acid (150 to 250°C). The values in water for the octahydrate decreased from 0.033 *m* at 25°C to 8×10^{-6} *m* for a lower hydrate at 350°C. The assumption that several sets of ionic species saturate the sulfuric acid solutions was tested by extended Debye-Hückel theory, which suggested that the 3-2 samarium sulfate may behave predominantly as a 2-2 sulfate at high temperatures, thus producing $\text{Sm}_2(\text{SO}_4)_2^{2+}$ and SO_4^{2-} ions in solution. Similar treatment of Lietzke and Stoughton's solubilities of lanthanum sulfate in sulfuric acid at 135 to 160°C was not inconsistent with this suggestion. Based on behavior as a 2-2 salt, thermodynamic functions for the solubility of samarium sulfate hydrate at 150 to 250°C were obtained, together with some comparisons from the solubilities of lanthanum sulfate hydrate.

¹ Summary of paper appearing in *J. Inorg. Nucl. Chem.* 37, 2171 (1975).

2. Computer Sciences Division.

2.1.8 Proton Spin Relaxation in Hydrous Melts¹

C. Girard² A. L. Bacarella
J. Braunstein L. L. Brown
B. M. Benjamin

With the aim of understanding the mechanisms of transport behavior in hydrous melts, which will be important in the application of these media in low-temperature thermal energy storage, in water electrolyzers, and for the use of some geothermal brines, we have measured proton spin relaxation times in water and in salt solutions³ and compared them with the macroscopic transport properties such as viscosity and the diffusivities of solute ions and of water.⁴ The basic model of spin relaxation in aqueous media was employed to resolve the correlation times for rotational and translational motion.⁵ For hydrous melts in the range $\text{Ca}(\text{NO}_3)_2\text{-}2.8\text{H}_2\text{O}$ to pure water [i.e., $\text{Ca}(\text{NO}_3)_2\text{-}\infty\text{H}_2\text{O}$], the translational correlation time increases with increasing electrolyte concentration (charge density) to a much greater extent than does the rotational correlation time, which is analogous to the effect of high pressure on relaxation in liquids.⁶ Since the Grotthuss mechanism of enhanced proton mobility via proton displacements along hydrogen bonds (rather than by diffusive jumps) may be conceived of in terms of rotational motion of water molecules, these studies should be

Fig. 2.2. Logarithmic plot of relaxation rate vs transport-reduced concentration variable. N_H = proton concentration, D = diffusivity (proton or Cd^{2+}), η = viscosity, T = absolute temperature. (a) N_H/D : $\circ$ = H_2O , proton; $\diamond$ = $\text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$, proton; $\blacksquare$ = $\text{Ca}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, proton; $\blacktriangle$ = $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, proton; $\blacklozenge$ = $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, proton; $\bullet$ = $\text{Ca}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, Cd^{2+} ; $\square$ = $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Cd^{2+} ; $\triangle$ = $\text{Ca}(\text{NO}_3)_2 \cdot 2.8\text{H}_2\text{O}$, Cd^{2+} ; (b) $N_H \eta/T$: $\circ$ = H_2O ; $\diamond$ = $\text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$; $\bullet$, $\blacksquare$ = $\text{Ca}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$; $\blacktriangle$ = $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\blacklozenge$, $\square$, $\blacklozenge$ = $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; $\triangle$ = $\text{Ca}(\text{NO}_3)_2 \cdot 2.8\text{H}_2\text{O}$.

useful in characterizing the range of Grotthus-enhanced mobilities in concentrated aqueous electrolytes. A striking empirical correlation has been observed in plots of the relaxation rate vs a reduced translational variable, using available viscosity and

diffusivity data. Results for water between its freezing and boiling points, our results for hydrous melts of $\text{Ca}(\text{NO}_3)_2 \cdot R\text{H}_2\text{O}$ with water mole ratios $R\text{H}_2\text{O} = 2.8, 4.0$, and 8.0 at several temperatures, and results taken from the literature for several other salts fall on a common line, although the relaxation rate spans three orders of magnitude.¹ This correlation, shown in Fig. 2.2, provides a simple empirical relation between the macroscopic properties and the relaxation rates. If, in this correlation, solute ion (e.g., Cd^{2+}) diffusivity is used instead of proton (water) diffusivity or melt viscosity, the hydrous melt data fall on different lines, suggesting different mechanisms for proton mobility and metal cation mobility.

1. Summary of a paper to appear in *J. Chem. Phys.* (in press).
2. Visiting scientist, Centre College, Danville, Kentucky.
3. J. Braunstein, A. L. Bacarella, B. M. Benjamin, L. L. Brown, and C. Girard, *J. Electrochem. Soc.* 124, 844 (1977); *Proceedings of the International Symposium on Molten Salts*, ed. J. Pemsler, J. Braunstein, D. R. Morris, K. Nobe, and N. E. Richards, The Electrochemical Society, Princeton, N.J., 1976, pp. 544-59.
4. J. Ambrus, C. T. Moynihan, and P. B. Macedo, *J. Electrochem. Soc.* 119, 192 (1972); C. A. Angell, *J. Phys. Chem.* 70, 3988 (1966); J. Braunstein, L. Orr, A. R. Alvarez-Funes, and H. Braunstein, *J. Electroanal. Chem.* 15, 337 (1967); P. M. Gammell and R. Meister, *J. Chem. Phys.* 64, 4287 (1976); C. T. Moynihan and C. A. Angell, *J. Phys. Chem.* 74, 736 (1970).
5. N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* 73, 679 (1948).
6. G. B. Benedek and E. M. Purcell, *J. Chem. Phys.* 22, 2003 (1954).

2.1.9 Diffusion in Concentrated Aqueous Calcium Chloride Solutions

M. Furrer¹ J. Braunstein

Calcium chloride is a constituent present at significant concentrations in some geothermal brines. The hexahydrate is a possible candidate as a phase-change thermal energy storage medium for home heating and cooling. Details of transport behavior in hydrous melts are important to an understanding of nucleation, crystallization, and melting rates in the use of these melts. Previous studies of diffusivity, viscosity, electrical conductance, and proton spin relaxation in calcium nitrate melts^{2,3} have shown that the temperature dependence of transport properties such as equivalent conductance in these melts is non-Arrhenius and may be characterized by a Fulcher-type equation,

$$\Lambda = AT^{1/2}e^{-\left(\frac{k}{T-T_0}\right)},$$

where T_0 is a hypothetical zero-mobility temperature near the glass-transition temperature. Isotherms follow an analogous dependence on concentration,

$$\Lambda = A'e^{-\left(\frac{k/Q}{N_0-N}\right)},$$

implying the simple relation

$$Q = \frac{T - T_0}{N_0 - N},$$

where N_0 is a hypothetical zero-mobility salt concentration, between the concentration dependence and temperature dependence of the transport properties.⁴ Since the hydrous melts of calcium nitrate supercool readily to form glasses, whereas calcium chloride melts do not (a useful feature for thermal energy storage media), and since nitrate ion offers the possibility of special modes of proton transport involving hydrogen bonds between water molecule oxygens and nitrate ion oxygens, it is worthwhile to compare details of transport behavior in the nitrate systems and in systems with simple ions. We therefore measured, chronopotentiometrically, solute ion (cadmium) diffusivities in calcium chloride hydrous melts at concentrations between 5 and 80 moles of water per mole of CaCl_2 and at temperatures between 25 and 90°C. The diffusion coefficients in this range span two orders of magnitude. The cadmium ion diffusion coefficients are 20 to 30% higher in the CaCl_2 hydrous melts than in the $\text{Ca}(\text{NO}_3)_2$ hydrous melts at comparable composition and temperature, and the Arrhenius energies are about 20% higher. A consistent set of values of N_0 , T_0 , and Q could be found for temperatures less than a factor of 2.3 higher than the glass-transition temperature and for salt concentration greater than 7 N , providing a useful correlation of transport properties in CaCl_2 , not only for the Cd^{2+} diffusivities but also for literature values^{5,6} of Ca^{2+} tracer diffusivity,⁵ proton (NMR) diffusivity,^{6,7} fluidity,⁸ and electrical conductance.⁹

1. Visiting scientist, Swiss Federal Institute for Reactor Research, Wuerenlingen, Switzerland.

2. C. A. Angell, *J. Chem. Phys.* 46, 4673 (1967).

3. J. Braunstein, A. L. Bacarella, B. M. Benjamin, L. L. Brown, and C. Girard, *J. Electrochem. Soc.* 124, 844 (1977); *Proceedings of the International Symposium on Molten Salts*, ed. J. Pemsler, J. Braunstein, D. R. Morris, K. Nobe, and N. E. Richards, The Electrochemical Society, Princeton, N.J., 1976, pp. 544-59.

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2.1.10 X-Ray Diffraction Study of Uranyl Complexes in Water at Low Concentration

A. H. Narten

The hydrolysis of the uranyl ion, UO_2^{2+} , has been investigated by a large number of workers with different techniques. Most authors agree on the presence of a complex with the general formula $(\text{UO}_2)_n(\text{OH})_m$, with the numbers $n, m > 2$, strongly dependent on the ionic medium and pH selected for the studies. The only recent x-ray diffraction study¹ concerns concentrated (3 M) acid solutions of uranyl chloride, and these data have led to the conclusion that the predominant complexes contain only two or three uranium atoms separated by a distance of 3.86 Å and joined by double oxygen bridges. We here report results from both large- and small-angle x-ray scattering studies of dilute (<0.05 M) alkaline solutions of uranyl chloride in water containing small amounts of $\text{N}(\text{CH}_3)_4\text{OH}$.

The purpose of the large-angle study was to determine the internuclear distances between nearest neighbors in the uranyl complex. The solution studied contained about 1000 water molecules per uranyl ion (0.1 mole % U) with a pH of 12.2. Data collection and reduction with a diffractometer designed for the study of liquids has been described elsewhere,² and the correlation function $G(r)$ derived from the data is shown in Fig. 2.3 (center). Also shown (top) is the function $G(r)$ for pure water,³ properly weighted for comparison with the curve for the solution.

For an analysis of the solution data, we consider that only contributions from water molecules, from uranium atoms, and from chlorine ions are "seen" by x rays at these concentrations. Furthermore, deviations in the mutual arrangement of water molecules from that found in the pure solvent cannot be detected. Hence, we have subtracted the weighted structure function of pure water from that of the solution and performed a Fourier transformation on the difference curve, Fig. 2.3 (bottom). Direct comparison of the functions $G(r)$ for pure water and for

Fig. 2.3. Correlation functions derived from large-angle x-ray diffraction. Top, pure water; center, UO_2Cl solution; bottom, difference.

the solution reveals the following features characteristic of the solution:

1. A peak at 1.8 Å, which must be ascribed to the $\text{U}=\text{O}$ distance in the UO_2^{2+} ion.
2. A broadening of the first-neighbor water-water peak at 2.85 Å in the solution.
3. A peak at 3.9 Å, which must be ascribed to $\text{U} \dots \text{U}$ interactions in the complex.

The difference curve, Fig. 2.3 (bottom), reveals two additional features:

4. A peak at 2.6 Å, which we interpret as a $\text{U} \dots \text{O}$ distance in the complex.
5. A peak at 3.1 Å, which we ascribe to a $\text{Cl}^- \dots \text{O}$ distance.

The features (1-5) derived from our results are consistent with a complex having as the basic unit two oxygen atoms, probably OH^- , bonded to uranyl ions at a mean distance of 2.6 Å, significantly shorter than the mean $\text{O} \dots \text{O}$ distance of 2.85 Å found in water. The two oxygen atoms serve as a double bridge between two uranium atoms separated by a mean distance of 3.9 Å. These results agree well with earlier results¹ obtained for concentrated acid solutions of uranyl chloride.

The purpose of the small-angle study was to determine the size of the uranyl complexes. This was found⁴ to be in excess of 100 Å, depending strongly on the pH of the solutions.

These results demonstrate that the combined methods of large- and small-angle x-ray scattering are sufficiently sensitive to determine the size and shape distributions of polymeric species involving heavy atoms at low concentrations.

1. M. Aberg, *Acta Chem. Scand.* **24**, 2901 (1970).
2. A. H. Narten and H. A. Levy, p. 311 in *Water: A Comprehensive Treatise*, vol. 1, ed. F. Franks, Plenum, New York, 1972.
3. A. H. Narten and H. A. Levy, *J. Chem. Phys.* **55**, 2263 (1971).
4. R. W. Hendricks, private communication.

2.2 GEOTHERMAL ENERGY

2.2.1 Precipitation and Scaling in Dynamic Geothermal Systems

E. G. Bohlmann A. J. Shor
P. Berlinski

Modification of the 100-gpm titanium loop¹ for the silica scaling studies has been completed, and shake-down operations have confirmed design objectives:

- Operation to 300°C.
- 150°C ΔT in the segmented heat exchanger scaling test section.
- 3 to 7 fps flow in the heat exchanger with Reynolds numbers at 10,000 to 50,000.
- Amorphous silica saturator column providing silica concentrations consistent with loop dynamics and temperature solubility equilibrium.
- Heat exchange data satisfactory for the following scaling.

Data of interest are automatically logged and processed by a Hewlett-Packard 3050B data acquisition processor system. The central unit is a 9825 computer with scanners, x-y plotter, printer, tape storage, and DVM peripherals on an HP interface bus, with provision for additional peripherals as required. Software is saved on a special two-track high-speed tape cartridge of about 250K byte capacity. An "Executive" program operates 24 programmable tasks, each of which can be scheduled with a timer-clock calendar at any period on a selected priority basis.

A once-through system (OTS),⁽¹⁾ also using an amorphous silica column to produce high-temperature silica-saturated brine which is subsequently supersaturated by air cooling in a Pyrex-pipe scaling test section, has been used to study the behavior of silica in such brines during this period. Procedures for sampling, scale characterization and cleanup, elimination of control valve plugging, and preparation of silica stock solutions for other laboratory investigations have been developed with this system.

Observations of scale formation during the OTS operations indicated that seeding during inadvertent shutdowns (usually resulting from control valve plugging) was the dominant—and probably essential—factor in initiating scale formation under the conditions investigated thus far: 0.1 M NaC₂H₃O₂, 0 and 1 M NaCl, pH 4.5 to 6, 600 to 1000 ppm SiO₂. Scales formed after seeding are typically very hard and adherent when deposited at temperatures above 100°C, but show a gradual transition to a friable nonadherent material easily removed with a test-tube brush at deposition temperatures less than about 60°C. Figure 2.4 shows the amount of scale deposited as a function of deposition temperature; these

Fig. 2.4. Run OT-2; silica deposition vs temperature of deposition.

deposits formed in ~15 hr after a 13-hr shutdown to promote seeding. Conditions during scale formation were 0.1 M NaC₂H₃O₂, 1 M NaCl, 725 ppm SiO₂, pH 6.0, 1 fpm flow rate. No silica formed in 58 hr of uninterrupted operation under the same conditions before the seeding shutdown. Deposits formed after seeding characteristically show minimum deposition at 55 to 60°C, no substrate effects, and maximum (>90%) deposition in the bottom 120° of the cooled piping.

The first run in the dynamic loop system has just been completed. Conditions were the same as for the OTS run described above except that the silica concentration ranged from 750 to 925 ppm and the brine

flow rate in the heat exchangers ranged from 4 to 2 fps. Evaluation of the results is still in progress, but they appear quite similar to those observed in the OTS.

I. E. G. Bohlmann, A. J. Shor, and P. Berlinski, *Precipitation and Scaling in Dynamic Geothermal Systems*, ORNL/TM-5649 (October 1976).

2.2.2 Ionization Equilibria of Silicic Acid and Polysilicate Formation in Aqueous Sodium Chloride Solutions to 300°C⁽¹⁾

R. H. Busey R. E. Mesmer

The experimental study of the ionization behavior of silicic acid and polysilicate formation in basic solutions has been completed by precision potentiometry, using titration techniques in the hydrogen-electrode concentration cell. Polysilicate formation was studied in 1 M NaCl solutions at temperatures from 60 to 290°C and at Si(IV) concentrations 0.005 to 0.05 M. Results from titration experiments are given in Fig. 2.5, where n is the average number of OH⁻ ions bound per silicon in solution (hydroxyl number). At the lowest silica concentration, only mononuclear species occur over a wide temperature and pH range. At hydroxyl numbers from ~0.7 to 1.0, small polysilicates which equilibrate rapidly occur at higher Si(IV) concentrations. In a 0.02 M Si(IV) solution at 60°C, the maximum polysilicate formation is ~25%, but in the same solution at 250°C, only ~3% of the silicon is present as the polynuclear species.

In another series of experiments where the objective was to determine the equilibrium quotient Q_{11} for the reaction

as a function of temperature and ionic strength, the results are represented by the expression

$$\begin{aligned} \log Q_{11} = & \frac{2.34669 \times 10^3}{T} + 2.57979 \ln T \\ & - 18.4014 + 0.0964146I - 3.02800 \times 10^{-7}IT^2 \\ & + 0.529703f(I)I + 0.0157\phi I. \end{aligned} \quad (2)$$

In this equation, $f(I)$ is a function of ionic strength (suggested in the formulation of Pitzer²) to express

Fig. 2.5. Effect of silicon concentration and temperature on the hydrolysis of silicic acid, $\text{Si}(\text{OH})_4(\text{aq})$, in 1 *m* NaCl. The approximate silicon concentrations are indicated, and the curves were calculated from equilibrium quotients derived from a computer fit of the data with $\text{Si}_4(\text{OH})_{18}^{2-}$, the assumed polynuclear species.

the effect of ionic strength on the interaction coefficients in the Brönsted-Guggenheim approach for activity coefficients, ϕ is the osmotic coefficient for NaCl solutions, and the assumption is made that ΔC_p is a constant. The thermodynamic quantities at saturation pressure for reaction (1) are derivable from expression (2). The reaction proceeds to a lesser extent to the right in a regular fashion as the temperature is increased.

1. Summary of a paper submitted to *Inorg. Chem.*
2. K. S. Pitzer, *J. Phys. Chem.* 77, 268 (1973).

2.2.3 Solubility of Amorphous Silica in Aqueous Sodium Nitrate Solutions to 300°C

W. L. Marshall

In geothermal energy production, deposition of scale on heat exchanger surfaces is a major problem. Deposits of amorphous silica and its related silicates, together with carbonates, are the chief antagonists.

These substances all show decreasing solubilities as the temperature of the geothermal solution is lowered in heat exchangers. Although the solubility of amorphous silica in water at both low and high temperatures has been studied in detail, there is little information on its solubility in salt solutions. Since geothermal waters generally contain moderate amounts of dissolved salts, it is important that we know solubility characteristics in these solutions. The objectives of this study are directed toward both the above goal and the fundamental interpretation of high-temperature solution behavior for later predictions.

By using apparatus and techniques developed earlier in this program, we have determined the solubility of amorphous silica in aqueous solutions of sodium nitrate from 0 to 6.5 *m* and at temperatures from 100 to 300°C. Solution phases were obtained for analysis after times varying from 1 to 24 hr; equilibrium appeared to be established within 2 hr. Values in water, the end point for each set of isothermal data, agreed moderately well with those

Fig. 2.6. Solubilities of amorphous silica in NaNO₃-H₂O solutions at 100 to 300°C.

published. Figure 2.6 gives the solubility data obtained, and these values show smooth correlations with molality of sodium nitrate, literature values in water, and temperature. The solubilities decrease with increasing salt concentrations as might be expected for a neutrally charged dissolved species.

These first studies were made in sodium nitrate solutions because of the inertness of our titanium alloy vessels to the high-temperature nitrate solutions. The solubilities should be reasonably comparable with behavior in sodium chloride solutions at least to 1 *m*; this expectation will be experimentally tested.

2.2.4 Corrosivity of Geothermal Brines

F. A. Posey A. A. Palko
A. L. Bacarella

The salinities of the hydrothermal brines located in the western part of the U.S.A. are usually very high, and as a result, they are corrosive to standard metallic materials of construction. Furthermore, most of these hypersaline brines form scales on the surfaces of containment materials as either the temperature or pressure is lowered. These two problems, which may be interrelated, have thus far seriously impeded large-scale utilization of the energy available in geothermal brines. The purpose of these studies,¹ which are sponsored by ERDA's Division of Geothermal Energy, is to develop a basic understanding of corrosion processes of ferrous metals, especially carbon steel, in synthetic brines which simulate the aggressive concentrated salt solutions encountered during conversion of the heat content of geothermal brines into

electrical energy. A quantitative knowledge of the kinetics of corrosion processes in synthetic brines and the influence of such variables as solution composition and temperature will assist in establishing a scientific basis for interpretation of field corrosion tests, on-line corrosion measurements, and plant corrosion experience, and perhaps suggest means for control or mitigation of corrosion during various stages of plant operation.

Principal emphasis in these studies is placed on the investigation of electrochemical aspects of corrosion of carbon steel, since this material has been proposed for most engineering applications. Literature data on the electrochemistry of corrosion of ferrous materials under geothermal conditions are virtually nonexistent; nearly all studies in concentrated chloride solutions have been restricted to those at room temperature. From a corrosion standpoint the components of brines that are most likely to affect the kinetics of interfacial reactions, in addition to acid or alkaline pH, are chloride, carbonate, sulfide, silicate, and perhaps low levels of heavy-metal ions which occur in natural brines. We are investigating the effects of these species on corrosion kinetics individually and in combination over the temperature range 25 to 200°C by use of electrochemical techniques.

Experimental measurements below 100°C are being carried out in a conventional laboratory electrochemical cell; measurements made above 100°C make use of a refreshed, stirred titanium autoclave system. A schematic diagram of the system is shown in Fig. 2.7. A diaphragm pulse pump forces deaerated test solution into the stirred autoclave, and pressure within the autoclave (typically 200 to 500 psig) is regulated by an adjustable letdown valve. Test specimens are mounted on a Teflon-insulated titanium contact rod, and an external saturated calomel reference electrode is bridged into the autoclave. The counter electrode is a coil of titanium wire wound on Teflon spacers. Provisions are available for control and monitoring of the autoclave temperature and for recording of the (room-temperature) pH of the solution entering and leaving the autoclave.

We have studied the polarization behavior and corrosion rate of type A212B carbon steel, a typical pipeline steel, in 4 *M* NaCl at pH 3, 4, 5, and 7 all the way from room temperature to 200°C. The results show several features of interest, including the observation that the specific rate of the anodic iron dissolution reaction actually decreases with increasing temperature in the vicinity of 200°C. This behavior may be a result of greatly increased hydrogen ion activity at elevated temperatures, which could reduce

Fig. 2.7. Schematic diagram of refreshed, stirred titanium autoclave system for electrochemical studies.

the surface concentration of adsorbed "hydroxy" reaction intermediates which determine the rate of the iron dissolution reaction. Alternatively, enhanced adsorption of chloride ions at elevated temperatures could displace adsorbed reaction intermediates in the iron corrosion reaction. The inhibiting effect of adsorbed chloride ions on the corrosion of carbon steel in concentrated chloride solutions is being investigated in detail as a function of pH and temperature below 100°C. Other measurements are concerned with the variation of the pitting potentials of representative stainless steels in deaerated synthetic brines, since the relationship of the pitting potentials of austenitic stainless steels to their spontaneous corro-

sion potentials has not been established for brines encountered under geothermal conditions. Further experimental details and the results of the measurements obtained so far may be found in periodic progress reports.^{2,3}

1. This work is a cooperative effort with J. C. Griess and J. H. DeVan of the Metals and Ceramics Division.

2. F. A. Posey and A. A. Palko, *Corrosivity of Geothermal Brines Prog. Rep. June 1976*, ORNL/TM-5688 (December 1976).

3. F. A. Posey, A. A. Palko, and A. L. Bacarella, *Corrosivity of Geothermal Brines Prog. Rep. December 1976*, ORNL/TM-5863 (April 1977).

3. Chemistry in Support of Fusion Reactor Technology

Tritium inventories in fusion reactor systems will be about 10^8 Ci and must be contained to prevent loss to the environment. The fuel cycle includes extracting and processing tritium from the blanket, and recycling tritium and deuterium from the exhaust gas. Methods for effective tritium management, both for containment and in the fuel cycle, must be developed simultaneously with other aspects of fusion reactor technology. This program is dedicated to providing fundamental knowledge about tritium management in fusion reactor systems. The primary objective is to obtain basic chemical information on the behavior of tritium in fusion systems and materials. Topics for investigation include (1) measurement of equilibria in the lithium-hydrogen isotope systems; (2) measurement of equilibrium tritium solubility in solid blanket materials such as lithium-aluminum alloy and LiAlO_2 ; (3) determination of the permeabilities for the hydrogen isotopes through clean metals that may be used in steam generator systems, and then the determination of the effects of in situ surface oxidation to impede permeation; (4) measurement of the kinetics for the surface oxidation and determination of the chemical compositions of the oxide films; and (5) evaluation of the chemistry, kinetics, and thermodynamics of processes that are proposed for tritium management.

3.1 EQUILIBRIA IN HYDROGEN ISOTOPE-FUSION REACTOR BLANKET SYSTEMS

F. J. Smith J. F. Land
G. M. Begun J. T. Bell
A. M. La Gamma de Batistoni¹

The development of controlled thermonuclear reactors with lithium blankets requires complete vapor-liquid equilibrium data on the hydrogen isotope-lithium system. This information is necessary to design tritium management programs for recovery of bred tritium from the blanket and minimize the loss of tritium to the atmosphere. The mutual solubilities and isotopic exchange of hydrogen and deuterium in lithium have been measured for the plateau region (two-phase coexistence region) at 700, 800, and 850°C. Both the total pressure and the individual partial pressures of H_2 , HD, and D_2 have been determined as a function of the mole fraction of LiH and LiD in the liquid phases with varying hydrogen-deuterium ratios. All of the results at 800°C for the plateau region ($0.96 > N_{\text{LiH}} +$

$N_{\text{LiD}} > 0.33$) are shown in Fig. 3.1. The results were independent of whether the initial additions were hydrogen, deuterium, or a mixture and did not depend on the relative amounts of the two coexisting phases. The equilibrium partial pressures depended only on the relative amounts of the isotopes in the system. The total equilibrium pressure in the mixed hydrogen-deuterium-lithium system follows the relationship

$$P_{\text{total}}^{1/2} [\text{torr}^{1/2}] = -3 \left(\frac{N_{\text{LiH}}}{N_{\text{LiH}} + N_{\text{LiD}}} \right) + 15.9 .$$

Partial pressures of hydrogen and deuterium are represented by

$$P_{\text{H}_2}^{1/2} [\text{torr}^{1/2}] = 12.9 \left(\frac{N_{\text{LiH}}}{N_{\text{LiH}} + N_{\text{LiD}}} \right) ,$$

$$P_{\text{D}_2}^{1/2} [\text{torr}^{1/2}] = 15.9 \left(\frac{N_{\text{LiD}}}{N_{\text{LiH}} + N_{\text{LiD}}} \right)$$

Fig. 3.1. Mutual solubility of hydrogen and deuterium in lithium for the plateau region at 800°C.

respectively. The equilibrium partial pressure of HD is defined by the pressures of H_2 , D_2 , and the gas-phase equilibrium constant for the reaction $H_2 + D_2 \rightleftharpoons 2HD$. At 800°C it is²

$$K(g) = 3.8 = \frac{P_{HD}^2}{P_{H_2} P_{D_2}}$$

Similar relationships were observed at 700 and 850°C. The equilibrium isotope effect, K , expressed by

$$P_{D_2}^{1/2} / P_{H_2}^{1/2} = K(N_{LiD} / N_{LiH})$$

is 1.28, 1.23, and 1.17 at 700, 800, and 850°C respectively.

The plateau boundaries of the two-phase region for the mixed hydrogen-deuterium-lithium system are identical to those for the single isotopes, and the boundaries are independent of the hydrogen-deuterium ratio. At 800°C the boundaries are given by the sum of the mole fraction relationship $N_{LiH} + N_{LiD} = 0.33$ and $N_{LiH} + N_{LiD} = 0.96$.

1. Comision Nacional de Energia Atomica, Argentina.
2. H. L. Johnston and E. A. Long, *J. Chem. Phys.* 2, 389 (1934).

3.2 SORPTION OF HYDROGEN ISOTOPES BY METAL GETTERS

G. M. Begun F. J. Smith
J. F. Land

Most current designs of advanced fusion reactors employ molten lithium as a blanket material in which tritium is formed by neutron absorption. Tritium concentrations in the blanket must be kept low (<100 ppm by weight) in order to minimize permeation into secondary systems and losses to the surroundings. Tritium must be recycled to the reactor by removing it from the blanket and purifying it. Experiments in the Chemical Technology Division¹ have shown that a promising method of removing tritium from liquid lithium is sorption on a hydrogen-gettering material. The material which shows the most promise at present is yttrium. Several studies of the yttrium-hydrogen system have been reported in the literature. These measurements do not cover the complete range of temperatures and pressures of interest. No measurements have been reported for the yttrium-deuterium or yttrium-tritium systems. We are therefore undertaking the investigation of these systems.

Samples of sponge and ingot yttrium have been obtained as well as yttrium turnings. Using the Sieverts' apparatus previously described,² several runs have been made on the yttrium-hydrogen system. Sponge and ingot yttrium samples were used, and equilibrium hydrogen vapor pressures were determined in the range 0.1 to 0.6 atom ratio H/Y and at temperatures ranging from 500 to 950°C. Below 500°C the equilibrium pressures were too low to measure with the present apparatus. Rapid equilibrium was observed at the higher temperatures for both sponge and ingot yttrium samples. The results of these experiments were tabulated and graphed and found to agree well with the literature values.³ Samples of ingot yttrium were found to react

with hydrogen at a measurable rate at temperatures as low as 200°C, and sponge yttrium reacted even at room temperature. At these low temperatures, reaction occurred largely at the surface, and yttrium dihydride was the principal product.

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2. *Proc. Symp. Tritium Technol. Relat. Fusion React. Sept., 1974*, ERDA-50, p. 42 (June 1975).
3. L. N. Yannopoulos, R. K. Edwards, and P. G. Wahlbeck, *J. Phys. Chem.* 69, 2510 (1965).

3.3 PERMEATION OF CONSTRUCTION MATERIALS BY HYDROGEN ISOTOPES

J. T. Bell J. D. Redman
F. J. Smith

Tritium permeabilities of clean Incoloy 800, clean type 316 stainless steel, and W-3.5% Ni-1.5% Fe alloy were determined over the 500 to 1100 K range. The data can be expressed as $DK = 6.77 \exp(-19700/RT)$ for Incoloy 800, $DK = 0.533 \exp(-16260/RT)$ for 316 SS, and $DK = 0.00788 \exp(-14930/RT)$ for the ternary alloy. Permeation rates for tritium through Incoloy 800, 316 SS, and the ternary alloy were determined at various feed-gas pressures from 35 to 782 torr, with HT pressures from 1.5×10^{-4} to 33.1×10^{-4} torr (corresponding to T_2 pressures from 1.67×10^{-10} to 37.2×10^{-10} torr). With each material, the permeation rates were dependent on the square root of the tritium pressure.

Isotope effects on hydrogen permeabilities of nickel have been determined by comparing our measured tritium permeabilities with the published permeabilities for deuterium¹ and protium.² The ratio of protium permeability to the permeability of either heavier isotope can be greater than the square root of inverse mass ratios. This high ratio results because permeability is the product of diffusivity and solubility, and the observed isotope effects on permeability are the products of the effects on diffusivities and solubilities. Furthermore, the isotope effect on permeabilities is also the product of the effect on the permeability constants and the effect on the exponential term containing the apparent activation energy. The isotope effects of the heavier isotopes are to reduce the permeability constants and the apparent activation energies. The activation energy, ΔE , appears in the negative exponential term as

$$DK = (DK)_0 e^{-\Delta E/RT},$$

and thus the effect of the heavier isotopes is to increase the exponential term. Then the isotope effect on permeability, DK , is the product of the effect to decrease the permeability constant, $(DK)_0$, and the effect to increase the exponential term. Since the total effect includes the exponential term, the isotope effect does vary with temperature.

Studies on the effects of in situ steam oxidation at 660°C to impede tritium permeation through Incoloy 800 were also continued. Oxide layers formed by oxidation with steam at partial pressures of 0.32, 0.70, and 0.94 atm for 150 days decreased the permeability by factors of 250, 304, and 492 respectively. Calculations based on various fusion reactor designs indicate that permeation rates through the heat exchanger into the steam system must be 10^2 to 10^3 times less than the rates for the bare construction materials. An example of steam oxidation to reduce the tritium permeability of Incoloy 800 is shown in Fig. 3.2. The initial effect is to reduce the permeability rapidly; during this time the surface is covered completely by the oxide. Then the slower but continuous decrease in permeability is the result of the oxide growing thicker. Table 3.1 shows impedance factors imposed by steam oxidation on Incoloy 800. With each of the steam pressures the factors increase with time; and, at any time, the factors increase with steam pressure. This second point indicates that the diffusion of the oxidizing components from the bulk alloy to the surface is faster than the oxidation. This poses the question: At what steam pressure will the diffusion rate control the

Fig. 3.2. Permeation of tritium through Incoloy 800 exposed to steam at 0.94 atm and temperatures cycling between 640 and 660°C.

Table 3.1. Oxides formed in situ will impede tritium permeation through Incoloy 800 at 660°C

Steam pressure	Impedance factors at days		
	24	150	176
0.32	76	250	302
0.70	100	304	350
0.94	199	494	

oxidation rate? Only further experimentation at higher pressures can provide the answer.

Stress effects on the oxide layers can cause defects which diminish the permeation impedance factors. Severe thermal shock affected the physical character of the oxide layers such that the permeability increased to within a factor of 10 of that for the clean Incoloy 800. However, the defects in the oxide in three experiments were annealed by continued oxidation at stable temperatures. Mild temperature cycles, $\pm 20^\circ\text{C}$ every 30 min, did not affect the permeabilities. Ion microprobe techniques for the chemical analysis of the oxides on the permeation samples have been evaluated. These techniques give the oxygen profile through the oxide layer and the relative amounts of the different metals in the oxide layer. Such analyses have now become an integral part of the permeation studies.

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3.4 STEAM OXIDATION OF INCOLOY 800

J. T. Bell F. J. Smith
J. D. Redman

Small tab samples of Incoloy 800 are being oxidized in low-pressure steam atmospheres, and the surface oxides formed are being analyzed with the assistance of W. H. Christie of the Analytical Chemistry Division. The thickness and the chemical composition of the oxide coatings are determined by ion microprobe techniques, and the results are compared with results from the permeation studies. The purpose of these oxidation studies is to better understand the role of the oxide coatings in decreasing the tritium permeation of Incoloy 800. Several tabs having different pretreatments were tested in the first experiment with 0.3 atm of steam at 660°C. Some tabs were not changed, some were mechanically lapped and buffed, and some were lapped and electropolished. The samples which had been lapped and then electropolished formed oxide coatings that were thicker and harder to remove by ion polishing than were the oxides on other samples. Elemental analysis of the oxide film on the tab samples indicated an outer iron oxide layer followed by an oxide layer enriched in chromium, silicon, and manganese. There was a corresponding depletion of these elements in the metal.

4. Chemistry of Transuranium Elements and Compounds

4.1 ABSORPTION SPECTROPHOTOMETRY AND X-RAY DIFFRACTION STUDIES ON THE ANHYDROUS HALIDES OF TRANSCURIUM ELEMENTS¹

R. L. Fellows² R. G. Haire
J. R. Peterson³ J. P. Young⁴

The systematic study of the anhydrous transcurium halides by absorption spectroscopy and x-ray diffraction was continued.⁵ This broad-based microchemical investigation seeks to prepare and study these elements in valence states of II, III, and IV. The preparative techniques are basically the same as outlined previously.⁵ An effort has been made to investigate the divalent state of californium and einsteinium by reducing their trihalides (Cl, Br, I) with hydrogen. The trihalides and oxyhalides of these elements are now well characterized, although the quality of x-ray data on einsteinium compounds is limited by the rapid destruction of their crystallinity by self-irradiation. Studies on the tetravalent state have also been initiated by examining preparations of ²⁴⁸CmF₄.

Recently, x-ray data have been obtained for BkI₃, BkOI, and EsI₃. A crystal structure is now known for all the trihalides of einsteinium except the fluoride. Both BkI₃ and EsI₃ crystallize in the BiI₃-type hexagonal structure. Lattice parameters obtained for BkI₃ are $a_0 = 7.584(4)$ Å and $c_0 = 20.87(1)$ Å. For EsI₃, the approximate parameters are $a_0 = 7.53$ Å and $c_0 = 20.84$ Å. A tetragonal PbFCl-type structure was found for BkOI, whose parameters are $a_0 = 3.986(1)$ Å and $c_0 = 9.149(2)$ Å.

Mixtures of the transcurium elements and selected lanthanide elements have also been studied. The impetus for examining these mixtures resulted from early unsuccessful attempts to prepare pure divalent einsteinium halides by hydrogen reduction. Five different lanthanide elements (La, Sm, Eu, Gd, and Yb) were selected on the basis of their ionic radii and

reducibility. A lanthanide-actinide compound resembling M₆Cl₁₃ or M₅Cl₁₁ (M = lanthanide) has been prepared; the latter compounds have been recently reported by other workers.^{6,7} The first absorption spectrum for divalent einsteinium was also obtained from a lanthanide-einsteinium mixture.

Development of a new apparatus for the chemical conversion step has vastly improved control over the chemical synthesis, permitting cyclic, consecutive oxidation-reductions to be carried out on the same sample. Using this new apparatus, it is now possible to prepare pure dihalide samples of both californium and einsteinium.

4.1.1 Dimorphism in BkBr₃

Changes in absorption intensity have been used to monitor solid-state phase transitions in BkBr₃. The transition in BkBr₃ can be followed spectrally because the coordination symmetry of the berkelium ion changes from *O_h* in the 6-coordinate monoclinic (high-temperature) form to *C_{2v}* in the 8-coordinate orthorhombic (low-temperature) form. The absorption spectra of these two crystal forms are presented in Fig. 4.1. The most noticeable change in the BkBr₃ spectrum is the overall intensity of the *f-f* transitions in the orthorhombic form. This change is significantly greater than that expected from changes in crystal density and is fully consistent with the view of the significance of symmetry and centers of inversion on transition probabilities.⁸ The ingrowing Cf³⁺ (apparent in Fig. 4.1 as small bands at 11,500 and 13,200 cm⁻¹) exhibits the 8-coordinate structure of the "host" BkBr₃, even though pure CfBr₃ does not form the orthorhombic crystal modification. Spectrophotometry is a more sensitive and rapid method than x-ray diffraction and is very useful for studying phase changes accompanied by spectral changes.

The kinetics of the phase transition were also followed spectrophotometrically. Representative re-

Fig. 4.1. Absorption spectra of the orthorhombic and monoclinic crystal forms of BkBr_3 .

Fig. 4.2. Spectrophotometric study of BkBr_3 phase transformation; kinetic study of 6- to 8-coordination transition.

sults for the conversion of the monoclinic form to the orthorhombic form at different temperatures are given in Fig. 4.2. These results, by monitoring the absorbance at constant wavelength, typify the behavior of all Bk^{3+} transitions as well as those of the ingrowing daughter Cf^{3+} .

4.1.2 Characterization of the First Preparation of CfCl_2

Investigations of the divalent state of californium are particularly interesting, since stability of divalency is enhanced in the very heavy actinides. The

question of Cf(II) stability was addressed by Nugent et al.,⁹ who predicted that Cf(II) would have a II $\rightarrow$ III oxidation potential similar to that of Sm(II) . Subsequent experimental work¹⁰ supported this prediction. Since SmCl_2 was the first divalent lanthanide prepared,¹¹ it is ironic that previous attempts to prepare CfCl_2 were unsuccessful, particularly in light of the recent preparations of CfBr_2 ¹² and CfI_2 .¹³

We have recently been successful in our efforts to prepare CfCl_2 by hydrogen reduction of CfCl_3 , using the new preparative equipment noted above.

Samples prepared to date have contained only about 1 to 5% Cf(III) . In contrast to the green-colored CfCl_3 which melts at 545°C , CfCl_2 is amber-colored and melts above 650°C .

The absorption spectrum of CfCl_2 is given in Fig. 4.3. A comparison of the absorption band intensities of CfCl_2 with those of CfI_2 (ref. 14) is particularly interesting. The most intense features of the CfI_2 absorption spectrum are the $f-f$ bands at 9.1 , 11.1 , and 17.9 ($\times 10^5$) m^{-1} while other bands exhibit considerably lower intensities. Many of these low-intensity absorption bands exhibit enhanced intensity in the CfCl_2 spectrum; the broad band at 10×10^5 m^{-1} is of questionable origin. Intensity should be enhanced if the site symmetry of the Cf(II) ions is lower in the dichloride than in the diiodide. In CfI_2 , californium is in a 6-coordinate, octahedral environment in both the rhombohedral CdCl_2 -type and the hexagonal CdI_2 -type crystal structures. Based on spectroscopic evidence, a coordination number greater than 6 is expected for CfCl_2 . The preliminary interpretation of CfCl_2 x-ray diffraction patterns indicates that CfCl_2 forms the orthorhombic PbCl_2 -type crystal structure in which the cations are 9-coordinate.

Fig. 4.3. Absorption spectrum of CfCl_2 .

4.1.3 The First Preparation and Characterization of an Es(II) Compound

Einsteinium chemistry to date has centered on the trivalent state. Separations behavior in aqueous solution has historically indicated that einsteinium is found in the 3+ valence state. Theoretical treatment of the absorption spectrum of aqueous einsteinium also indicates the trivalent state. Those few compounds for which x-ray data have been obtained are also trivalent einsteinium compounds.^{15,16}

The reduction potential of Es(III) → Es(II) has been predicted to be in the range of -1.2 to -1.3 V in aqueous solution.⁹ This potential indicates that Es(III) should be easier to reduce than Cf(III). Recent polarographic experiments confirm the predicted ease of reduction¹⁰ of Es(III), but Es(II) has been prepared only in the solid state as a dopant in various matrices.¹⁷⁻¹⁹

We have recently succeeded in preparing solid-state Es(II) compounds by the following reaction:

where X = Cl, Br, I. The evidence for Es(II) is based on the disappearance of the Es(III) absorption spectrum and the simultaneous appearance of a new and unique spectrum that we attribute to Es(II) (Fig. 4.4). Reoxidation of the Es(II) with the appropriate HX results in the reversion to Es(III).

The absorption spectrum of Es(II) in the visible and near-infrared region consists of bands whose intensities and full-widths at half maximum (FWHM) are characteristic of *f-f* transitions. The nephelauxetic shifts accompanying the change in halide are comparable to those of the trivalent einsteinium cation, paralleling the behavior seen in the Cf(II)-Cf(III) halide systems.

4.1.4 Characterization of Oxyhalides of Trivalent Einsteinium

The oxyhalides (AnOX) are often ubiquitously found during the preparation of actinide (An) halides (X = Cl, Br, I). The exact mechanism of formation is not known, but three potential mechanisms are considered to be of primary importance: (1) direct reaction of Es³⁺ with water trapped in the quartz container, (2) reaction of einsteinium with SiO formed during seal-off of the capillary (most significant when the capillary contains hydrogen), and (3) direct reaction of EsX₃ with the quartz container. This last reaction may occur during lanthanide trihalide preparations and becomes more significant with the heavier halogens. Any combination of these reactions must be considered, and the possibilities are complicated by the energetic decay of ²⁵³Es (~3660 kcal mole⁻¹ min⁻¹).

In order to study the oxyhalides, EsOCl, EsOBr, and EsOI were prepared via the following reactions:

This scheme permits determination of the melting point of the intermediate EsX₃, an important check for sample purity.

The oxyhalides are opaque and are of poorer crystallinity than the corresponding trihalides. Although determinations of einsteinium crystal structures by x-ray diffraction are difficult due to the rapid degradation of the crystal by self-irradiation, EsOCl has been shown to have the PbFCl-type, tetragonal crystal structure.¹⁹ The compounds EsOBr

Fig. 4.4. Absorption spectrum of EsCl₃.

and EsOI probably have the same structure, since all known trivalent actinide and all but three trivalent lanthanide oxychlorides, oxybromides, and oxyiodides exhibit this structure.

The poor crystallinity of the oxyhalides may be reflected in their spectra. For example, EsOI (Fig. 4.5) absorption band widths (FWHM) as well as the band shapes are reminiscent of solution spectra: relatively broad bands of high intensity. The low coordination symmetry might also cause the spectrum to exhibit this type of behavior. Band positions are shifted to generally higher energy than those of the corresponding trihalide. As in other actinides and lanthanides, however, these nephelauxetic shifts are not consistent in magnitude for the different absorption bands.

Fig. 4.5. Absorption spectrum of EsOI.

4.2 INVESTIGATION OF THE REDUCTION OF TRIVALENT EINSTEINIUM AND CALIFORNIUM BY POLAROGRAPHY¹

C. Musikas² J. R. Peterson³
R. G. Haire

The increasing stability of the divalent state for the higher members of the transcurium elements suggests that polarography and cyclic voltammetry may be used to experimentally measure the valence changes of californium and einsteinium. With polarography of californium in acetonitrile, the californium III → II reduction wave can be observed.⁴ Efforts have been made to examine einsteinium in acetonitrile by polarography and to develop microtechniques for cyclic voltammetry of californium in aqueous media.

The extremely high specific activity of the most available isotope, ²⁵³Es, poses two major experimental problems. First, the alpha radiation on the acetonitrile solvent generates interfering decomposition products. This has been overcome by developing microtechniques that require only 5- to 10-μg quantities of einsteinium. Second, an anhydrous einsteinium compound must be prepared that is soluble in acetonitrile and that is stable enough to dissolve in the solvent before it decomposes from self-irradiation. Initial attempts to use perchlorate salts formed by evaporating to dryness a perchloric acid solution of einsteinium were unsuccessful. These salts rapidly decompose to form oxygenated salts that do not dissolve in acetonitrile. More recent efforts have employed freshly prepared anhydrous einsteinium trichlorides. The dissolution rate of these trichlorides is a function of their surface area; a single 10-μg piece of einsteinium trichloride, most desirable for transfers, provides the poorest dissolution behavior.

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The dissolution rate is especially important with einsteinium compounds, since the radiolytic decomposition of the solvent is a function of dose and time. Initial results of polarography experiments with einsteinium in acetonitrile appear promising for measurement of the einsteinium III $\rightarrow$ II reduction wave.

Microtechniques for performing cyclic voltammetry and polarography in aqueous solutions have also been developed; we hope to measure the III $\rightarrow$ II reduction of californium in very dilute acid solutions. Experiments substituting 30 μ g of samarium for californium have been successful, and the initial work with californium will immediately follow the einsteinium work.

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4.3. X-RAY DIFFRACTION STUDIES OF CALIFORNIUM UNDER HIGH PRESSURE

J. H. Burns J. R. Peterson¹

The behavior of the crystal structure of californium metal under pressures up to 140 kbars has been studied by use of a diamond-anvil type miniature x-ray diffraction camera.² For testing the apparatus and technique, the phase transitions in silver iodide and cerium metal were produced and identified. Calibration of the camera dimensions was achieved by measuring the diffraction pattern of thorium oxide. In order to study californium metal, previously prepared samples³ having a mass of about 10 μ g were pressed between tiny aluminum discs; these served to encapsulate the californium, and the aluminum acted as an internal standard for pressure calibration through compression of its lattice.

Californium metal in the expanded face-centered cubic form,³ valence two, was used as the starting sample because it was expected to transform under pressure to the collapsed form having valence three. No such transformation was observed to occur, however, with the pressure applied in each case for about a week at room temperature. A contraction of

the cubic lattice volume of about 8% at 140 kbars was measured, and from this a preliminary estimate of the compressibility of californium metal was obtained. On release of the pressure, the lattice parameter returned to its original value.

Similar measurements are being made using trivalent californium metal as the starting material.

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4.4 ENERGY-DISPERSIVE X-RAY DIFFRACTION STUDIES OF TRANSURANIUM ELEMENTS

J. H. Burns C. E. Bemis

Experiments were carried out to test the feasibility of employing energy-dispersive x-ray diffraction in studies of highly radioactive samples having masses of only a few micrograms. The goal is to obtain crystal-structure data from einsteinium compounds in times short relative to those in which radiation damage to the sample or blackening of photographic films have been limiting factors.

In applying the energy-dispersive method, the tiny sample is irradiated with polychromatic x rays, and the diffraction is measured at a single, well-defined angle using a Si(Li) detector. The x rays (and gamma rays, if any) entering the counter are recorded by a multichannel pulse-height analyzer, and the intensities are displayed as a function of energy. In the patterns thus obtained are (1) maxima corresponding to characteristic x rays used in irradiating the sample, e.g., MoK α , (2) fluorescent x rays from elements in the sample, (3) possibly gamma rays, and (4) the x-ray diffraction maxima. These diffraction lines can be sorted out and translated, by use of Bragg's Law, into interplanar spacings of the crystalline sample.

Samples of thorium oxide, curium bromide, and californium metal have been examined by us using this method, and diffraction patterns were obtained using quantities as low as ten micrograms. Improvements in the equipment and technique are underway to increase the sensitivity enough to allow the study of einsteinium compounds.

X
no
data

4.5 RECENT WORK ON THE TRANSCURIUM ELEMENT-OXYGEN SYSTEMS

R. G. Haire

Studies on oxide systems of the transcurium elements have continued. Some of the oxide work was part of a collaborative study with Battelle Pacific Northwest Laboratories, Richland, Washington. Since einsteinium is the highest member of the actinide series expected to be available in microgram quantities in the foreseeable future, the einsteinium-oxygen system will be the last series studied.

Manometric and x-ray diffraction work has been completed on the californium-oxygen system for $1.7 > \text{oxygen/californium} > 1.5$.^{1,2} In that study, rhombohedral Cf_7O_{12} was prepared, and oxygen overpressure isotherms and x-ray data were obtained for the metal oxides between Cf_2O_3 and Cf_7O_{12} . Subsequent work on the californium-oxygen system has dealt with oxides between Cf_7O_{12} and CfO_2 ; the latter is thermally unstable, with its stepwise decomposition beginning at about 300°C in air.

Recent studies on the berkelium-oxygen system were aimed at correlating oxygen-to-metal ratios obtained by manometric measurements with oxide crystal structures and lattice parameters between Bk_2O_3 and BkO_2 . Efforts to prepare Bk_7O_{12} have been unsuccessful. This compound would have had significance because the expected rhombohedral structure would have provided an independent check on stoichiometry, since this structure exists over a narrow composition range. Thus, only bcc and fcc structures were observed for a number of oxide compositions from Bk_2O_3 to BkO_2 .

Due to the half-lives of ^{249}Bk and its ^{249}Cf daughter, mixtures of these two elements are often encountered, and the behavior of the californium in different berkelium-californium oxides was investigated as a function of metal composition. Up to californium contents of about 35 mole %, the californium is oxidized to the dioxide in air atmospheres, although under the same conditions pure californium yields Cf_7O_{12} . Mixtures containing greater amounts of californium are being investigated.

The effects of self-irradiation of berkelium and californium oxides as a function of time have been studied by x-ray diffraction. With Cf_2O_3 in vacuum, a classical type of lattice expansion with dose was observed, with the maximum expansion being similar to that reported for lattice expansions in PuO_2 and Cm_2O_3 . Self-irradiation of CfO_2 can bring about a

loss of oxygen (reduction) and/or lattice expansion; the net effect of these two processes is dependent on both sample size and atmosphere. The effect of self-irradiation on berkelium oxides from its beta emission is smaller but becomes complicated by the moderately rapid (about 5% per month) ingrowth of the californium daughter in the berkelium oxide.

Efforts were also made to gather more information on the einsteinium-oxygen system. Previously, only the bcc form of Es_2O_3 was known from electron diffraction work; it was stable up to 1000°C .³ Based on an ionic radii comparison with the lanthanide elements, a monoclinic and perhaps a hexagonal form of Es_2O_3 should exist. Higher oxides of einsteinium are not expected based on estimated oxidation potentials. Electron diffraction evidence for both of these crystal modifications has been obtained, but the structures were formed from self-irradiation rather than by high temperature treatment. Modification of the crystal structure of $^{244}\text{Cm}_2\text{O}_3$ by self-irradiation has been reported in the literature.⁴

The melting point of Es_2O_3 has been measured to be $1650 \pm 50^\circ\text{C}$, which agrees with a value extrapolated from the melting points of Bk_2O_3 and Cf_2O_3 . The melting point of Cf_2O_3 was remeasured by this technique; the value of 1730°C is identical within the experimental limits to the previously reported value.⁵ The melting points of Bk_2O_3 , Cf_2O_3 , and Es_2O_3 do not follow the trend shown by the heavier lanthanides, which increase rather than decrease across the second half of the series.

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4.6 CRYSTAL STRUCTURE OF BARIUM NEPTUNYL(V) TRIACETATE DIHYDRATE

J. H. Burns C. Musikas¹

This acetate complex was one of several compounds^{2,3} studied to evaluate the effect of various factors on the strength of $\text{Np}=\text{O}$ bonds in neptunyl ions. By measuring the bond lengths of NpO_2^+ and NpO_2^{2+} ions in nearly identical crystalline environments, the effect of changing

valence from Np(V) to Np(VI) can be assessed. Crystals of $\text{BaNpO}_2(\text{CH}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$ were grown from concentrated acetate solution containing Ba^{2+} and NpO_2^+ , and the structure was determined from x-ray diffraction data.

Linear NpO_2^+ entities present in the crystal have six oxygen atoms from three acetate ions in a planar hexagon around their equator. These hexagonal bipyramids are cross-linked by sharing their acetate oxygen atoms with Ba^{2+} ions, each of which has six oxygen atoms from different acetate ions and two H_2O molecules in its coordination polyhedron. The oxygen atoms of the NpO_2^+ ion are unshared, and the $\text{Np}=\text{O}$ bond lengths are $1.85(2)$ Å. A comparison with the bonds in the NpO_2^{2+} ion can be made by considering the structure of $\text{NaNpO}_2(\text{CH}_3\text{CO}_2)_3$, in which the neptunyl ion has the same equatorial ligand

and a very similar configuration.⁴ These structures are illustrated in Fig. 4.6. In the latter case the $\text{Np}=\text{O}$ bond length is $1.71(4)$ Å. The $\text{Np}=\text{O}$ bond is weaker in NpO_2^+ than in NpO_2^{2+} as indicated by a bond length change of 0.14 Å, caused by the addition of a nonbonding electron in NpO_2^+ .

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Fig. 4.6. Stereoscopic drawing of the environment of the NpO_2^+ ion in $\text{BaNpO}_2(\text{CH}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$ (above) and the NpO_2^{2+} ion in $\text{NaNpO}_2(\text{CH}_3\text{CO}_2)_3$ (below).

4.7 METHOD FOR THE RAPID CHEMICAL SEPARATION AND STUDY OF ELEMENTS 104 AND 105

R. J. Silva G. D. O'Kelley
J. R. Tarrant

All available evidence supports the idea that elements 104 and 105 should fall into the groups IVB and VB of the chemical periodic system.¹ From extrapolations of the trends in the chemical properties of the other elements in these groups and from interpretations of the relativistic Hartree-Fock calculations, element 104 is expected to exhibit chemical behavior similar to that of hafnium and zirconium, and 105 is expected to be similar to tantalum and niobium.¹ Thus, one can obtain information on the chemical properties of elements 104 and 105 by comparing their behavior with the homolog elements in chemical separations.

The longest-lived isotopes of these heavy elements are $^{261}\text{104}$ and $^{262}\text{105}$ with half-lives of about 70 and 40 sec respectively. About 5 atoms/hr of $^{261}\text{104}$ and about 2 atoms/hr of $^{262}\text{105}$ can be produced at the Oak Ridge Isochronous Cyclotron by bombarding ^{248}Cm and ^{249}Bk , respectively, with ^{18}O ions. Because of these restrictions, any separation scheme for studying these elements must be specific for one atom at a time, require only about 1 min, and be amenable to a repetitive series of experiments that may extend over several days. Separations based on ion exchange column techniques satisfy these requirements.

The cations of niobium and tantalum are unstable in acid solution without the presence of complex-forming anions. Fluoride complexes these elements strongly and has been used extensively in niobium and tantalum separations.² Fluoride ions produce soluble complexes of hafnium and zirconium but insoluble compounds with the trivalent actinides. Further, zirconium forms positively and negatively charged complex ions with fluoride, depending on the HF concentration.³ We have developed a separation scheme for 104 and 105 based on these charge changes and differences, using solvent extraction chromatography with a cation exchanger as the organic phase.

We measured distribution coefficients for tracer quantities of ^{181}Hf and ^{182}Ta , using HF solutions as the aqueous phase and the cation exchanger HDEHP or the anion exchanger aliquot 336 as the organic phase. From these data, one can determine the charge on the complex ions formed under various

concentration conditions. For example, tantalum forms a complex ion in 0.01 M HF solutions that is extracted primarily into the anion exchanger, while Hf is extracted primarily into the cation exchanger. Both elements are extracted chiefly into the anion exchanger from 0.1 M HF solutions. Therefore, hafnium and zirconium in 0.01 M HF would be expected to be retained by a cation exchange column, while niobium and tantalum should pass through the same column. Subsequently, hafnium and zirconium could be stripped from the column with 0.1 M HF. Figure 4.7 shows the separation of niobium from zirconium, and hafnium from tantalum, using this scheme. The cation exchange column was 2 mm in diameter and 1 cm long. The stationary organic phase was 0.01 f HDEHP in benzene absorbed onto the inert support Bioglass. Separations, accomplished in about 1 min, yielded 80 to 90% recovery of the niobium and tantalum but only about 50 to 60% recovery of the zirconium and hafnium due to tailing from the column.

An automatic system under construction will carry out all the steps necessary for the separation using mechanical devices. This will involve sample dissolution, cation exchange column manipulations, sample drying, and sample counting. The entire

Fig. 4.7. Separation of ^{95}Nb from ^{95}Zr , and ^{182}Ta from ^{181}Hf tracers, via solvent extraction chromatography. The stationary organic phase was 0.01 f HDEHP in benzene, and the mobile aqueous phase was hydrofluoric acid.

process will be controlled by a Hewlett-Packard 9820 programmable calculator.

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4.8. RADIOLUMINESCENCE SPECTRA OF EINSTEINIUM COMPOUNDS¹

J. P. Young² R. L. Fellows³
R. G. Haire J. R. Peterson⁴

The radioluminescence spectra of solid-state einsteinium compounds can be studied using a microscope-spectrophotometer. A complete characterization of the origins of these emissions will require much research, but we have made advances in our understanding of these origins. The emissions appear to be impurity sensitized. What are believed to be carefully purified einsteinium compounds often exhibit no radioluminescence. Doping einsteinium starting material with Ca^{2+} , La^{3+} , Eu^{3+} , Sm^{3+} , or Yb^{3+} consistently yields halide products that exhibit radioluminescence. Hydrogen-reduced lanthanum-einsteinium bromide has a radioluminescence spectrum different from the starting tribromide, indicating that reduction has occurred.

One sample of Es_2O_3 radioluminesced strongly when the argon gas overpressure was less than 100 torr. This effect probably relates to some form of nonradiative energy transfer that is enhanced in the presence of a sufficient quantity of gas. Although the radioluminescence of einsteinium compounds is impurity sensitized, the spectral peaks appear to arise from both Es^{3+} and daughter Bk^{3+} energy levels. From studies of the effect of elevated temperature on individual emission bands in the spectrum, it appears that some of the excited levels, particularly in Bk^{3+} , are quite isolated and are therefore relatively unquenched by heating the solid-state compound.

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4.9. SELF-LUMINESCENCE OF SEVERAL FLUORITE-STRUCTURE HALIDES DOPED WITH CURIUM OR BERKELIUM¹

C. B. Finch² R. L. Fellows³
J. P. Young⁴

The self-luminescence emission spectra of several fluorite-structure halides doped with 0.1 cation % ^{244}Cm or ^{249}Bk were measured in the wavelength range 200 to 700 nm at 298 to 600 K. The hosts included CaF_2 , SrF_2 , BaF_2 , and SrCl_2 for curium, and BaF_2 and SrCl_2 for berkelium. The room-temperature spectra of the curium-doped fluorites have relatively sharp peaks ($\text{FWHM} \approx 1 \times 10^5 \text{ m}^{-1}$) at approximately 600 nm, and broad bands ($\text{FWHM} \approx 6 \times 10^5 \text{ m}^{-1}$) with maxima at 300 nm for the fluorides and 400 nm for SrCl_2 . The 600-nm peaks appear to be associated with the curium dopant, and they remain unquenched at 600 K. The 300- and 400-nm bands are attributable to host anion centers and disappear on sample heating from room temperature to 500 K. The room-temperature spectrum of berkelium-doped BaF_2 displays only the anion-related band at 300 nm, while that of berkelium-doped SrCl_2 has both an anion band at 400 nm and a peak at 520 nm, also believed to be a host or host impurity effect. The luminescence intensity of all the hosts decreases during room-temperature storage but can be partially restored by annealing at 600 to 1000 K. Annealing is accompanied by strong thermoluminescence and optical bleaching.

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4.10 X-RAY TRANSITION AND ELECTRON BINDING ENERGIES IN URANIUM AND NEPTUNIUM

M. O. Krause C. W. Nestor, Jr.¹

Transition energies of the major M x rays of uranium and neptunium and electron binding energies of the M and N levels of uranium metal, uranium oxide, and neptunium oxides have been measured with an electron spectrometer, and as a complement these energies have been calculated in the Dirac-Fock (DF) formalism with Desclaux'

program that we recently established at ORNL.^{2,3} At an accuracy of about 0.1 eV, which we achieved in the experiment, the data can serve as a proving ground for this rather sophisticated theoretical formalism. This is possible because higher-order corrections arising from quantum electrodynamic effects, although of nearly the same relative importance for any electron level of the atom, are less than 0.1 eV for the *M* and *N* levels in the actinide region. These effects may amount to 100 eV in the innermost shells. Quantum-electrodynamic effects may be revealed in experiments dealing with the outermost shells of free atoms, since the experimental sensitivity obtainable would be of the same order as the effects. In Tables 4.1 and 4.2, some of the transitions and levels studied

Table 4.1. Experimental and theoretical transition energies (eV) in uranium and neptunium and the difference $\Delta E = E(\text{DF}) - E(\text{expt})$

Level	Line	Expt	DF ^a	ΔE
<i>M₅N₇α₁</i>	U	3171.4(1)	3174.0	2.6
	Np	3260.7(1)	3263.2	2.5
<i>M₄N₆β₁</i>	U	3336.7(1)	3338.3	1.6
	Np	3434.2(2)	3435.8	1.6
<i>M₄N₂ζ₂</i>	U	2455.7(3)	2446.6	-9.1
	Np	2521.6(1.2)	2513.6	-8.0

^aFree-atom values.

Table 4.2. Electron binding energies (eV) in uranium and neptunium

Level	Line	Expt ^a	DF ^b	ΔE^c
<i>M₄ (3d_{3/2})</i>	U	3724.9(3)	3434.8	9.9
	U	3727.4(4)	3734.8	7.4
	Np	3848.5(7)	3857.0	8.5
<i>M₅ (3d_{5/2})</i>	U	3548.8(3)	3559.3	10.5
	U	3551.3(4)	3559.3	8.0
	Np	3663.4(6)	3671.9	8.5
<i>N₂ (4p_{1/2})</i>	U	1269.2(5)	1288.2	19.0
	U	1271.7(8)	1288.2	16.5
	Np	1326.9(1.4)	1343.4	16.5
<i>N₇ (4f_{7/2})</i>	U	377.4(2)	385.3	7.9
	U	380.0(4)	385.3	5.3
	Np	402.6(4)	408.7	6.1

^aFirst uranium entry is for the metal; second entry and neptunium values are for the oxides.

^bFree-atom values.

^c $\Delta E = E(\text{DF}) - E(\text{expt})$.

are displayed. Except for the *N₂* and *N₃* levels the DF predictions obtained from differences of configuration-average total energies lie within about 2 eV of the experimental values, if the data of the metals and oxides are converted to free-atom data by subtraction of 5 to 7 eV. This conversion is accomplished automatically by a measurement of the transition energies (see Table 4.1). The 2-eV residual can presumably be accounted for by abandoning the single-particle model and including many-body effects as demonstrated recently for the *K* shell of neon.⁴ In the case of the *N_{2,3}* subshells the discrepancy of 10 eV between experiment and theory has not been recognized although it occurs in other heavy elements and for other *p* electrons. We suspect that interactions between the hole in the 4*p* level and the open shell configurations of the 5*f* and 6*d* levels may be responsible for this large energy shift. Strong effects have been observed for the 5*p* level, which is in closer proximity to the 5*f* and 6*d* shells. We hope to pinpoint the origin of this discrepancy, by using the multiconfiguration Dirac-Fock model.

1. Computer Sciences Division.
2. O. Keski-Rahkonen and M. O. Krause, *Phys. Rev. A* 15, 959 (1977).
3. M. O. Krause, C. W. Nestor, Jr., and J. H. Oliver, *Phys. Rev. A* June/July issue (1977).
4. H. P. Kelly, *Phys. Rev. A* 11, 556 (1975).

4.11 TEST OF INTERMEDIATE COUPLING

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M. Frilley ¹	S. Shafrath ²
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In the medium-*Z* range of the periodic chart, neither the *L-S* coupling scheme, which is an excellent approximation at low *Z*, nor the *j-j* coupling scheme, which is generally a good description at very high *Z*, is satisfactory in describing the electron interactions. Evidently, some intermediate coupling in which the various states of the same symmetry, contributing to the same *J* value, are allowed to mix is appropriate. However, the details of the transition region between pure *L-S* and pure *j-j* coupling have not yet been delineated.

In this work^(4,5) the intermediate coupling scheme was probed for the inner shells of the atoms for $26 \leq Z \leq 80$ by measuring the intensity ratio of the *Kα₁* to *Kα₂* hypersatellites. Consider Fig. 4.8: The initial

Fig. 4.8. Radiative decay scheme for an atom with both K electrons missing. Initial and final states are characterized in the L - S and j - j coupling scheme and by their parity.

state is 1S with $J=0$ and both K electrons missing; the final state is a $J=1$ state, namely $K^{-1}L_2^{-1}(^1P)$ if a $K\alpha_2^h$ ($K\alpha_2$ hypersatellite) transition has taken place, and $K^{-1}L_3^{-1}(^3P)$ if a $K\alpha_1^h$ x ray has been emitted. In L - S coupling, only $K\alpha_2^h$ is allowed, $K\alpha_1^h$ being a so-called intercombination line; in j - j coupling, both $K\alpha_1^h$ and $K\alpha_2^h$ are allowed, since $\Delta J=1$, and their intensities are expected to correspond to the statistical 2:1 ratio. In intermediate coupling the 1P and 3P wave functions belonging to $J=1$ can mix, and, as a consequence, both hypersatellites may occur with intensities determined by the mixing coefficients. As experiments carried out for Fe, Cu, In, and Hg have shown,^{4,5} the mixing or configuration interaction is weak for elements with $Z \lesssim 30$ and strong for $Z \gtrsim 60$. In fact, for iron and copper the $K\alpha_1^h$ line is barely discernible, but for mercury this line is nearly twice the strength of the $K\alpha_2^h$ line, as shown in the well-known diagram of $K\alpha_1$ and $K\alpha_2$ x rays.

Figure 4.9 shows a plot of the theoretical predictions obtained in an intermediate coupling calculation.^{5,6} Agreement between experiment and

Fig. 4.9. Variation of the intensity ratio of the $K\alpha$ hypersatellite lines originating from an atom doubly ionized in the K shell. Curve indicates the theoretical prediction. (Source: T. Åberg, unpublished.)

theory is good, showing how intermediate coupling provides a gradual transition between extreme L - S and j - j coupling.

Only the electrical dipole transitions were considered in this work. Transitions to the $K^{-1}L_2^{-1}$ and $K^{-1}L_3^{-1}$ final states are allowed, but none to the $K^{-1}L_1^{-1}$ state.

1. Laboratoire Curie, Institut du Radium, Paris, France.
2. University of North Carolina, Chapel Hill.
3. Technical University of Helsinki, Finland.
4. J. P. Briand, A. Touati, M. Frilley, P. Chevallier, A. Johnson, J. P. Rozet, M. Tavernier, S. Schafroth, and M. O. Krause, "The Structure of $K\alpha$ Hypersatellite Spectra of Cu, Ni, and Fe as a Test of Intermediate Coupling," *J. Phys. B* **9**, 1055 (1976).
5. J. P. Briand, A. Touati, M. Frilley, P. Chevallier, A. Johnson, J. P. Rozet, M. Tavernier, S. Schafroth, M. O. Krause, and T. Åberg, "The Structure of $K\alpha$ Hypersatellite Spectra: A Test of Intermediate Coupling," *Abstr. Contrib. Pap., 2d Int. Conf. Inner Shell Ionization Phenomena*, March 29-April 2, 1976, Freiburg, Germany.
6. T. Åberg, unpublished data.

4.12 SUPERCONDUCTING QUANTUM INTERFERENCE DEVICE (SQUID) FOR THE DETERMINATION OF MAGNETIC SUSCEPTIBILITY OF ACTINIDE MATERIALS¹

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S. E. Nave²

In the past year we have constructed a sensitive micromagnetic susceptibility apparatus and have independently tested each of the components. The overall system sensitivity and noise levels are being determined. A cross-sectional diagram of the low-temperature section of this apparatus is shown in Fig. 4.10. The crosshatched areas of this diagram remain immersed in a liquid-helium Dewar, and asymmetric pickup coils are located in the geometric center of a 55-kG superconducting magnet. The outer stainless steel tube removes or inserts the temperature sensors and heater, which are thermally connected to the copper ballast. Thermometers of several varieties are used: (1) a germanium resistance probe, (2) a platinum resistance probe, (3) a carbon resistance probe, and (4) two Chromel-Alumel thermocouples. Temperature stability is maintained by a Scientific Instruments cryogenic controller. Samples are held in a 0.025-in.-OD gold tube that is encased in a 0.053-in.-OD quartz tube. The gold tube is held firmly by a copper chuck that contacts the copper ballast. The chuck, gold tube, and sample may be independently positioned or removed from the copper ballast through a vacuum interlock for sample exchange. Two 0.0625-in.-ID, 50-turn, asymmetric superconducting coils detect the magnetic flux difference when the sample is moved from one coil to the other in the presence of a large external magnetic field. Approximately 9% of the flux change is coupled into a SQUID (superconducting quantum interference device) element through another superconducting coil in series with the asymmetric pair. The sensitivity

of the SQUID element is about $10^{-3} \phi_0$, where $\phi_0 =$ one flux quantum $= 2 \times 10^{-7} \text{ G} \cdot \text{cm}^2$. If external noise does not reduce system sensitivity, the typical error in magnetic susceptibility for a 1- μg actinide sample should be

$$\Delta\chi = \pm 6.75 \times 10^{-11} \text{ cm}^3/\text{g}.$$

For a paramagnetic system

$$\chi = (N_0\rho/M)(n^2\mu_B^2/3kT),$$

where $n =$ the number of Bohr magnetons per atom. If we assume for a typical actinide that $\rho = 20 \text{ g/cm}^3$ and $M = 250 \text{ g/g-mole}$,

$$\chi = 150 \times 10^{-6} \text{ cm}^3/\text{g}$$

for $n = 1$ Bohr magneton per atom at 4.2K. This leads to a system detectability

$$\Delta\chi/\chi \sim 4.5 \times 10^{-6}/n^2$$

for samples of actinides produced in microgram quantities.

This is an enormous increase in sensitivity over that obtained by Fujita.³ For a 1- μg sample of californium (with $n \sim 9$), Fujita obtained a sensitivity of $\Delta\chi/\chi \sim 0.1$. Our device is designed to be about 10^6 times more sensitive and should facilitate the study of picogram quantities in the future.

1. Supported in part by ERDA contract E-(40-1)-4447 with the University of Tennessee, Knoxville.

2. Physics Department, University of Tennessee, Knoxville.

3. D. K. Fujita, *Some Magnetic, Spectroscopic, and Crystallographic Properties of Berkelium, Californium, and Einsteinium*, UCRL-19507 (1969), pp. 1-175.

ORNL-DWG. 77-8213

Fig 4.10. Low-temperature magnetic susceptibility apparatus for microgram quantities of the actinides through SQUID measurements.

5. Separations Chemistry

5.1 SPECTROPHOTOMETRIC STUDIES OF SOLUTIONS CONTAINING RADIOACTIVE MATERIALS

5.1.1 Photochemistry of Aqueous Uranium and Plutonium Solutions

L. M. Toth M. M. Osborne
H. A. Friedman J. T. Bell

The effect of visible ultraviolet radiation on aqueous plutonium and uranium solutions has been investigated as part of a continuing program in actinide photochemistry. Although many of the aqueous redox equilibria have been previously well characterized, little attention has been directed at the photochemistry of these ions. Aside from fundamental considerations, photochemical studies of the actinides are important in nuclear fuel reprocessing, in nuclear waste management, and in environmental control.

Infrared spectra of the plutonium(IV) polymer formed during hydrolysis of plutonium(IV) in aqueous solution have been measured in an effort to relate changes in bonding to the polymer aging process. The polymers were prepared and aged in aqueous inorganic acid solutions, precipitated by the addition of NaOH, and dispersed in KBr or Nujol mulls for spectral measurements from 200 to 4000

cm^{-1} . Surprisingly, the plutonium(IV) polymer was found to have a high affinity for atmospheric CO_2 , absorbing it during routine handling procedures with the accompanying formation of CO_3^{2-} ligands. Figure 5.1 shows a typical spectrum of plutonium(IV) polymer that had been handled (A) solely in an N_2 glove bag and (B) in the laboratory atmosphere. The strong bands at 1350 and 1500 cm^{-1} in Fig. 5.1B have been assigned to the separate components of the degenerate ν_3 vibrational mode of CO_3^{2-} . The weaker band at 850 cm^{-1} is assigned to the $\nu_2(\text{CO}_3^{2-})$ mode. It was shown that CO_3^{2-} could easily be mistaken for the structurally analogous NO_3^- ion on the basis of infrared measurements also and probably has resulted in the misinterpretation of thorium(IV)-polymer infrared spectra.

Aging of the polymer produced measurable changes in the 1000 cm^{-1} region, where a sharp band at 1010 cm^{-1} was found to decrease in intensity, while a broad band centered at 950 cm^{-1} grew in. Although these two bands were not assigned in this study, their presence supported the contention that aging effects involve chemical as well as physical changes.

Photoredox studies involving PuO_2^{2+} and Pu^{4+} were extended to include the effect of formic acid and hydrazine as reductants. In general, the photoreduction of PuO_2^{2+} can be written as

Fig. 5.1. Infrared spectrum of plutonium(IV) polymer (A) prepared in inert atmosphere and (B) prepared in laboratory air.

where R is the reductant, and R_{ox}^+ is the corresponding by-product. The photochemical reduction of Pu^{4+} , using the above reductants, was investigated and generally can be written as

Using these fundamental reactions, we have shown experimentally that 300-nm light increases the rate of hydrazine reduction of Pu^{4+} to Pu^{3+} by a non-optimized factor of 6. We have also shown that the same ultraviolet light of 1-W intensity increases the Pu-U separation factor of plutonium by at least a factor of 18 when a 1.4 M HNO_3 solution containing 3.7 mM Pu^{4+} , 4.7 mM UO_2^{2+} , and 0.5 M hydrazine nitrate was exposed for 30 min and then contacted with a 30% TBP-dodecane solution. These data are shown in Table 5.1. A patent application for this process has been filed. These data strongly encourage further consideration of photoredox schemes as alternate procedures in the Purex process being considered for the reprocessing of spent LWR and LMFBF fuels.

Table 5.1. Effect of light on the reductive extraction of Pu^{4+} from TBP into aqueous nitric acid-hydrazine solution

	Dark sample (After 1.5 hr)	Light sample (0.5 hr light exposure followed by 1.0 hr in dark)
Aqueous layer	33% Pu^{3+} 3% U	90% Pu^{3+} 3% U
TBP layer	67% Pu^{4+} 97% U	10% Pu^{4+} 97% U

5.1.2 Chemistry of Fission Products in Refrigerant-12 Media

L. M. Toth D. W. Fuller

The work concerned with the development of processes for LMFBF fuels is not reported here this year in compliance with regulations which stipulate that such information must be distributed solely under the category UC-79—Liquid-Metal Fast Breeder Reactors. The results of our studies have been summarized in the LMFBF Reprocessing Program quarterly progress reports for periods Jan. 1 to Mar. 31, 1976, ORNL/TM-5463; Apr. 1 to June 30, 1976, ORNL/TM-5556; July 1 to Sept. 30, 1976, ORNL/TM-5668; and Oct. 1 to Dec. 31, 1976, ORNL/TM-5768.

The associated effort in LWR fuel reprocessing is being reported separately in a series of quarterly progress reports. The results of the investigations carried out during this report period have been summarized in the LWR Fuel Reprocessing and Recycle Program quarterly reports for periods Jan. 1 to Mar. 31, 1976, ORNL/TM-5447; Apr. 1 to June 30, 1976, ORNL/TM-5547; July 1 to Sept. 30, 1976, ORNL/TM-5660; Oct. 1 to Dec. 31, 1976, ORNL/TM-5760; and in similar reports.

5.2 CHROMATOGRAPHIC STUDIES OF HYDROMETALLURGICAL SEPARATIONS

F. J. Hurst

The increasing need for pure zirconium and pure hafnium in the nuclear industry has created renewed interest in their separation and recovery. Of many methods developed, only two have been used on an industrial scale: the hexone-thiocyanate system and the tributylphosphate-nitric acid system. Both of these solvent extraction processes suffer disadvantages such as solvent degradation, excessive corrosion, and solids formation that interfere with continuous operation. The purpose of this study is to determine the feasibility of high-pressure ion exchange techniques, such as those described previously to separate cobalt and nickel,¹ to define and effect this separation. Previous work² has shown that a sulfuric acid treatment is the most economical way to dissolve the reaction product obtained after opening up the zircon sand feed with caustic. Electromigration and cation exchange experiments have shown that cationic species, present at low concentrations of H_2SO_4 , are converted to anionic and uncharged species at high acid concentrations. In addition, the complex-forming tendencies of the zirconium and hafnium ions are quite different in the sulfate system, and the minor constituent (hafnium) is more strongly held by cation exchange resins, a situation which makes commercial-scale separation more practical.

In our study, the eluted metal ions were detected continuously by the formation of fluorescent complexes with a fluorogenic reagent (morin) which was mixed with the column stream as it exited from the ion exchange column. Since morin is not specific for either metal ion, identifications of the peaks were made using the stable isotopes ^{90}Zr and ^{180}Hf . Distribution ratios for zirconium and hafnium calculated from retention volumes obtained by eluting samples, prepared in a number of ways, from 15- to 25- μ Dowex 50W-X8 resin with sulfuric acid

Fig. 5.2. Effect of H_2SO_4 concentration on sorption of zirconium and hafnium complexes by Dowex 50W-X8 resin.

solutions decreased sharply as the acid concentration was increased from 0.5 to 3 N (Fig. 5.2). At the lowest acid concentration tested (0.5 M), only one zirconium and one hafnium species were observed. However, as the acid concentration was increased, two zirconium complexes emerged. Depending on the method of preparation, either one or the other species was present, and under some conditions both species were present: One decreased with the same slope as the hafnium; the other decreased less sharply, decreasing the separation factor from 9 to 4.5 over the range tested.

1. F. J. Hurst, "Separation of Cobalt from Nickel in Ammonia-Ammonium Carbonate Solutions Using Pressurized Ion Exchange," *Hydrometallurgy* 1, 319-38 (1976).

2. B. A. J. Lister and L. A. McDonald, "Some Aspects of the Solution Chemistry of Zirconium," *J. Chem. Soc.*, pp. 4315-30, 1952.

5.3 RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID

W. D. Arnold

Octylphenyl acid phosphate (OPAP) is a commercially available mixture of mono-octylphenyl phosphoric acid (MOPPA) and dioctylphenyl phosphoric acid (DOPPA) that is being evaluated as an extractant for recovering uranium from wet-process phosphoric acid. The reagent also contains neutral and acidic impurities that affect its performance. Tests were continued to determine the composition of the commercial reagent and to measure its long-term stability and uranium extraction performance.

Hydrolysis of a commercial OPAP sample by gently refluxing with water (1 ml/g of OPAP) resulted in loss of about 20% of the titratable fraction of the reagent (Fig. 5.3). In subsequent treatments of the hydrolyzed material, the DOPPA concentration did not change, but the MOPPA concentration continued to decrease at a slower rate. The major hydrolysis product in the aqueous phase was orthophosphoric acid, probably formed by the decomposition of complex phosphates containing P-O-P bonds. In the later contacts, the aqueous samples contained both MOPPA and H_3PO_4 , suggesting a combination of dissolution and hydrolysis. The nonacidic (nontitrating) fraction of the OPAP increased with succeeding hydrolyses from

Fig. 5.3. Effect of hydrolysis on OPAP composition. Commercial OPAP sample hydrolyzed successively by gentle reflux with water (1 ml of H_2O per g of OPAP) for 20 hr.

essentially none in the starting material to 18% after the first hydrolysis and to 27% after the fifth. We are trying to identify this material by liquid chromatographic techniques and are also working with the producer to reduce the readily hydrolyzable fraction of the reagent. Extraction tests with the hydrolyzed material showed that uranium extraction decreased slightly with increasing hydrolyses and that iron extraction was essentially unaffected.

A continuous countercurrent cyclic test designed to study the long-term stability and uranium extraction performance of OPAP was completed with moderate loss of uranium extraction capability, probably caused by partial crystallization and/or poisoning of the extractant. The system contained two extraction stages and two stripping stages. Flow rates were 5 ml/min for the organic (0.3 *M* twice-hydrolyzed OPAP in Kermac 470B), 20 ml/min for the acid feed (wet-process green acid containing 0.17 g of U/liter and 5.8 *M* H_3PO_4), and 0.25 ml/min for the strip solution (10 *M* H_3PO_4 containing NaClO_3 to oxidize and strip the uranium). The system operated continuously for more than 440 hr with excellent physical performance. It operated essentially unattended at night and on weekends and required no additions of organic after start-up. Based on clarity and appearance of the organic, phase separation improved as the run progressed. Some solids accumulated at the extraction settler interfaces but did not interfere with operation. During the period between roughly 150 and 250 hr of operation, a crystalline yellow solid deposited on the extraction settler walls above the organic-aqueous interfaces and in the organic lines. This material also did not interfere with operation and appeared to stop forming after about 250 hr.

The composition of the organic changed differently during the test than would be predicted on the basis of earlier batch solubility loss measurements;¹ the DOPPA concentration decreased, and the MOPPA concentration did not change. Most of the concentration change occurred during the period that the crystalline material was being deposited on the settler walls, a finding which suggests that the crystals contained part of the reagent. Analysis of the crystals is not complete, but we have determined that the major components are carbon, hydrogen, and phosphorous, and that they contain phosphoric acid and iron. The DOPPA concentration decreased during the test from 0.188 *M* to 0.115 *M*, equivalent to almost 40% of the initial concentration. The DOPPA:MOPPA ratio decreased from an initial value of 1.6:1 to approximately 1:1 after about 250 hr,

and then both the concentrations and the ratio were essentially unchanged for the remainder of the test.

In order to minimize the organic inventory, the time required for a cycle of the organic, and the volume of feed acid required, the system contained an insufficient number of extraction stages for complete uranium recovery, and only about 75% recovery was expected. Based on feed and raffinate analyses, the recovery was about 70% in the early part of the test and decreased to about 50% at the end. The analyses indicate a steady decrease in recovery throughout the test and do not show any abrupt change during the period that the DOPPA concentration was changing. Batch extraction tests with organic removed from the system do indicate more decrease during this period, but it is less pronounced than the change in DOPPA concentrations. The organic darkened in color during the test, and the color cannot be removed by scrubbing the organic with acids or with bases. This darkening suggests poisoning of the organic with material extracted from the acid, and such poisoning could account for both the decreased uranium recovery and the apparent loss of DOPPA concentration. We are not able to say at this point whether the decrease in uranium recovery was caused by reagent loss, reagent poisoning, or a combination of the two. We are making tests to determine which is the cause and to determine whether the nonacidic fraction of the hydrolyzed reagent is involved. Other areas of investigation include the separation and identification of reagent components by liquid chromatographic techniques, measurement of reagent solubility in process diluents, and the separation of purified fractions of MOPPA and DOPPA fractions from the OPAP mixture. Work is planned on the evaluation of oxidants for uranium valence control in the stripping system and on the development of methods for removing organic matter (humus) from phosphoric acid before uranium recovery.

1. *Chem. Div. Annu. Prog. Rep. Nov. 1, 1975*, ORNL-5111, p. 55.

5.4 DETERMINATION OF RADON EMANATION COEFFICIENTS IN URANIUM MILL TAILINGS

F. J. Hurst

A problem of growing national concern is the emanation of radon gas from western uranium mill tailings. At present, most of these ores are processed

with sulfuric acid, although a few high-lime ores are treated with sodium carbonate for economic reasons. In either case, most of the radium remains with the waste tailings and is the source of radon emanation and its daughters. We have recently completed a study, in conjunction with the Chemical Technology Division, to determine the effectiveness of nitric acid for treating these ores. Our aim is to leach essentially all of the radionuclides (U, Ra, Th, Po, and Pb) from the ore so that the waste tailings will be less hazardous.

Our major part in this program was to determine radon emanation coefficients (i.e., the ratio of radon escape to radon production in the sand grains) from representative samples of uranium ores and tailings from the major mining districts of the United States. To accomplish this goal, we adopted existing emanation techniques to better fit our needs.

Emanation coefficients measured for five ore feed samples ranged from 9 to 35% and averaged 24%. After treatment with sulfuric acid, emanation coefficients were significantly lower and varied over a narrower range, 9 to 17%, averaging 12%; emanation coefficients from alkaline-leached tailings were higher than those obtained before leaching, ranging from 14 to 45% and averaging 30%. Even after essentially all of the leachable radium (88 to 99%) was removed from the ore feed and tailings samples by treatment with nitric acid, the residues continued to emanate radon. Although the percentage of radon emanating varies over a rather wide range, from 8 to 43%, the total amount emanating is rather small (0.02 to 0.12 pCi of radon per hr per g of residue) and represents a substantial reduction (90% or better) from that emanating from the sulfate tailings.

An interesting sidelight of the study was the discovery of "hot" sand grains in the HNO₃-leached residues. After exhaustive leaching of the samples with nitric acid, the radium concentration in the residue ranged from 15 to 54 pCi/g for seven samples tested, corresponding to a range of 88 to 99% removal. At the same time, over 99.5% of the uranium was leached from the samples, giving evidence that the residual radium may be bound differently from the bulk of the radium. Further treatment with hydrofluoric acid showed that this radium could not be removed short of complete dissolution of the sample. Gamma analysis of small (5- to 8-g) amounts of the leached residues showed considerable variation in radium concentration. On further fractionation, sand grains were isolated that

analyzed several orders of magnitude higher (estimated up to 50 μ Ci of Ra/g) than the bulk sample.

I. A. D. Ryon, F. J. Hurst, and F. G. Seeley, *Nitric Acid Leaching of Radium and Other Significant Radionuclides with Nitric Acid from Uranium Ores and Tailings*, ORNL/TM-5944.

5.5 DISPERSION OF MISCIBLE FLUIDS IN PACKED BEDS

S. Y. Shiao K. A. Kraus

The idea of using miscible phase displacements to increase the recovery of crude oil has been under active study for more than three decades. Most of this work has been done on the nature and extent of the mixing zone which develops between the two miscible materials for many situations, including the two phases having different viscosities and densities.

The stability of the displacing fluid front is affected by viscosity and density of the two fluids. If the more viscous fluid displaces the less viscous fluid, the boundary is viscosity stable, and the state of flow is viscosity favorable. If the less dense fluid is on top of the more dense fluid, the boundary is gravitationally stable, and the state of flow is called density favorable.

It is known that an unfavorable viscosity ratio and/or an unfavorable density difference can cause fingering of the displacing fluid into the displaced fluid, that is, cause instability of the boundary. The effect of the density difference of the viscosity ratio and of flow rate on the mixing zone length has been studied by various investigators. However, the particle size of the packed material has not been sufficiently taken into consideration in these studies. In addition, most of the previous work was carried out either in a vertical or in a horizontal packed column. In practice, all sorts of flow directions can occur in the displacement of oil in the oil reservoir.

The objectives of this study, therefore, are to investigate the effect of the particle sizes of the packed material together with the density difference, viscosity ratio, and flow rate of the fluids on the stability of the boundary; to investigate the effect of the inclination of the packed beds on the stability of the boundaries; and possibly to derive a theoretical model to predict the displacement behavior. We also hope to extend these studies to boundaries with immiscible fluids.

We present here (Figs. 5.4 and 5.5) a few preliminary experiments which compare the extent of boundary dispersion when miscible fronts pass through packed beds containing particles of different sizes. The figures compare dispersion under conditions when both density differences and viscosity ratios are favorable and when they are unfavorable. The feed solutions were ethanol-water mixtures. These show, as a function of composition, a viscosity maximum and a monotone decrease in density and, thus, allow formation of boundaries with all four types of combinations of favorable and unfavorable viscosity and density gradients. The packed beds were made from screened sands and were approximately 6 cm high. Boundary mixing was monitored by passing the effluent through a Sodev densitometer, which allows density measurements with parts-per-million precision in a few seconds and can be operated under static and continuous flow conditions. The instrument was slightly modified to allow continuous recording of a function closely related to the density of the solution.

As shown in Figs. 5.4 and 5.5, the breakthrough curves are highly symmetrical, sharp, and have 50% displacement near one pore volume when both density (ρ) and viscosity (μ) gradients are favorable. [Displacement is computed from the density ratio $(\rho - \rho_1)/(\rho_2 - \rho_1)$, where the subscripts identify the displaced and displacing fluids.] When they are

Fig. 5.4. Dispersion of miscible boundaries. (A) $\Delta\rho = +0.0387$ g/cm³, $\mu_{\text{water}}/\mu_{\text{alcohol}} = 0.494$; (B) $\Delta\rho = -0.0376$ g/cm³, $\mu_{\text{alcohol}}/\mu_{\text{water}} = 1.99$ [30 cc of sand (20–30 mesh), 25°C, flow rate = 0.066 cm/min, 25.3 wt % ethanol in water].

Fig. 5.5. Dispersion of miscible boundaries. (A) $\Delta\rho = +0.0387$ g/cm³, $\mu_{\text{water}}/\mu_{\text{alcohol}} = 0.494$; (B) $\Delta\rho = -0.0381$ g/cm³, $\mu_{\text{alcohol}}/\mu_{\text{water}} = 2.015$ [30 cc of sand (80–170 mesh), 25°C, flow rate = 0.066 cm/min, 25.3 wt % ethanol in water].

unfavorable, the displacing fluid breaks through very much earlier, and the breakthrough curves become highly asymmetrical. This effect is particularly dramatic with the column containing 20- to 30-mesh sand. The effect is much smaller but still significant with the column prepared with the finer sand (80 to 170 mesh), demonstrating the expected importance of particle size on the dispersion of these miscible fronts.

5.6 PHASE STUDIES OF AQUEOUS SALT SOLUTION-ALCOHOL-HYDROCARBON SYSTEMS

5.6.1 Properties of Water-Organic-Electrolyte Systems

Patience C. Ho Michele A. Moio¹
Kurt A. Kraus

Several years ago we carried out a rather extensive program on the properties of water-organic-electrolyte systems. At that time the objective was to develop information which might help explain the salt-rejecting properties of organic hyperfiltration membranes. We have now begun a new program in this area with the objective of elucidating the complex phenomena which occur in the enhanced oil recovery process, commonly termed "micellar flood." In this process the oil-bearing formation is treated with a surfactant solution, which usually also contains a so-called cosurfactant (typically a low-molecular-weight alcohol) to mobilize the residual oil. (The surfactant solution is followed by a "polymer" solution with

controlled viscosity; this field, while also of interest to the division at present, is not of principal interest here.)

A class of surfactants of considerable practical import are aromatic sulfonates containing long aliphatic side chains. While the present program eventually will include these special materials, we have elected to carry out first a systematic study of the properties of benzene sulfonates containing only short side chains. We hope that some clarification of the properties of the complex micellar fluids could be obtained from a study of these simpler systems which do not form micelles. These sulfonates are organic salts which can significantly increase the solubility of the hydrocarbon in the cosurfactant-water mixture. We, of course, are interested also in the effect of other salts such as simple inorganic salts and other organic salts such as aliphatic and aromatic carboxylates.

In our preliminary survey we are examining three hydrocarbons: toluene, decane or dodecane, and cyclohexane. The cosurfactants which we are considering include methyl and ethyl alcohols, the various isomeric forms of propyl and butyl alcohol, some higher alcohols, and several cellosolves and carbitols. Currently we are including in the study of electrolytes monovalent and divalent chlorides and perchlorates, thiocyanates, and salicylates as well as the sulfonates mentioned. Our principal interest at present is to identify the compositions at which the systems change from two liquid phases to one liquid phase. This information can relatively easily be obtained by determining "cloud" points in samples for which the weight percent of the various components is established. While most of the systems studied are four-component systems, in the "cloud" point determination we have considered them as pseudo three-component systems by the simple device of keeping the water-salt ratio constant.

A typical set of results from the toluene-*n*-butanol-water system in the presence of three different sodium sulfonates is shown in Fig. 5.6. In the absence of the sulfonates, water and butylalcohol are not completely miscible. The presence of the sulfonates (2.5 moles per kg of water) removes this miscibility gap and leads to typical binodal curves (Fig. 5.6). The two-phase region decreases substantially as the sulfonates are changed from those of benzene to toluene to xylene, that is, as increasing number of methyl groups are attached to the benzene ring. Thus, even without micelle formation, aliphatic side chains on the sulfonates can significantly

Fig. 5.6. Effect of sulfonates on the phase relations in the toluene-*n*-butanol-water system (2.5 moles of sodium sulfonate per kg of water; diagram gives weight percent of the contents).

increase the solubility of the hydrocarbon in water containing the "cosurfactant."

Our examination of the effect of inorganic salts on the miscibility of alcohol-water-hydrocarbon systems had as its objective classification of salts according to salting-in and salting-out properties. From the usual Hofmeister series, we expected that perchlorates added to the alcohol-water-hydrocarbon systems would cause considerable salting-in of water. Salting-in occurred when the alcohol was butyl carbitol, but not with many of the other alcohols studied. For example, with the various propanols and butanols, sodium perchlorate generally caused salting-out of water, while magnesium perchlorate and lithium perchlorate caused salting-in. The extent of the effect depended greatly on which isomer of the alcohol was used. Chlorides (NaCl , MgCl_2) generally caused salting-out of water in the various toluene-alcohol systems studied. As expected, sodium salicylate caused salting-in. However, unexpectedly, thiocyanate did not. The salting-in effects seem to depend strongly on the isomeric form of the alcohol and on the salting-in agent. This surprising effect is demonstrated in Fig. 5.7, which compares the maximum water contents (at the cloud point) of a number of 1:1 toluene-alcohol mixtures, with the third component being water or concentrated aqueous solutions of NH_4SCN , sodium-salicylate, or *p*-toluene sulfonic acid.

Fig. 5.7. Effect of solutes on maximum water content of toluene-alcohol (1:1) solutions.

5.6.2 Micellar Solutions and Lyotropic Liquid Crystals

D. H. Smith S. A. Templeton¹

We have begun the study of various properties of quaternary systems composed of water, hydrocarbon, surfactant, and alcohol (cosurfactant). These systems are of great interest in applications such as the micellar-flood method of enhanced oil recovery and in more fundamental research areas such as model membranes, micellar catalysis, and the structures of lyotropic mesomorphs.

The initial aspect of this work is the determination of phase boundaries, since virtually no phase diagrams are available for these four-component systems. Beginning with the L_1 phase of sodium octanoate-*n*-decanol-water, for which the ternary phase diagram was known, we have measured the solubility of *p*-xylene and found solubilization changes corresponding to the second and third critical micelle concentrations (CMCs) of the sodium octanoate-water system. This is evidence for the structural connection between the second and third CMCs and the C-to-D and D-to-E mesomorphic phase transitions respectively which we have hypothesized. The significance of cosurfactants for costs of oil recovery can be seen from the experimental result that a few percent of cosurfactant can increase the solubilization by the surfactant severalfold.

We are also investigating this system by NMR chemical shift and relaxation time measurements in order to better understand the solubilization mechanisms. The concentration dependence of the xylene chemical shift does not fit the conventional two-site model for solubilized hydrocarbon, and it is anticipated that relaxation time experiments in progress will help us to relate the chemical shift variations to the micelle structural changes occurring at the second and third CMCs.

In a homologous series of ionic surfactants the first CMC of a given member depends on the length of its alkyl chain, and van der Waals forces between neighboring alkyl groups play a critical role in many other surfactant properties. In order to better understand these interactions, we have begun the accurate calculation of the intermolecular forces and molecular motions in various crystalline forms of the solid alkanes. Heats of sublimation and activation energies for rigid-molecule rotation were calculated for the triclinic form of all even-carbon-numbered paraffins from hexane through hexadecane. Not surprisingly, both the heat of sublimation and the activation energy were found to be linear functions of the chain length, which could be separated into methyl- and methylene-group contributions. More novel was the finding of three subminima in the molecular rotation potential. It is anticipated that similar subminima will be found for the monoclinic structure which exists at higher temperatures and that these will presage a disordered, "premelting" hexagonal phase bridging the ordered solid and the liquid structures. The properties of the hexagonal phase are of particular interest, since they are expected to mimic many of the structural features of the micellar and mesomorphic phases.

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5.7 FILTRATION STUDIES

5.7.1 Mechanism of Formation of Dynamic Membranes

G. B. Tanny¹ J. S. Johnson, Jr.
D. Freilich¹ C. G. Westmoreland

Since the inception of dynamically formed membranes at ORNL some 12 years ago, considerable information concerning their transport properties has been accumulated. Rejections of electrolytes, for example, have been shown to be consistent with

expected ion exchange and other properties of the substance (hydrous oxides, organic polyelectrolytes, etc.) from which they are formed. They are comprised of thin deposited layers on or near the surface of the porous supports. With respect to mechanism of membrane formation, it became clear fairly early that one picture initially conjectured—a layer of solution concentrated in additive at the surface by convection, with its thickness controlled by diffusion back into bulk solution—was not applicable; persistence of membranes over shutdowns and in absence of additives precluded that possibility. However, with that negative exception, relatively little has been established concerning the processes involved in dynamic formation of membranes.

Research in cooperation with Weizmann Institute has been under way on this subject. Efforts have been concentrated on hydrous zirconium(IV) oxide-polyacrylate membranes, the choice when substantial salt rejections are required. The primary approaches have been electron microscopy, analyses of the zirconium(IV) content of membranes, and inferences from time dependence of fluxes during membrane formation.

Operations necessary to prepare samples for electron microscopy introduce some uncertainty in

interpretation of pictures. However, examination of membranes formed on Acropor and Millipore filter sheets confirmed that the hydrous oxide layer was a thin deposit on the surface, penetrating but little into the porous support, although the thickness appeared to be several times the few microns inferred in earlier work. The oxide was amorphous. Addition of the polyacrylate layer changed the appearance in no substantial way, except that damage from beams used in the measurement seemed less.

In formation of the hydrous oxide sublayer, there appears to be a rapid plugging of pores near the surface initially, followed by a more gradual buildup of cake thickness. During subsequent exposure to polyacrylic acid (PAA) at low pH and at concentrations in the range usually used in membrane formation (up to a few hundred ppm), flux behavior (Fig. 5.8) does not appear consistent with precipitation of a gel layer at the interface. In such cases, one expects build-up of layer thickness, with a concomitant decrease in flux, until the rate of convection of PAA toward the interface is balanced by diffusion away. Steady-state fluxes are not reached as rapidly² as usual when this model is applicable, and the flux is not dependent on PAA concentrations as strongly as one would expect. However, results seem consistent

Fig. 5.8. Flux decline during formation of PAA layer on hydrous zirconium(IV) oxide membranes on 0.45- μ Acropor AN (950 psi, 15 fps, 30°C, 0.05 M NaCl).

with a mechanism involving plugging of pores in the hydrous oxide layer by PAA.

The sharp drop of flux when membrane formation is completed by raising pH to neutrality presumably results from the greater drag on permeating water by the ionized (salt) form of the polyacrylate.³ The membrane formed from 1% PAA appears somewhat different from those formed at more usual polyacrylate concentrations, but a gel polarization model does not seem applicable here either.

In the course of this study, an interesting, not altogether understood, observation was made of properties of hydrous zirconium(IV) oxide membranes on 0.45- μ Acropor AN supports [a filter sheet of poly (vinyl chloride co acrylonitrile) on a nylon fabric]. Eight membranes were formed simultaneously under what were thought to be identical conditions. However, the hydrous zirconium(IV) oxide membrane properties fell in two classes—five had rejections of $45 \pm 2\%$ and fluxes of 900 ± 100 gpd/ft², and the other three had rejections of 34% at 640 gpd/ft² (0.05 M NaCl, 950 psi, 15 fps circulation velocity, 25°C). After formation of the polyacrylate layer, fluxes for the two sets overlapped within scatter, but rejections of the first set were $89 \pm 6\%$ and of the other, $73 \pm 2\%$. Review of the history showed that direction of feed flow relative to orientation of the sections of sheet in the roll from which they were cut was perpendicular for the two sets. Examination of the Acropor under a microscope established that there was a different number of strands in the weaves parallel and perpendicular to the long dimension of the roll. This difference apparently causes the difference in membrane properties, as well as a more wrinkled appearance after formation of the set supporting membranes of higher rejection.

1. Weizmann Institute of Science, Rehovoth, Israel. Research partially sponsored by the U.S.-Israel Binational Foundation.

2. W. F. Blatt, A. Dravid, A. S. Michaels, and L. Nelson, pp. 47-97 in *Membrane Science and Technology*, ed. J. E. Flinn, Plenum, New York, 1970.

3. J. Th. G. Overbeek and D. Stigter, *Recl. Trav. Chim. Pays-Bas* 75, 543 (1956).

5.7.2 Sulfate Rejection by Hydrous Zirconium(IV) Oxide and Hydrous Zirconium(IV) Oxide-Polyacrylate Membranes at High pH

C. G. Westmoreland J. S. Johnson, Jr.

Hydrous zirconium(IV) oxide is a cation exchanger at high pH, and higher rejection from basic solution for salts of divalent anions (coions) than for

monovalent anions would be predicted. However, zero sulfate rejections were reported to us from another laboratory, and because of importance in some potential applications, as well as intrinsic interest, we have reexamined rejections of sulfate from basic solutions in more detail than previously.¹ Hydrous zirconium(IV) oxide membranes were formed on four 0.27- μ Selas ceramic tubes by conventional procedures; their rejections of NaNO₃ from 0.05 M solutions, pH 4, were $38 \pm 2\%$, and fluxes were 250 ± 15 gpd/ft² (950 psi, 15 fps, 25°C).

Figure 5.9 summarizes results at high pH. In the first cycle, as a baseline, one of the membranes was tested with a 1,1 salt, 0.05 M NaCl from pH 10 to 0.1 M NaOH and back. Conductivity rejections reflect both NaCl and NaOH removal; a lower rejection of hydroxide than chloride is apparent. The decline in rejection at high pH is somewhat greater than

Fig. 5.9. Hyperfiltration properties of hydrous zirconium(IV) oxide and hydrous zirconium(IV) oxide-polyacrylate membranes in alkaline media (950 psi, 15 fps, 25°C, 0.27- μ Selas ceramic tubes).

expected for increased total electrolyte concentration and reflects an unexpected effect of high pH. There is also an irreversible drop in flux seen in the repeat at pH 10, apparently caused by exposure to highly alkaline conditions, since it also occurred with fresh membranes in the other two cycles.

A fresh hydrous zirconium(IV) oxide membrane was added for the second cycle, with 0.025 *M* Na₂SO₄. Sulfate rejections, as expected, were higher than those of NaCl (cycle 1) at the same equivalent concentration, though the trend to lower rejection was qualitatively similar.

It seemed of interest to see what effect the change in properties of hydrous zirconium(IV) oxide membranes at high pH would have on dual-layer membrane properties. A polyacrylate layer was formed on these two membranes and one not exposed to high pH, by contacting with polyacrylic acid at low pH. Rejection of 0.05 *M* NaNO₃ was 85 ± 5% and fluxes were 49 ± 15 gpd/ft². With the remaining hydrous zirconium(IV) oxide membrane, these were tested with Na₂SO₄ solution in cycle 3. Rejections of sulfate, as expected, were higher by membranes with a polyacrylate layer, and, also in agreement with

earlier experience, there was a serious deterioration in properties of dual-layer membranes on exposure to high pH, presumably because of displacement of polyacrylate from the membrane.

To illustrate variability which may be encountered, results of another test with a hydrous oxide membrane having a somewhat higher rejection of Na₂SO₄ (initially about 40% at pH 10) than these membranes are summarized in Fig. 5.10. The first cycle, to pH ~12, showed sharply increased rejection and reduced flux. In the second cycle, fluxes and sulfate rejection (70 to 80%) varied little over the pH range. Reasons for these differences in behavior shown in Figs. 5.9 and 5.10 are not clear.

We conclude that sulfate salts are rejected at high pH and that the lack of rejection observed elsewhere must have resulted from other constituents or conditions. There appear to be irreversible effects on hydrous zirconium(IV) oxide membrane properties of exposure to high pH, though a history of such exposure does not seem to have much effect on polyacrylate layers formed subsequently.

I. A. J. Shor, K. A. Kraus, W. T. Smith, and J. S. Johnson, Jr., *J. Phys. Chem.* 72, 2200 (1968).

Fig. 5.10. Rejection of Na₂SO₄ by hydrous zirconium(IV) oxide membranes at high pH (950 psi, 15 fps, 25°C, 0.27- μ Sela ceramic tube).

5.7.3 Hyperfiltration Properties of Clay Membranes

J. S. Johnson, Jr. C. G. Westmoreland

With the growing interest in a variety of aqueous chemical processing applications, membranes whose salt rejection is unfavorably low for desalination merit reexamination. The ion exchange properties of clays imply that compact layers of them should filter salt by ion exclusion, and this process has been demonstrated both for clay packs elsewhere and for dynamically formed bentonite membranes in our early investigations of the dynamic class. An additional motivation for another look at this time is our involvement in enhanced-oil-recovery and nuclear-waste-isolation programs, in which the chemistry of clays is an important factor. We selected bentonite as an example of a "soft" clay and kaolin as a "hard" type. Of particular interest was the effect of pH and of divalent counterions, Ca(II) in these experiments. Membranes were formed initially from 0.05 *M* NaNO₃ solution containing 100 ppm of the clays.

After removal of clay from the feed, there was a drift in properties toward higher rejection and lower flux over a considerable period. For bentonite this can be seen in the first pH scan in Fig. 5.11. The flux and rejection of the final point at neutral pH, however, were fairly representative of subsequent measurements under the same conditions. After this scan, addition of 0.005 *M* $\text{Ca}(\text{NO}_3)_2$ dropped rejection from about 60% to 35% and flux from about 110 gpd/ft^2 to 70 gpd/ft^2 . Rejection of a 1 *M* neutral NaNO_3 solution was 25%; flux was 70 gpd/ft^2 . Properties seem relatively stabilized in a subsequent pH scan with 0.05 *M* NaNO_3 , and the effect of pH did not seem to be great. Rejection properties of membranes on 0.4- μ Nuclepore and 0.27- μ Sela ceramic supports were approximately the same as for the Acropor.

Following the second 0.05 *M* NaNO_3 scan, a 0.025 *M* $\text{Ca}(\text{NO}_3)_2$ feed was tested. Rejections and fluxes were lower. In a procedure aimed at speeding removal of $\text{Ca}(\text{II})$, a 0.05 *M* HNO_3 solution was circulated; rejection was 27% and flux was 80 gpd/ft^2 . Subsequently, a recheck with 0.05 *M* NaNO_3 at pH

6.3 (rejection 66%, flux 70 gpd/ft^2) indicated that there had been no major irreversible shift in membrane properties.

Kaolin membranes seemed to form more slowly, particularly on ceramic supports. The formation solution containing clay was circulated overnight, in contrast to about an hour for bentonite. There was again a rather extended period of drift in membrane properties, but eventually they stabilized. The rejection by a membrane on Acropor at neutral pH changed from 48% before a pH scan to 46% after, and flux changed from 105 gpd/ft^2 before to 115 gpd/ft^2 after. Rejection at pH 3.2 was 13%, flux was 200 gpd/ft^2 ; at pH 10 they were 43% and 84 gpd/ft^2 . Behavior on Nuclepore and ceramic supports was similar.

The trends in rejection properties with concentration of NaNO_3 and with presence of a divalent counterion are qualitatively what one would expect. Changes in flux may reflect changes in clay dimensions occurring in transition from monovalent to divalent replaceable cation forms. They do not reflect strongly the apparent several-fold increase in clay volume observed with bentonite in contact with 0.05 *M* salt over volume in contact with 1 *M* salt at atmospheric pressure.

Fig. 5.11. Hyperfiltration properties of a bentonite membrane (950 psi, 15 fps, 25°C, 0.45- μ Acropor AN).

5.7.4 Applied Studies

J. S. Johnson, Jr. L. J. Breithaupt¹
C. G. Westmoreland J. T. McKinnon¹
A. J. Shor P. H. Hayes²

We have continued to give substantial attention to practical aspects of filtration. One critical factor is commercial availability of suitable porous supports. In evaluation of Mott Metallurgical Corporation stainless steel tubes, dynamic membranes of good performance were formed. Filteraid was necessary, but a satisfactory technique using fine carbon powder during the formation of hydrous zirconium(IV) oxide sublayers, rather than in a pretreatment step, was worked out. Oil-water separations by membranes, important in many environmental and energy contexts, have been erratic; work with well-defined aqueous-hydrocarbon systems now suggests that many difficulties have arisen from surfactants, added or already present in the oils. Tests of phenolic compounds typical of coal-conversion aqueous streams established that good separation by dynamic ion exchange membranes depends on the pH being high enough for the phenols to be in salt form.

We shall discuss in more detail our major applied effort—participation, funded by the U.S. Environmental Protection Agency, in a pilot-plant program, cooperative with the International Paper Company, on treatment of effluents from wood pulping by the kraft process. Since the previous annual report,³ the hyperfiltration and ultrafiltration units were completed, shipped to the IPCo Moss Point, Mississippi,

installation, and put into initial operation. The ultrafiltration unit before shipment is pictured in Fig. 5.12. It provides for tests of 19-tube bundles of Sela ceramic tubes (not installed in the picture), offering a total membrane area of about 20 ft². Alternatively, a UCARSEP carbon-tube module can be accommodated (open flange position). A Goulds multistage centrifugal pump is capable of delivering 50 gpm at up

Fig. 5.12. Pilot plant for dynamic ultrafiltration membranes before shipment.

to 600 psi, a rate which allows attainment of circulation velocities of about 20 fps past ceramic test sections.

Only preliminary results have been obtained at this writing. Fluxes and contaminant removals by dynamic hydrous zirconium(IV)-silicon(IV) oxide membranes in the ultrafiltration unit have been favorable (Fig. 5.13). Color rejection was over 99%,

Fig. 5.13. Ultrafiltration of caustic extract by dynamically formed hydrous Zr(IV)-Si(IV) membranes on 19-tube bundles of Sela ceramic tubes.

and after the first few days, total organic rejections were mostly >98%. Chloride rejections, as expected and desired, were low. Fluxes for some reason increased in the early stages to gratifying values around 100 gpd/ft². After the period covered in the figure, brine concentration was continued to over 12% solids, with good removals; flux at this point was still about 65 gpd/ft². Most shutdowns resulted from power interruptions.

Initial experience with hyperfiltration of pulp-washing (decker) effluents has not been as favorable. Rejections by dynamically formed hydrous zirconium(IV) oxide-polyacrylate membranes have been good—organic, >99%; color, essentially complete; and chloride rejections, 80 to 90%, values which indicate from laboratory experience that total sulfur rejection (the low-molecular-weight component of primary interest) will be satisfactory. Flux declines, however, have been rapid, from about 50 initially to 20 gpd/ft² one week after start-up. The rate of tube breakage has been disturbingly high.

Extended operation will be necessary to establish the practicality of this approach to treatment of pulping effluents, but the initial ultrafiltration results, at least, are encouraging.

1. Erling Riis Laboratory, International Paper Company, Mobile, Ala.
2. Engineering Technology Division.
3. *Chem. Div. Annu. Prog. Rep. Nov. 1, 1975*, ORNL-5111, p. 52.

6. Chemicals for Enhanced Oil Recovery

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Conventional methods of production of petroleum recover on the average only about a third of the oil in the fields. Techniques removing even a small fraction of presently unrecoverable oil would contribute substantially to relief of liquid-fuel shortages in the midterm. One approach long under investigation involves injection of surfactants into formations to free oil. The enormous requirements for expensive chemicals and the presently limited capacity to manufacture them are major factors discouraging implementation of micellar flooding. About a year ago we began, under sponsorship of ERDA/Petroleum, Natural Gas, and Oil Shale Technology, a search for useful chemicals, or raw materials for their production, in waste streams or in natural products. The effort can be divided into what are basically organic chemical studies by Baldwin and co-workers, which have so far concentrated on pulp-mill wastes, and microbiological production of chemicals, so far mainly mobility-control polymers, by Compere and Griffith.

The chemistry of systems which may be encountered is complex; it involves interactions of oil-field brines whose concentration and constituents vary over wide ranges, of petroleum containing tens or hundreds of different hydrocarbons, of surfactants, of cosurfactants (usually alcohols), of polymers, and of a multiplicity of minerals, with wide variations of temperature and hydrodynamic conditions. The intricacy can be illustrated by the surprising specificity, extensively investigated by Wade and co-workers at the University of Texas,² of a given brine-surfactant combination for a mixture of hydrocarbons having a favorable value of what they call an "equivalent average carbon number" (EACN), to which organic compounds contribute from one for each carbon for straight-chain alkyl groups to essentially zero for carbons in aromatic rings. Sharp

minima, in which interfacial tensions between aqueous and hydrocarbon phases vary several orders of magnitude over two or three EACN, have been observed.

The complexity of the systems implies that our venture is a long shot, but the potentially enormous payoff makes the gamble in our opinion worthwhile. Some of the basic research on phase behavior and flow through porous media, described in other sections of this report, will be helpful, and programs on ion exchange aspects of surfactant and mineral systems, recently approved, will also strengthen the search.

1. Chemical Technology Division.

2. R. L. Cash, J. L. Cayias, R. G. Fournier, J. K. Jacobson, T. Schares, R. S. Schechter, and W. H. Wade, paper 5813, Preprints of Symposium on Improved Oil Recovery, Society of Petroleum Engineers, Mar. 22-24, 1976, Tulsa, Oklahoma.

6.1 WASTES FROM PULPING OF WOOD

The surfactant flooding process for improving the yield from oil wells has been envisioned to include solutions that may contain, in addition to the surfactant, a cosolvent to improve mutual solubility, a sequestrant to regulate the action of calcium and magnesium ions, a sacrificial agent to minimize the loss of surfactant to geologic formations, and a mobility control agent to regulate viscosity. The need for large volume and low cost has prompted us to consider the wastes from the wood-pulping industry as sources of chemicals.

Two processes for wood-pulping were found in 1964 to produce the waste products listed in Table 6.1. The most readily accessible material is the black liquor, for which a typical composition is shown in Table 6.2.

Table 6.1. Organic by-products formed in pulping processes in the U.S.A. in 1964

Kraft pulping (tons)		Sulfite pulping (tons)	
Thiolignin	8,800,000	Lignin sulfonic acid	1,920,000
Fatty and resin acids	405,000	Hexoses	550,000
Formic acid	600,000	Pentoses	87,000
Acetic acid	840,000	Acetic acid	140,000
Acids derived from carbohydrates	4,900,000	Formaldehyde and small amounts of ethyl alcohol, furfural, and acetone	18,000
All other organics (phenols, etc.)	650,000		

Source: C. H. Hoyt and D. W. Goheen, p. 833 in *Lignins*, ed. K. V. Sarkanen and C. H. Ludwig, Wiley-Interscience, New York, 1971.

Table 6.2. Typical composition of pine kraft black liquor (total solids about 20%, pH around 11)

	% of total solids
Alkali lignin (including soluble phenols)	41
Extractives (fatty and rosin acids)	3
Hydroxy acids and lactones	28
Acetic acid	5
Formic acid	3
Methanol	1
Sulfur	3
Sodium	16
Total	100%

Source: J. Maxton, p. 670 in *Lignins*, ed. K. V. Sarkanen and C. H. Ludwig, Wiley-Interscience, New York, 1971.

The main component (alkali lignin, thiolignin or kraft lignin) is a mixture of high-molecular-weight compounds soluble in base and insoluble in acid. Among the functional groups present in this compound are phenols, methoxyls, alcohol, ether, and carboxyls. While this is a polymer, there are no regular repeating units, but the empirical formula is usually expressed in units of propyl benzene with linkages through the alkyl chains.

Westvaco supplies a number of derivatives of kraft lignin. Indulin AT, the product that apparently results from acidification of the black liquor, is reported to contain polymers of molecular weight exceeding 100,000, with a maximum frequency around molecular weight 7000. Polyfon F, a sulfonated kraft lignin produced by Westvaco, is reported by them to have an ion exchange capacity around 3 meq/g, a maximum molecular weight around 50,000, with maximum frequency around molecular weight 4600.

Interfacial tension measurements were made with black liquor (from International Paper Company, diluted with nine volumes of water) and 0.5% Polyfon F (Westvaco) against *n*-octane. The results, 2.9 and 3.6 dynes/cm respectively, are much higher than the millidynes/cm range usually stated to be required for oil displacement.

Second in importance are the hydroxy acids (saccharinic acids) and lactones that have value as sequestering agents. A solution of the sodium salts of mixed saccharinic acids was prepared from kraft black liquor by the method of Green.¹ The sequestering capacity of saccharinic acids was compared with other compounds, using a modification of the method of Mehlretter, Alexander, and Rist.² Their method is based on the visual observation of precipitation of calcium oxalate in the presence of various sequestering agents. We have modified their method by using our surfactants (sulfonates, carboxylates) instead of oxalate and by using a commercial turbidimeter to attempt quantification of the precipitate.

The effectiveness of sodium saccharinate was compared with sodium gluconate and sodium citrate because they have been studied as sequestrants in other systems and because both might be available by fermentation of suitable wastes.

Comparison of the three materials (Fig. 6.1) shows saccharinate to be between gluconate and citrate in sequestering ability in the presence of TRS 10-80, a petroleum sulfonate surfactant. It is apparent that in this system a large excess, even of citrate (the most effective of the three), is required to reduce the amount of precipitation.

Preliminary results with 0.01 *M* sodium oleate, 2×10^{-3} *M* CaCl₂, and 0.01 *M* sodium citrate reveal that sequestering in the presence of oleate presents a greater problem than with sulfonates. In this oleate system the turbidity was the same whether citrate was present or not (650 arbitrary units). Sequestering of Ca(II) was obtained when the sodium salt of EDTA was used instead of citrate (one arbitrary unit). It must be pointed out that the use of EDTA does not appear to be practicable, either on the basis of its price or supply.

Turbidities leave much to be desired as criteria for usefulness of sequestrants in this application, since small fractions of material distributed in large aggregates may have turbidities as high as large fractions in small species. Interfacial tensions would give a better indication, but the presence of precipitate makes their determination by the spinning-drop method difficult. The pervasiveness of

Fig. 6.1. Sequestering of Ca(II) in 0.04 M TRS 10-80 and 2×10^{-3} M CaCl_2 .

precipitation does raise questions about the utility of sequestrants in surfactant banks. Perhaps a more effective way to use them would be in the preflush frequently carried out to modify salinity of formation brine. They would not in this case be competing with strongly complexing surfactant for multivalent cations, but might be able to reduce hardness in the brines, clays, etc., enough to mitigate deleterious effects.

Interfacial tension measurements with sodium oleate. Sodium oleate was selected as a model of some components of tall oil. When tested against various hydrocarbons, a minimum interfacial tension (measured by the spinning-drop technique) was found for an equal molar mixture of *n*-undecane and *n*-dodecane (see Fig. 6.2). Note that the minimum interfacial tension (55 millidynes/cm) is somewhat higher than the minima reported for favorable sulfonates (approximately 1 millidyne/cm).

Sodium oleate gels. It is well known that sodium oleate in water forms gels under certain conditions. Sodium chloride (a component of some oil-field brines) increases gel formation in sodium oleate

Fig. 6.2. Interfacial tension—sodium oleate (0.002 M sodium oleate, 0.1 M sodium chloride).

Table 6.3. Viscosity of sodium oleate solutions (20°)

Sodium oleate (moles/liter)	Sodium chloride (moles/liter)	Isopropyl alcohol (%)	Viscosity (cP)
0.1			1.3
0.2			1.8
0.5			71
0.002	1		1.1
0.01	0.25		2.2
0.01	0.5		Curds
0.1	0.05		1.4
0.1	0.1		3.0
0.2	0.24		Curds
0.35	0.14		Curds
0.1		5	1.8
0.1	0.1	5	1.5
0.2	0.24	5	43
0.35	0.14	5	142

solutions. We have used viscosity (Brookfield viscosimeter) as a measure of the effect of sodium chloride and isopropyl alcohol on sodium oleate solutions. Table 6.3 shows that at 0.5 M sodium oleate the viscosity has increased dramatically over that at 0.2 M. The increase in viscosity and curd formation by sodium chloride was reduced by including 5% isopropyl alcohol in the solution.

Cosolvents. Cosolvents are added to the surfactant mixture to increase the solubility of the several components. It has already been mentioned that isopropyl alcohol reduces the viscosity of sodium chloride-sodium oleate solutions. We have observed that butyl carbitol, Carbowax 20 M, and bis-ethoxyethyl ether reduce the turbidity produced when TRS 10-80 and calcium chloride or magnesium chloride are mixed. These were the most effective cosolvents of a number that have been tested. We plan to measure their effect on interfacial tension. These solvents had very little effect on calcium oleate precipitates.

Sulfonate surfactants. TRS 10-80 is a commercial sulfonate (Witco) resulting from the sulfonation of petroleum fractions. The product, while a complex mixture, is cheap, available in large quantities, and represents the presently favored type of surfactant for tertiary oil-field treatment. An EACN of 8 was found for the minimum interfacial tension (see Fig. 6.3). Inconsistencies were observed during these tests (while the test equipment was still new) that could not be confidently attributed to either the surfactant or the testing technique. A homogeneous sulfonate of known structure was synthesized for use as a standard surfactant. The following sequence was used to prepare *p*-(3-pentadecyl) phenyl sodium sulfonate:

The EACN was found to be 1 (toluene) for minimum interfacial tension measurements (see Fig. 6.4)

1. J. W. Green, *Tappi* 39, 472 (1956).
2. C. L. Mehlretter, B. H. Alexander, and C. E. Rist, *Ind. Eng. Chem.* 45, 2782 (1953).

Fig. 6.3. Interfacial tension—petroleum sulfonate (0.2% crude TRS 10-80, 1% NaCl, 8000 rpm, 27°C).

Fig. 6.4. Interfacial tension—*p*-(3-pentadecyl) phenyl sodium sulfonate (0.08% surfactant, 0.4% NaCl, 3.5% *i*-butyl alcohol, 6000 rpm).

6.2 MICROBIOLOGICAL PRODUCTION OF MOBILITY-CONTROL POLYMERS

Polymers are among the materials required in some procedures for enhanced recovery of petroleum from depleted wells. The polymer is used to increase viscosity and thus inhibit fingering in floods and premature breakthrough of drive water to producing wells. Increased viscosity is particularly necessary in the slug following a surfactant injection, and may be desirable in the surfactant solution also, as well as for improving sweeps in (secondary) waterfloods. It is projected that roughly 1 lb of polymer will be required per barrel of incremental oil. If projections of a million barrels of oil per day by these approaches are realized, amounts of polymer comparable to production of acetic acid, ethanol, or acetone would be required.

Currently, the leading candidates are partially hydrolyzed polyacrylamide and xanthan gum, a complex carbohydrate-based polymer produced by *Xanthomonas campestris*. The biopolymer has certain advantages over the synthetic; it is, for example, less shear degradable and less affected by brine hardness. It was developed by the Northern Regional Research Laboratory of the Department of Agriculture and is marketed by Kelco, some of it as food additive. For several reasons it may be difficult to scale production up to the level required for desired impact on oil recovery.

The polymer is produced from glucose at a pH near neutral with heavy supplementation of the organism. It is difficult to remove the *X. campestris* organisms, which are about $1\ \mu$ in length, from the highly viscous culture broth. The polymer is amine substituted, which implies that the nitrogen requirement for polymer production may be high. The *X. campestris* organism does not adapt well to continuous culture in that it has a spontaneous reversion to a strain genetically unable to produce polymer. The family of xanthomonads to which *X. campestris* belongs are generally plant pathogens which cause wilt and yellows in a variety of economically important food crops, including sugar cane, alfalfa, apples, cucumbers, cabbages, and strawberries.

For our purposes, an organism with simple nutrient requirements—say, inorganic salts and a carbon source, with potential adaptability to waste carbon sources—rather than one requiring proteins and vitamins is preferable. To avoid cumbersome and expensive precipitation procedures, relatively small-scale field production near points of use may be desirable; this implies growth under conditions

discouraging contamination by other organisms, such as extreme pH values or high salt concentrations, and in filaments or cells large enough to permit easy removal of the organism from the culture broth. Lack of serious pathogenic properties and high polymer production efficiency, perhaps one-third to two-thirds conversion of input carbon to polymer, would be other favorable qualities.

Two groups of organisms were chosen for examination. One of the groups is a family of fungi which produces scleroglucans. These are large, high-viscosity polymeric molecules having unsubstituted glucose monomers. The polymer has a backbone with 1,3-linked glucoses which have a high proportion of beta linkages and side branches consisting of a single glucose linked beta 6,1 to the backbone. Organisms which produce these polymers are found in the genera *Sclerotium*, *Helotium*, and *Stromatinia*. Some previous work on the production of polysaccharides by these organisms was performed by the Pillsbury Corporation using either glucose or sucrose as the major carbon source. The organisms fulfill most of

Fig. 6.5. Polymer production by *Sclerotium rolfii* ATCC 15206 on Pillsbury salts and glucose.

the criteria for an ideal organism, and the polymers obtained from these organisms are similar in many respects to those produced by *X. campestris*. Another group of organisms which produces interesting polymers is the black yeast family. These organisms produce polymers which are acetylated glucosamines alternating with acetylated glucuronic acids. The organisms, other than the requirement for the amine nitrogen, fulfill many of the requirements for polymer production.

The scleroglucan-producing organisms seemed more promising and have been studied first. *Sclerotium rolfsii* ATCC 15206 was tested under a variety of growth conditions, the polymer production was measured, and the polymer was characterized against xanthan gum. Polymer production during a

single fermenter batch run (Fig. 6.5) reached a maximum at around 15 g/liter. This represents a production efficiency of about 50% from the input glucose. The peak occurred about 50 hr after the start of the fermentation. Polymer production was measured by removing aliquots from the fermenter and preparing the polymer according to the scheme shown in the upper left arrow of Fig. 6.6. The polymer was then precipitated by addition of isopropanol, lyophilized in tared bottles, and weighed.

Figure 6.6 summarizes results obtained with different methods of dispersing polymeric material in fermenter broth to enhance viscosity. The initial values indicate scatter in sampling the rather heterogeneous mass comprising the broth. The step

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Fig. 6.6. Viscosities of fermentor sample of laboratory-produced glucan after various treatments. Blend, 60 sec at low speed of blender; heat, 90°C for ~30 min; neutralize, pH 6.5-7.0. Numbers refer to viscosities in centipoise, measured at 60 rpm. Brookfield LVF, spindle No. 3, temperature, 25 ± 1°C.

producing the largest increase in viscosity in all cases was blending. The sequence neutralization, heating, and blending seemed somewhat better than the others, and we have adopted it for preparation of culture broth for polymer recovery.

Polymer properties vary substantially with fermentation conditions, and the variables are not yet completely under control. We have measured several properties of interest in this application from a fermentation producing a batch of favorable quality. The viscosities under various conditions of our *Sclerotium* polymer, which we shall refer to as "glucan," are compared with measurements we made under similar conditions of samples of commercial xanthan gum, "Xanflood."

Figure 6.7 shows the effect of shear. The ordinate is labeled "comparative viscosity" because with the Brookfield attachments and the vessels used, computation of the shear rate was not feasible. The effects of increasing shear are similar for the two polymers. Figure 6.8 shows the temperature dependence of viscosity.

The effects of concentration, of pH, and of hardness on viscosity are major factors in the choice of polymers. Figure 6.9 shows the effects of pH. The 1500-ppm scleroglucan solution shows less than 10% variation in viscosity across a pH range of 2 to 10. The xanthan gum solution has a relatively constant viscosity between pH 4 and 10, but does show a marked decrease in viscosity between pH 2 and 4. Neither polymer shows a significant variation in

Fig. 6.7. Dependence of viscosity of glucan solution on rpm. Comparison with Xanflood (Brookfield LVE, 25°C).

Fig. 6.8. Temperature dependence of viscosity (1500 ppm polymer in water; shear rate, 14 sec⁻¹).

viscosity as the sodium chloride concentration in the suspending solution changes between 0.01 and 0.5 M (Fig. 6.10).

Hardness seems to have relatively little effect. The viscosity of a 1000-ppm solution in 0.05 M NaCl of a glucan preparation containing 0.16 millimole of Ca(II) + Mg(II) per gram of polymer was 34.8 cP. After concentration of these divalent cations was reduced to 0.002 millimole of Ca(II) + Mg(II) per gram of polymer by contact with the sodium form of the cation exchanger Dowex 50W-X8, viscosity was 32.4 cP. [The mole ratio Ca(II)/Mg(II) in the preparation was 2:1.] Replacement of sodium by calcium in the solution at constant chloride concentration also affected the viscosity only slightly. When the supporting electrolyte was changed from 0.05 M NaCl to 0.025 M CaCl₂ [1000 ppm Ca(II)], the viscosity of a 500-ppm polymer solution increased from 18.8 cP to 19.4 cP.

Fig. 6.9. Dependence of viscosity on pH (1500 ppm polymer 0.05 M NaCl, 25°C; numbers indicate order of measurement; shear rate, 14 sec⁻¹).

Fig. 6.10. Dependence of viscosity of glucan on NaCl concentration (1500 ppm polymer, 25°C; shear rate, 14 sec⁻¹).

Figure 6.11 illustrates the effect of polymer concentration on viscosity in 0.05 M NaCl. The xanthan gum develops a slightly higher viscosity at concentrations lower than around 500 ppm in water. At concentrations higher than 500 ppm or in 0.05 M NaCl over most of the range, the viscosities of solutions at a given glucan concentration are equal to or higher than those at the same concentration of Xanflood.

The testing performed to date indicates that at least this batch of scleroglucan polymer compares favorably with commercially available xanthan gum. However, much more has to be done, in addition to identifying sources of irreproducibility and opti-

mizing procedures, before its practical utility is established. Some information on adsorbability on minerals typical of oil-bearing formations must be obtained. Some measurements eventually necessary, for example, stability over extended periods at elevated temperature and performance in core flood tests, are outside the scope of this program. Further work here is needed to indicate whether it is possible to produce an organism which will satisfactorily meet the test of producing high-quality polymers from cheap or waste carbon sources, such as wood molasses. Finally, we hope to suggest more efficient configurations than stirred-tank batch systems to carry out fermentations.

Fig. 6.11. Concentration dependence of viscosity of solutions containing polymer produced by *Sclerotium rolfsii* (glucan). Comparison with Xanflood (Brookfield LVF, 60 rpm, 25°C).

AE S?
Fuel cells

7. Molten-Salt Systems

7.1 MOLTEN CARBONATE FUEL CELL PROGRAM

7.1.1 Electrochemical Studies of Transport and Thermodynamic Properties in Molten Alkali Carbonate Mixtures

H. R. Bronstein J. Braunstein

Direct electrochemical utilization of fuels at elevated temperatures offers one means of electrical energy generation that is potentially more efficient and less noxious than combustion of the fuels.¹ One of the promising candidates is the molten carbonate fuel cell operated with gaseous mixtures containing hydrogen and carbon monoxide derived from hydrocarbon or carbonaceous fuels and water. Basic supportive research for the molten carbonate fuel cell program has been initiated at ORNL with experimental measurements and theoretical interpretation of the physicochemical behavior of molten carbonate electrolytes and their interactions with electrodes, gases, and containment materials.² A survey of the recent literature on alkali carbonates has been incorporated into a compilation and critical review to be assembled for the molten carbonate fuel cell program³ with the aim of identifying information gaps where additional research is needed. Areas of needed research directly related to division expertise were materials compatibility and fundamental transport and thermodynamic properties, including transference numbers, diffusivities, and activities of components in alkali carbonate melts.

For greater flexibility in design of equipment for electrochemical studies in alkali carbonate melts, additional refractory insulators besides the commonly used high-density alumina and lithium aluminate are being sought. One likely candidate was pyrolytic boron nitride, which from thermodynamic calculations based on data in the JANAF tables indicated possible stability in carbonate melts under reducing conditions. Tests in a molten ternary eutectic melt of $(\text{Li-Na-K})_2\text{CO}_3$ indicated a rather restricted usefulness. Below 550°C no visible sign of attack or weight loss occurred after a 5-hr exposure.

At higher temperatures, 600 to 700°C , attack does occur.

Solid sodium beta-alumina, a sodium ion conductor,⁴ is being evaluated for its resistance to attack by molten carbonates and its use as an ionic membrane in an electrochemical cell for the measurement of thermodynamic properties:

Single crystals of sodium beta-alumina bathed in the molten ternary alkali carbonate melt $(\text{Li-Na-K})_2\text{CO}_3$ at temperatures exceeding 725°C for periods as long as ten days showed no visible sign of reaction with the melt. Chemical analysis showed some replacement of sodium ions by potassium ions⁵ but not by lithium ions of the melt. These results suggest that sodium beta-alumina may be usable in cell [A] with melts of $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$, and possibly $\text{K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ melts, since the mobility of sodium ions is very much greater than that of the potassium ions in sodium beta-alumina. A tube of this material⁶ will be incorporated into an experimental cell.

In the operation of carbonate fuel cells under high current densities, changes in the alkali ion ratios may occur at the electrode because of mobility differences.⁷ An apparatus for determination of composition profiles in alkali carbonate-lithium aluminate tiles similar to those employed in fuel cells is illustrated in Fig. 7.1.⁸ The nickel electrodes were preconditioned at 565°C with a 50-50 vol % $\text{CO}_2\text{-O}_2$ mixture to convert them to Ni-NiO electrodes for the electrode reactions

A PAR model 173 potentiostat/galvanostat and model 179 digital coulometer were used to electrolyze a tile for 5 hr at a current density of 40 mA/cm^2 . The carbonate tile has been sectioned and polished, and

the composition profile is being analyzed using x-ray fluorescence and ion probe scanning techniques.

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Fig. 7.1. Electrolytic cell for composition profiles in molten carbonate mixtures.

7.1.2 Thermochemistry of Alkali Carbonates

S. Cantor D. E. Heatherly

A critical evaluation of the thermochemistry of materials used in molten-salt fuel cells began with an examination of the data for Li_2CO_3 , Na_2CO_3 , and K_2CO_3 compiled in the JANAF tables.¹ Several errors and omissions were uncovered in this examination, primarily in the temperatures and enthalpy of solid-state transitions.

Based on this indicated need for improved thermodynamic information, we initiated a calorimetric study of these compounds using the (Perkin-Elmer) differential scanning calorimeter, an instrument ideally suited for determining enthalpies of transition and changes of heat capacity that occur in the range -65 to 727°C . Preliminary DSC measurements over this temperature range were carried out with samples of carbonate dried and purified at 425°C by passing CO_2 over analytical- or reagent-grade starting materials. A summary of results is presented in Table 7.1.

Of the three carbonates, only Li_2CO_3 showed first-order transitions: at 410°C and at $\sim 725^\circ\text{C}$, the melting point. All the transition temperatures observed in the DSC studies have been previously noted;² however, the type (i.e., whether first order or second order) of transition has not been clear. Better resolution of transition energetics in Na_2CO_3 and K_2CO_3 will be obtained when we measure heat capacities with the DSC.

Review of the thermochemistry of alkaline carbonates has included the deriving of activity coefficients from phase equilibria. Values of activity coefficients of the component carbonates have been computed from liquidus temperatures in the systems $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ and $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$. These are listed in Table 7.2. It was found that deviations from ideality are greater in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ than in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$. Excess partial molar free energies calculated from the activity coefficients tend to be roughly 0.5 kcal/mole more negative than partial molar heats of mixing;³ thus, these binary molten carbonate solutions do not fit a regular solution model. These activity coefficients should be applied with some caution, since there could be solid solubility (especially of Li_2CO_3 in Na_2CO_3), although there is no evidence for this in the two binary systems.

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Table 7.1. DSC measurements in crystalline Li_2CO_3 , Na_2CO_3 , and K_2CO_3

	Transition temperature ($^\circ\text{C}$)	Type of transition	Interpretation of DSC thermograms
Li_2CO_3	410	First order	$\Delta H = 200 \pm 20 \text{ cal mole}^{-1}$
Na_2CO_3	357-360	Second order	Slight upsweep in C_p with temperature, then C_p abruptly decreases $\sim 6 \text{ cal mole}^{-1} \text{ deg}^{-1}$
	484-488	Second order	Roughly the same, except C_p decreases $\sim 9 \text{ cal mole}^{-1} \text{ deg}^{-1}$
K_2CO_3	420-422	Second order	Same features as for Na_2CO_3 ; C_p decreases $\sim 13 \text{ cal mole}^{-1} \text{ deg}^{-1}$

Table 7.2. Activity coefficients^a in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ and $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ derived from liquidus temperatures^b

$\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$			$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$		
Mole fraction Li_2CO_3	$\gamma_{\text{Li}_2\text{CO}_3}$	$\gamma_{\text{Na}_2\text{CO}_3}$	Mole fraction Li_2CO_3	$\gamma_{\text{Li}_2\text{CO}_3}$	$\gamma_{\text{K}_2\text{CO}_3}$
0.9	0.903		0.9	0.871	
0.8	0.780		0.8	0.680	
0.7	0.561		0.72	0.462	
0.6	0.500		0.62	0.301	
0.55 ^c	0.414		0.427		0.441
0.54 ^c	0.399		0.42		0.457
0.533 ^c	0.389		0.4		0.494
0.503 ^c		0.409	0.3		0.663
0.50 ^c		0.413	0.2		0.811
0.48		0.463	0.1		0.930
0.45		0.509			
0.4		0.579			
0.3		0.726			
0.2		0.843			
0.1		0.935			

^aCalculated from $\ln \gamma_N = \int_{T_M}^T (\Delta H_f / RT^2) dT$; N is mole fraction, T_M is the melting temperature (K) of the pure component, ΔH_f is the heat of fusion; heat of fusion and heat capacity taken from G. J. Janz et al., *Trans. Faraday Soc.* 59, 841 (1963).

^bMost liquidus temperatures taken from G. J. Janz and M. R. Lorenz, *J. Chem. Eng. Data* 6, 321 (1961).

^cLiquidus temperature from E. J. Cairns and D. I. MacDonald, *Nature* 194, 441 (May 5, 1962).

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here too*

7.2 TRANSPORT AND THERMODYNAMICS IN MOLTEN SALTS

7.2.1 Entropy Estimates of Garnets and Other Silicates

S. Cantor

To estimate third-law entropies of silicates, Saxena¹ has presented equations in which molar entropy at 298.15°K is linear with molar volume. The use of these equations is open to two criticisms: (1) the linear relationship between entropy and volume misses the well-known role of mass, and (2) for compounds with transition metal ions, magnetic contributions to entropy are neglected.

It has long been known² that the entropy of lattice vibration can be estimated satisfactorily in terms of atomic mass. Of course, volume will also be a factor. Indeed, the author³ has shown, from the Debye theory of specific heats, that lattice entropy S is related both to molar mass M and to molar volume V by the equation

$$S = A + \frac{3}{2} n R \ln MV^{2/3}, \quad (1)$$

where A is a term that is nearly constant for closely related compounds, n is the number of gram-atoms in a mole of the crystal, and R is the gas constant. For example, note the orthosilicate series with the formula $M_2\text{SiO}_4$:

		A (gibbs/mole)
Phenacite	Be_2SiO_4	-133.01
Forsterite	Mg_2SiO_4	-133.02
Ca-olivine	$\gamma\text{-Ca}_2\text{SiO}_4$	-135.36
Willemitte	Zn_2SiO_4	-136.47
	av	-134.47

The values of A were obtained from the experimental entropies critically compiled by Robie and Waldbaum.⁴ At 298.15°K, Ca-olivine is more stable than larnite ($\beta\text{-Ca}_2\text{SiO}_4$), and it is Ca-olivine that is correlated by Eq. (1). Saxena¹ excludes Ca-olivine from his correlation for orthosilicates presumably because his estimated entropy was too high by 9.15 gibbs/mole.

For crystalline silicates with transition-metal ions, the estimation of entropy requires an additional term

to account for the disorder of magnetic moments. For compounds of the first transition series, magnetic entropy S_m can be approximated⁵ from the spin quantum number S by the equation

$$S_m = R \ln (2S + 1). \quad (2)$$

For instance, S is 2 for Fe^{2+} and $5/2$ for Mn^{2+} . Thus we estimate entropies of the orthosilicates tephroite (Mn_2SiO_4) and fayalite (Fe_2SiO_4) from Eq. (2) by calculating lattice entropy from Eq. (1), using the average A (-134.47 gibbs/mole) obtained from the four diamagnetic orthosilicates.

The table following summarizes the results:

	lattice S [Eq. (1)]	magnetic S [Eq. (2)]	estd S	exptl S (ref. 4)
Mn_2SiO_4	30.30	7.12	37.42	39.0 ± 1.0
Fe_2SiO_4	29.83	6.40	36.23	35.45 ± 0.4

Another form of Eq. (1) is the expression

$$S_y = S_x + \frac{3}{2}nR \ln [(M_y V_y^{2/3}) / (M_x V_x^{2/3})]. \quad (3)$$

The subscript y refers to a compound whose entropy is to be estimated; x signifies a reference compound, that is, a compound chemically and structurally similar to y whose entropy is known. For instance, to estimate the entropy at 298.15°K of pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), we use grossularite ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) as the reference compound. Substituting in (3) the experimental data tabulated in ref. 1:

$$S(\text{pyrope}) = 57.7 + 1.5(20)1.987 \ln [403.15 \times 113.27^{2/3} / 450.454(125.3)^{2/3}] = 47.07 \text{ gibbs/mole}.$$

For a silicate with a transition-metal ion, the magnetic entropy must be added. For example, in rhodonite (MnSiO_3), S_m from Eq. (2) is 3.561 gibbs/g-atom. The lattice entropy at 298.15°K , estimated from enstatite (MgSiO_3) via Eq. (3), is 21.26 gibbs/mole. The sum, $3.561 + 21.26 = 24.82$ gibbs/mole, agrees closely with the experimental⁴ entropy of 24.5 ± 0.5 gibbs/mole.

It is instructive to compare Saxena's correlation¹ with the methods given here for estimating the entropy of another garnet. For andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$), the entropy at 298.15°K (78.7 ± 1.3 gibbs/mole) has been computed⁶ from heat capacity data.⁷ The molar volume, 131.65 cm^3 , is obtained

from the x-ray unit-cell parameter,⁸ $12.048 \text{ \AA}$. Substitution of 131.65 cm^3 in Eq. (2) of Saxena's paper¹ yields an entropy of 94.32 gibbs/mole. Since $S = 5/2$ for Fe^{3+} , $S_m = 2R \ln 6 = 7.12$ gibbs/mole. Again using grossularite as the reference compound in Eq. (2) above, we obtain 66.85 gibbs/mole as the lattice entropy of andradite; this added to the magnetic entropy gives an entropy of 73.97 gibbs/mole, an estimate much closer to the experimental value than is predicted from ref. 1.

A fuller exposition of this subject will shortly be published as a technical comment in *Science*.

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7.2.2 Thermodynamically Predicted Miscibility Gap in the BeF_2 -LiF System¹

C. E. Vallet J. Braunstein

We have reported on electrolysis of a beryllium anode in molten BeF_2 -LiF (53-47 mole %) at temperatures just above the liquidus for that composition.² At constant temperature the changing melt composition at the electrode surface approaches pure BeF_2 , and most of the isotherm lies below the liquidus. The dependence of electrode response on the current density suggested a dependence on nucleation rates in the metastable liquid phase.³ It was therefore of interest to determine the temperature-composition regions of stability and metastability of homogeneous liquid. Furthermore, since the fluoroberyllates have structures analogous to the silicates, it is of considerable interest to compare the respective coexistence curves. For silicates and borates, the calculation requires assumptions on the form of the activity coefficients because of the paucity of the data. Since activity coefficient data are available for LiF- BeF_2 mixtures, we were able to calculate the thermodynamically predicted miscibility gap,

shown in Fig. 7.2, by computer analysis of the free-energy-composition isotherms.

The spinodal (inner) curve indicates the limit between the regions of metastability and instability of a single liquid phase to small composition fluctuations. The binodal (outer) curve indicates the equilibrium compositions of the two coexisting liquid phases and delineates the separation between the composition regions of stability and metastability of a single liquid phase [i.e., between the binodal and spinodal curves the liquid is stable to small (e.g., diffusive) composition fluctuations, while between the spinodal compositions there is no thermodynamic barrier to the growth of nuclei and consequent phase separation]. Both curves are highly asymmetric, as in silicates and borates. As expected from the flattening of the liquidus line, the upper consolute point (534°C , 78 mole % BeF_2) is within the range of temperatures reported for the liquidus temperature at this composition. Separation into two liquid phases has not been observed in the binary system

$\text{LiF}-\text{BeF}_2$, although it has been found in the ternary system $\text{LiF}-\text{BeF}_2-\text{ZrF}_4$.⁴ The Cook-Hilliard relation⁵ between compositions on the spinodal and binodal curves was found valid. Verification of this relation for highly asymmetric miscibility gaps such as those in fluoroberyllate, silicate, and borate systems is important because of its wide use in estimating the properties and phase transformations in glass-forming systems in which data are incomplete.

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4. K. A. Romberger, J. Braunstein, and R. E. Thoma, *J. Phys. Chem.* **76**, 1154 (1972); R. E. Thoma, M. Insley, M. A. Friedman, and G. M. Hebert, *J. Nucl. Mater.* **27**, 166 (1968).
5. M. E. Cook and J. E. Hilliard, *Trans. Metall. Soc. AIME* **233**, 142 (1965).

Fig. 7.2. Phase diagram of the system $\text{LiF}-\text{BeF}_2$ with the calculated miscibility gap indicated on the right.

7.2.3 Numerical Solution of Electrochemical Flux Equations with Composition-Dependent Diffusion Coefficient and Transference Number¹

C. E. Vallet J. Braunstein

Finite-difference solution has been carried out for the nonlinear partial differential equations for diffusion and migration that arise in many electrochemical studies of binary mixtures of molten salts. Simulated chronopotentiograms have been computed, and Fig. 7.3 shows the relative concentration at the electrode surface for the following model cases with semi-infinite boundary conditions. The first two cases have analytical solutions that verified the algorithm (D is the interdiffusion coefficient, and M is a migrational term whose form depends on the mobilities of the ions and on the electrode reaction).

- I. Constant D , $M = 1$ (curve 0 of Fig. 7.3).
- II. Constant D , constant $M \neq 1$ (curve 3 of Fig. 7.3).
- III. Constant D , varying $M =$ transference number (curves 3a and 3b of Fig. 7.3). One of the two ion constituents of like charge crosses the electrode-electrolyte boundary. This case includes the analogs of electrodes in the Li-S battery with molten LiCl-KCl electrolyte and in some complex melts such as chloroaluminates.
- IV. Constant D , $M = T_L^C - X_L$ (curve 4 of Fig. 7.3). This case is analogous to a molten carbonate fuel cell electrode (T_L^C represents the transference number of Li^+ relative to carbonate, and X_L is the equivalent fraction of Li_2CO_3) in which the common ion crosses the boundary.
- V. D varying exponentially with composition, $M = 1$ (curve 2 of Fig. 7.3). This case corresponds to the composition dependence of D in systems analogous to LiF-BeF₂ or silicates.
- VI. D varying exponentially, M varying. The form of M was chosen to remain nearly constant and equal to unity over a broad range of composition and then fall rapidly, to provide an analog of LiF-BeF₂ mixtures. Case VI leads to a sigmoid plot of concentration at the electrode surface vs square root of time analogous to those observed in ED chronopotentiometry of 0.53 BeF₂-0.47 LiF mixtures,² as shown in Fig. 7.4.

The graphically evaluated initial limiting slope of the computer plot of relative concentration vs square root of time corresponds in all cases to the values of the diffusion coefficient and transference number in melt of initial (bulk) composition, justifying our earlier² chronopotentiometric evaluation of inter-

Fig. 7.3. Time dependence of concentration at electrode surface with varying diffusion coefficient or migrational term.

Fig. 7.4. Effect of decreasing diffusion coefficient D and decreasing transference number T on the time dependence of concentration at electrode surface. Comparison with experimental results in molten LiF-BeF₂.

diffusion coefficients in concentrated electrolytes. The computations demonstrate the errors inherent in attempts to use the chronopotentiometric transition time to evaluate diffusion coefficients of concentrated constituents.

The above computations open the way to predictive modeling of a wide variety of electrochemical devices, to more rigorous analysis of electrochemical scanning experiments, and to more convenient methods for the determination of composition-dependent transport parameters in binary electrolyte mixtures.

1. C. E. Vallet and J. Braunstein, "Solution of Electrochemical Flux Equations with Variable Diffusion Coefficient and Transference Number," paper 186, Symposium on Reaction Mechanisms, Models, and Computers, ACS Meeting, New Orleans, Mar. 20-25, 1977.

2. C. E. Vallet and J. Braunstein, *J. Electrochem. Soc.* 124, 78 (1977).

7.2.4 Migrational Polarization in Electrochemical Systems with Mixed Electrolytes at High Current Density¹

J. Braunstein C. E. Vallet

In the development of efficient batteries and fuel cells for energy storage and conversion, high-temperature devices reduce losses from ohmic, activation, and mass transport polarization, and from degradation of the thermal energy available from the primary source.² Molten salts permit high-temperature operation, and their mixtures offer a wide range of properties. Mass transport polarization may arise from two kinds of concentration gradients. The first is that of electroactive species which may be present at low concentration. A second, frequently overlooked, source is concentration gradients of the major constituents as a result of migrational separation induced by the current. Although the migrational effect on voltage is relatively small, the changes in composition at the electrode surfaces need to be considered in cell design and modeling.³

Composition profiles have been estimated by numerical solution of the diffusion-migration equation involving M , a migrational term appropriate to the electrode reaction and the form of the transference numbers; D , the interdiffusion coefficient; C , the concentration; ξ , the distance from an electrode; and I , the current density. The algorithm developed for simulation of chronopotentiograms⁴ with semi-infinite boundary conditions (see previous section) was modified for the two finite boundary conditions appropriate to a battery or fuel cell analog. Simulated composition profiles and their time dependence are shown in Figs. 7.5 and 7.6 for a battery analog,

$$(a) M = i_L^{Cl} \approx X_L,$$

and for a fuel cell analog,

$$(b) M = i_L^C - X_L, \quad i_L^C = \frac{C_L U_L}{C_L U_L + C_K U_K},$$

with constant but unequal mobilities ($U_L/U_K \sim 2$). Significant concentration gradients develop in a short time. In case (a) the concentration of lithium at the cathode falls to a steady-state value of about half its initial value in about 15 min. In case (b) the lithium steady-state concentration at the anode is nearly 20%

Fig. 7.5. Case (a): Molten-salt battery analog.

below the initial, indicating a composition gradient of nearly 40% across the electrodes. Actual composition gradients would be modified by convection (which is retarded, however, by the porous matrix containing the electrolyte), current variations, coupling to the flows of additional constituents and of thermal energy, effects of pore size, and edge effects. However, these computations indicate the magnitude of the driving force toward a composition gradient and suggest important consequences for the choice of electrolyte and operating conditions. Wetting behavior, gas solubility, and phase stability in the electrolyte can be expected to differ at the two

Fig. 7.6. Case (b): Molten-salt fuel cell analog.

electrodes, affecting electrolyte losses, corrosion, and the possible precipitation of unwanted solid phases.

1. J. Braunstein and C. E. Vallet, paper 379, Symposium on Electrode Materials and Processes for Energy Conversion and Storage, the Electrochemical Society, Philadelphia, May 8-13, 1977.

2. D. A. J. Swinkels, "Molten-Salt Batteries and Fuel Cells," chap. 4, pp. 165-223 in *Advances in Molten-Salt Chemistry*, vol. 1, ed. J. Braunstein, G. Mamantov, and G. P. Smith, Plenum, New York, 1971.

3. J. Braunstein, H. R. Bronstein, S. Cantor, D. E. Heatherly, and C. E. Vallet, *Molten Carbonate Fuel Cell Research at ORNL*, ORNL/TM-5886 (1977).

4. C. E. Vallet and J. Braunstein, "Solution of Electrochemical Flux Equations with Variable Diffusion Coefficient and Transference Number," paper 186, Symposium on Reaction Mechanisms, Models, and Computers, ACS Meeting, New Orleans, Mar. 20-25, 1977.

7.2.5 Electrochemical Measurements in Model Systems Simulating Molten-Salt Fuel Cells and Batteries

D. E. Heatherly C. E. Vallet

Experimental tests of the concepts and equations of migrational polarization¹ have been initiated in simple model systems for which the transport coefficients (diffusion coefficients and transference numbers) are known and which permit, more readily than do actual fuel cell and battery electrolytes, systematic evaluation of the effects of electrode separation, porosity of electrolyte matrix, electrolyte composition, and current density. Mass transport in the system $\text{KNO}_3\text{-AgNO}_3$, electrolyzed between silver electrodes, is analogous to that in the $\text{Li}(\text{alloy})/\text{LiCl, KCl}/\text{FeS}_x$ battery under charge and permits quantitative evaluation of the range of validity of the migrational polarization equation as well as visual observation of qualitative phenomena such as phase changes. Results of this simulation are needed to design experiments for investigation of possible segregation of components in molten LiCl-KCl , chloroaluminates and other electrolytes. Silica cells with silver electrodes have been constructed for electrolysis experiments with free electrolyte and with electrolyte confined in porous silica frits. Concentrations at the electrode surface have been determined as a function of time by monitoring the cell emf, and the porous frits can be sectioned and analyzed following electrolysis to determine the composition profile. Initial experiments with the free-electrolyte cells with different current densities show time dependence of the concentration at the anode surface for electrolysis times up to ~ 10 min consistent with the migrational polarization equations, but with a slightly higher diffusion coefficient than the literature² value. The discrepancy is in the direction expected from a convective effect, and similar experiments³ with the electrolyte confined in a porous matrix are consistent with a lower value of the diffusion coefficient. It has not yet been possible to test the steady-state equations because of extensive silver dendrite formation at the cathode at long electrolysis times.

Fig. 7.7. Time dependence of potassium concentration at the electrodes during electrolysis. Dashed line: calculated from equations of migrational polarization; symbols correspond to different experimental runs.

Probably for the same reason, the composition at the cathode surface follows the theoretical equation for up to ~ 25 sec. Conditions of temperature and composition which minimize dendrite growth are being sought. Figure 7.7 shows the time dependence of concentration at the anode, compared with the theoretical equation, for two current densities.

1. See sect. 7.2.4 of this report.
2. J. Richter, *J. Chem. Eng. Data* 18, 400 (1973).
3. MIT School of Chemical Engineering Practice, ORNL, CEPS-X-249, (February 1977).

7.2.6 Reduced Titanium Species in Metaborate Melts¹

L. O. Gilpatrick G. L. Johnson²
Lynda Johnston G. P. Smith

This research was conducted in support of a U.S. Bureau of Mines process for electroplating titanium diboride. The electroplating bath consists of a molten mixture of lithium and sodium metaborates (LiBO_2 and NaBO_2) in the weight ratio 2/1, respectively, to which is added a mixture of titanium dioxide and lithium and sodium titanates such that titanium constitutes about 1 wt % of the melt. The bath operates at approximately 875 to 900°C.

The purpose of the research was to apply spectroscopic methods in an effort to determine the chemical form in which titanium is present in such baths and why such baths tend to deteriorate during periods in which the electrolysis current is turned off. Although titanium is added in the 4+ oxidation state, the following evidence suggests that during electroplating a lower oxidation state is formed and plays an important role. (1) The bath operates under strongly reducing conditions. (2) During break-in electrolysis it turns very dark blue to black and does not yield a satisfactory plate until this dark coloration is well developed. Titanium in a lower oxidation state is a conspicuous possibility as the source of this color. (3) Unless the melt is agitated, a stratification of color develops. When this happens, the electrodeposit builds up much faster on the lower part of the cathode. (4) Titanium metal, which served as the anode in an early version of this process, is known to be attacked by the melt. A possible mode of this attack is reaction with titanium(IV) to produce a lower oxidation state. With this evidence in mind we set out to determine whether the dark coloration was due to a lower oxidation state of titanium and, if so, to characterize this state in so far as possible by spectroscopic methods.

Optical spectra in the visible and near-infrared regions (approximately 400 to 2500 nm) were measured at 900°C with Cary 14H high-temperature spectrophotometers. The melts were contained in diamond-windowed cells with graphite bodies inside a gastight chamber under purified argon.³ The solvent melt was LiBO_2 - NaBO_2 (67-33 mole %) to which was added a total of 1.0 mole % titanium in the form of TiO_2 , or titanium metal, or mixtures of these substances in various proportions.

It was found that the coloration of these melts is associated with a spectrum consisting of a broad band with a maximum at about 18.0 kK (1 kK = 1000 cm^{-1}) and a broad, well-formed shoulder at about 10.5 kK. This spectrum is attributed to Ti^{3+} coordinated to oxide ions in a geometry that has two different titanium-oxygen distances. The most probable coordination geometry is that of an octahedron with a large tetragonal distortion. The two absorption bands arise from electronic transitions between states of the $3d^1$ configuration of Ti^{3+} split by the ligand field.⁴

The concentration of Ti^{3+} was different for melts of different starting compositions and changed slowly over periods of many hours. For systems that contained Ti^{4+} but not titanium metal, relatively low

concentrations of Ti^{3+} were formed. Possible reduction reactions for this process include

When titanium metal was present, the following reaction occurred:

For this reaction the presence and relative partial pressure of sodium in the gas phase were monitored by photometric measurement of its resonance absorption lines at 16.956 and 16.973 kK.

In all cases most of the reaction took place within the 3- to 7-hr period before the first spectrum was measured. Thereafter the Ti^{3+} concentration changed at a much slower rate, and the direction of change (increase or decrease) depended on the starting composition. These slow changes are attributed to heterogeneous reactions involving the possible formation of insoluble boride, carbide, or oxycarbide phases.

1. Research sponsored by the U.S. Bureau of Mines under interagency agreement with ERDA.

2. Visiting scientist from Kenyon College, Gambier, Ohio.

3. L. M. Toth, J. P. Young, and G. P. Smith, *Anal. Chem.* **41**, 683 (1969); L. M. Toth and L. O. Gilpatrick, *J. Phys. Chem.* **77**, 2799 (1973).

4. C. R. Kurkjian and G. E. Peterson, *Phys. Chem. Glasses* **15**, 12 (1974); A. Paul, *J. Mater. Sci.* **10**, 692 (1975).

7.2.7 Hydrogen Reduction of UF_4 in Molten Fluoride Solutions¹

L. O. Gilpatrick L. M. Toth

The H_2 reduction equilibrium of UF_4 ,

has been measured in selected molten fluoride solutions from 500 to 800°C. Absorption spectrophotometry was used to determine UF_3 and UF_4 concentrations in equilibrium with a gas mixture containing HF in approximately 1 atm H_2 . By measuring all components as a function of temperature and melt composition, equilibrium quotient expressions for the reduction

$$\log_{10} Q^R = [\text{UF}_3][P_{\text{HF}}]/[\text{UF}_4][P_{\text{H}_2}]^{1/2} = a - (b/T)$$

have been obtained, where $a = 3.771, 3.587, 3.133$ and $b = 8900, 8225$, and 7296 for the $\text{LiF}-\text{BeF}_2$ solutions of 66-34, 57-43, and 48-52 mole % respectively. For an $\text{LiF}-\text{BeF}_2-\text{ThF}_4$ (72-16-12 mole %) solution, $\log_{10} Q^R = 3.952 - 9183/T$, where Q is in $\text{atm}^{1/2}$. These data are shown in Fig. 7.8. By defining the standard state for each solute so that its activity coefficient is unity when it is present in very low concentration in $\text{LiF}-\text{BeF}_2$ (66-34 mole %), activity coefficient ratios, $\gamma_{\text{UF}_4}/\gamma_{\text{UF}_3}$, for the other solvents have been calculated from the above expressions. These data have extended previous activity coefficients over wider temperature and solvent ranges.

1. Abstract of a paper in press in *J. Inorg. Nucl. Chem.*

Fig. 7.8. Equilibrium quotients for hydrogen reduction of UF_4 in selected molten fluoride solvents.

8. Environmental Chemistry

8.1 THE GLOBAL CARBON DIOXIDE PROBLEM¹

C. F. Baes, Jr. J. S. Olson³
H. E. Goeller² R. M. Rotty⁴

The concentration of carbon dioxide in the atmosphere has increased steadily from the preindustrial value of about 295 ppm in 1860 to the current value of 330 ppm. Since the beginning of accurate and regular measurements in 1958, the increase has accounted for about 50% of the carbon dioxide released by the burning of fossil fuels—currently the latter is 5×10^9 metric tons of carbon per year. The remainder of the flux from the burning of fossil fuel has been balanced by the take-up of carbon dioxide in the oceans and/or the land biota; but since many of the pools and fluxes of the carbon cycle are large compared with the fossil carbon flux, it is not clear how the carbon cycle has accomplished this. Yet many of these pools and fluxes are in turn dwarfed by the economic reserves of fossil fuel (perhaps 7400×10^9 tons of carbon). If the growth in the production of carbon dioxide from fossil fuels (typically 4% per year) continues, an appreciable fraction of this reserve could be consumed in the next 100 years, and the resulting atmospheric concentration of CO_2 could reach several times its preindustrial value. Estimates of the consequent warming (greenhouse) effect indicate increases in the average surface temperature of the earth that range from possibly acceptable to catastrophic. Clearly it is necessary to foresee more accurately the consequences of the continued use of fossil fuels by: (1) learning more of the carbon cycle (particularly ocean circulation, the effect of CO_2 on photosynthesis, and the effect of changing patterns of land use) in order to judge how the airborne fraction of the fossil carbon flux will change in the future; (2) most importantly, learning more about the climatic (particularly regional) effects of increased atmospheric CO_2 through a greatly increased and integrated climate study effort; and (3) learning how to predict the full impact of a given change in regional climate on man, his environment, and his society.

Only then can we judge how rapidly we can safely use our fossil fuel reserves.

1. This is an abstract of a report (ORNL-5194, August 1976) of an ad hoc committee appointed by A. Zucker to examine the present state of knowledge, what is presently being done, and what more needs to be done to assess the effects of increasing atmospheric carbon dioxide.

2. Program Planning and Analysis Office, ORNL.

3. Environmental Sciences Division, ORNL.

4. Institute for Energy Analysis, ORAU.

8.2 KINETIC MODEL FOR PREDICTING THE COMPOSITION OF CHLORINATED WATER DISCHARGED FROM POWER PLANT COOLING SYSTEMS

M. H. Lietzke

A kinetic model has been developed to predict the composition of chlorinated fresh water discharged from power plant cooling systems. This program should be useful in assessing the environmental impact of such water discharged from existing or proposed plants. The major concern is the toxic nature of the inorganic and organic chloramines that may persist for hours or even days in the waters of a river or estuary.

The model as formulated takes into account the forward and reverse rates of chemical reactions leading to the formation of monochloramine, dichloramine, and organic chloramine (modeled by methyl chloramine). In addition to these three equations, the model also includes a differential equation for the irreversible uptake of chlorine in satisfying the chlorine demand of the water. Input to the computer program consists of the operating characteristics of the cooling system and the chemical composition of the water (amounts of inorganic and organic nitrogen, chlorine demand, pH, and temperature). Output consists of the amounts of the chloramines and total residual chlorine in the

discharge water. A complete description of the model and a listing of the computer program are included in ORNL/NUREG-13.

Attempts are being made to obtain field data from an operating power plant for verification of the model.

8.3 COPRECIPITATION OF CADMIUM WITH CALCITE

G. Slocum¹ C. F. Baes, Jr.

A preliminary investigation has been made of the coprecipitation of Cd^{2+} with CaCO_3 (calcite) from aqueous 0.5 M chloride, to explore the mechanism involved and determine the potential application as a water treatment to remove cadmium. The mechanism of coprecipitation is expected to involve formation of a $(\text{Cd-Ca})\text{CO}_3$ solid solution. The following exchange equilibrium should apply:

with the equilibrium quotient

$$Q = \frac{[\text{Ca}^{2+}]X_{\text{CdCO}_3}}{[\text{Cd}^{2+}]X_{\text{CaCO}_3}} \quad (2)$$

and the equilibrium constant

$$K = Q \frac{g_{\text{Ca}^{2+}} \gamma_{\text{CdCO}_3}}{g_{\text{Cd}^{2+}} \gamma_{\text{CaCO}_3}}, \quad (3)$$

where $[i]$ and g_i are aqueous ion concentrations and activity coefficients, and X_i and γ_i are component mole fractions and activity coefficients in the solid solution. The available formation free energies give

$$K \sim 800 \quad (298^\circ \text{K}).$$

The first measurements, involving precipitation by stepwise addition of Na_2CO_3 to aqueous mixtures of CdCl_2 and CaCl_2 , gave a Q value of about 14. But analysis of the results was complicated because the composition of the precipitate changed continuously during the course of the experiment, perhaps producing changes in γ_{CdCO_3} and γ_{CaCO_3} , and therefore in Q . Also, recrystallization would alter the apparent value of Q . The latter effect suggests that $Q = 14$ is the lower limit for the range of solid composition involved (Fig. 8.1).

Subsequent experiments involved the slow removal of CO_2 from a nearly saturated $(\text{Cd}^{2+}-\text{Ca}^{2+})\text{CO}_3^{2-}$ solution, causing a partial precipitation

during which the $\text{Cd}^{2+}/\text{Ca}^{2+}$ ratio in each phase changed little. The results are summarized in Fig. 8.1. The error limits reflect uncertainties from the composition changes that did occur; the scatter of the data probably arises from analytical uncertainties. The results have been represented by the expression

$$\ln Q = 3.0X_{\text{CdCO}_3} + 3.2. \quad (4)$$

This gives for each activity coefficient in the solid phase,

$$\log \gamma_i = 1.5X_i^2. \quad (5)$$

If this representation is approximately correct, then

$$K = 110 \cdot g_{\text{Ca}^{2+}}/g_{\text{Cd}^{2+}}.$$

Combined with the estimate of $K \cong 800$, this suggests that the ratio $g_{\text{Cd}^{2+}}/g_{\text{Ca}^{2+}} \sim 0.14$, which is consistent with the stronger complexing of Cd^{2+} by chloride ion.

The values of Q should increase with decreasing chloride concentration. They are large enough to suggest that Cd^{2+} can be scavenged quite effectively by CaCO_3 precipitation, or recrystallization.

1. Great Lakes College Association-Oak Ridge Science Semester Participant, fall 1975.

Fig. 8.1. Variation of exchange quotient Q [Eq. (2)] with mole fraction of CdCO_3 in the calcite phase.

(Bio)

9. Biophysical Chemistry

9.1 PHOSPHORESCENCE QUENCHING OF POLY rA AT 77 K

R. M. Pearlstein F. Van Nostrand¹

We have been interested in the nucleic acids as model systems for the study of exciton transport and trapping. Last year we reported the results of a study also done at 77 K of fluorescence quenching, that is, singlet excitation transfer, in a system consisting of polyriboadenylic acid (poly rA) with bound dye in an aqueous medium containing glucose and sodium acetate.² The results showed that one molecule of either of the dyes proflavine or ethidium bromide per ~100 adenine bases in the poly rA reduces the observed fluorescence intensity to half the value it has for dye-free poly rA. However, these fluorescence quenching studies did not allow us to distinguish between two possible mechanisms for the excitation transfer: (1) one-dimensional exciton transport through the system of stacked bases in the polymer, with subsequent trapping of the exciton's energy at the site of an intercalated dye molecule; (2) direct transfer through space from base to dye by inductive resonance (Förster mechanism). These two possibilities are closely related to polymer conformation. Mechanism 1 requires a well-ordered helix; mechanism 2 requires a highly folded configuration with, at most, short well-stacked regions. Thus, if mechanism 1 applies, the system is useful as the originally intended model system; if 2 applies, new methods of study might be developed for the compact nucleic acid conformations found in chromosomes, ribosomes, or materials derived from them. To resolve this question of mechanism, we undertook the study whose results we now report.

Because the transfer of triplet-state excitation energy, unlike that of singlet-state, depends on intermolecular orbital overlap, triplet exciton migration in a nucleic acid is much more sensitive to the degree of base stacking than is singlet. It is known from experiments on the quenching of phosphorescence by metal ions that at 77 K, triplet excitons can migrate over at least 100 bases in well-stacked poly rA.³ We

therefore studied both dye and metal-ion quenching of poly rA phosphorescence.

Samples were prepared as described previously.^{2,4} All measurements were done at 77 K with a frequency-quadrupled Nd:YAG laser ($\lambda = 266$ nm) as excitation source. The laser was pulsed (width = 0.1 to 0.2 μ sec) at ~70 Hz. Phosphorescence was observed through a monochromator or an interference filter and detected by photon counting with a cooled photomultiplier. Gated pulse-handling electronics was used to exclude prompt fluorescence and to monitor and correct for laser intensity fluctuations. For time-dependent measurements, the sample was pulsed enough times to achieve a steady state; then the excitation was shuttered off, and the phosphorescence counts were stored in a 1024-channel analyzer used in its multiscaling mode.

Although our kinetic analysis is based primarily on poly rA phosphorescence, we checked that the dye-acceptor state is the singlet, rather than the triplet, by observing that the delayed fluorescence of the dye has complementary kinetics to that of the poly rA phosphorescence. The metal ions used, Co^{2+} or Mn^{2+} , quench only the poly rA triplet, not the singlet, and are themselves nonluminescent.

We find that ethidium bromide half-quenches the poly rA phosphorescence at a concentration of about one dye molecule per 200 bases, proflavine at about one per 500 bases, Co^{2+} at about one per 40 bases, and Mn^{2+} at about one per 25 bases. With metal-ion quenching, the decay of phosphorescence is essentially exponential with a lifetime, $\tau = 2.5$ sec, the same as that of unquenched poly rA, independent of the ratio of metal ions to bases. With dye quenching, the poly rA phosphorescence decay is markedly non-exponential, the rate of decay depending sensitively on dye type and on $[\text{dye}]/[\text{base}]$ as well as on time following excitation.

These results are much easier to explain by invoking mechanism 2 rather than 1. First, there is the observation that although the fluorescence is quenched with equal effectiveness by either dye, proflavine is more than twice as effective as ethidium

bromide at quenching phosphorescence. Thus, if there is one-dimensional triplet exciton migration it cannot be diffusion limited. But the metal-ion quenching results indicate a more limited range of triplet excitation migration in our poly rA system than in poly rA that is known to be well stacked. In the latter it is believed that trapping of the triplet excitation on bases at stacking faults limits the exciton range.^{3,5} If this is so, it is plausible that in our solvent, poly rA has more such faults, that is, has shorter well-stacked regions and is therefore more highly folded, than poly rA in solvents that form glasses at 77 K.^{3,5}

This view is reinforced by comparing the time-dependent results for dyes and metal ions.⁶ Our time-dependent results for metal-ion quenching are similar to those found in studies of well-stacked poly rA—on a time scale of milliseconds or longer the decay is exponential regardless of $[\text{ion}]/[\text{base}]$. This has previously been interpreted to mean that the competition between metal ion and host trap for the triplet exciton occurs on a much shorter time scale; if the host trap (an adenine base) “wins,” phosphorescence proceeds as in the unquenched situation, and if the metal ion wins there is no phosphorescence. The variant results for the dyes would imply that the dyes are able to quench triplet excitation directly from host trap sites. Why can the metal ions not do so? The answer is that the value of R_0 , the critical distance for excitation transfer from donor to acceptor by the Förster mechanism, is much greater for the dyes than for the metal ions. We estimate R_0 to be about 34 Å for transfer of the poly rA triplet to the ethidium bromide singlet, and about 49 Å for transfer to the proflavine singlet. For poly rA triplet transfer to Co^{2+} , R_0 is estimated to be about 11 Å, and about 4 Å for transfer to Mn^{2+} (ref. 7). Recalling that the transfer rate depends on R_0^6 , one sees that direct Förster transfer of the poly rA triplet to the less efficient of the two dye quenchers proceeds nearly a thousand times faster at any given distance than it does to the more efficient of the two metal-ion quenchers.

9.2 ANALYSIS OF TIME-DEPENDENT TRIPLET ENERGY TRANSFER FROM POLY rA TO BOUND DYE

R. M. Pearlstein¹ F. Van Nostrand¹
J. A. Nairn²

Polyriboadenylic acid (poly rA), a single-stranded nucleic acid polymer, apparently collapses into a folded conformation when frozen in an aqueous medium containing sodium acetate and glucose.³ In this conformation, singlet or triplet electronic excitation energy of the adenine bases in the polymer efficiently transfers to singlet states of bound dyes, with $[\text{dye}]/[\text{base}] = 1\%$ or less, by a direct process presumed to be the Förster mechanism.^{3,4} In this report we present quantitative evidence that the process *does* occur by the Förster mechanism, and give the value of parameters deduced from the fit of a theoretical model to the data.

The theoretical model was first proposed by Förster himself,⁵ and later slightly generalized by Eisinger and Siegel.⁶ This “FES” model was originally used to describe donor-acceptor excitation transfer between molecules in solution. Its two principal assumptions are that there is irreversible Förster transfer from each donor to acceptors, and that donors and acceptors are distributed randomly. The first assumption is well satisfied by our system, the second one approximately so if the individual poly rA strands are sufficiently compact. In the FES model the time decay of the quenched donor excited state in response to instantaneous excitation is given by

$$S(t) = S_0 \exp \left[- (t/\tau_D) - 1.4991 c(t/\tau_D)^{1/2} \right], \quad (1)$$

where τ_D is the unquenched donor state lifetime, and the reduced concentration is given by

$$c = (4\pi/3) \bar{R}_0^3 c_A, \quad (2)$$

in which c_A is the acceptor concentration, and the “actual” Förster critical distance⁷ is

$$\bar{R}_0 = (\phi I_{ov}/n^4)^{1/6}. \quad (3)$$

In Eq. (3), ϕ is the emission quantum yield of unquenched donor state per excited donor state, I_{ov} is the normalized spectral overlap integral of donor emission with acceptor absorption, and n is the refractive index of the medium.

Experimentally, our objective was to test the fit of the phosphorescence decay at 77 K of poly rA with bound dye both as a function of time and relative acceptor concentration,

1. Consultant.

2. *Chem. Div. Annu. Prog. Rep. Nov. 1, 1975*, ORNL-5111, p. 93.

3. J. Eisinger and R. G. Shulman, *Proc. Natl. Acad. Sci. U.S.A.* 55, 1387 (1966).

4. F. Van Nostrand and R. M. Pearlstein, *Chem. Phys. Lett.* 39, 269 (1976).

5. P. Szerenyi and H. H. Dearman, *J. Chem. Phys.* 58, 2467 (1973).

6. See sect. 9.2 of this report for a detailed analysis of the dye results.

7. M. Guéron and R. G. Shulman, *Annu. Rev. Biochem.* 37, 571 (1968).

$$r = c_A / c_D, \quad (4)$$

where c_D is the donor concentration. Here, c_A = [dye], and c_D = [base], where "base" designates the adenine bases of the poly rA. The experiments were performed with samples prepared as described previously,⁴ and using the pulsed laser excitation, pulse-handling electronics, and multiscaler also mentioned earlier,³ but with several important modifications. Equation (1) holds only when the donors are initially excited randomly with respect to the acceptors.⁶ In our earlier time-dependent work³ the sample was pulsed repeatedly until the phosphorescence achieved a steady state, a condition in which donors far from acceptors are preferentially excited. This did not matter in the earlier studies, since we were not interested then in quantitative details of the decay. For purposes of this study, however, such a steady-state initial condition leads to great complications in the comparison of theory and experiment because Eq. (1) must be replaced by a much less tractable expression.⁶ On the other hand, a steady-state initial condition is much easier to deal with experimentally, because the sample emits much more light than it does when excited by a single brief pulse of light. To perform the present experiments we therefore found it necessary to excite the sample with a single laser flash (0.1 μ sec duration), detect the poly rA phosphorescence through an interference filter with a cooled, long-wavelength-sensitive photomultiplier in a geometry having a large numerical aperture, allow the phosphorescence to decay for approximately half a minute while accumulating data, and then reexcite the sample with a second flash. This process was repeated ten or more times on a given sample, and the data were summed electronically in order to obtain adequate signal/noise ratios; close synchronization of laser flashes with the multiscaler start signal is essential in this procedure.

The data were analyzed by computer. Information from supplementary experiments was used to correct for the slight nonexponentiality of unquenched poly rA phosphorescence and for rapidly decaying background glow. The corrected data fit Eq. (1), within experimental error, over at least two orders of magnitude in time and approximately one order in fractional dye concentration for each of the two dyes, ethidium bromide and proflavine. Defining a quantity $Q \equiv c/r$, one sees from Eqs. (2) and (4) that Q is independent of both r and c_A . Since c_D should be constant for the two dyes, it follows from the definition of Q and Eq. (3) that the ratio of Q values for the two dyes should equal the square root of the corresponding ratio of overlap integrals if the FES model applies to our system. For the Q -value ratio we find 3.56 ± 0.26 , and for the square root of the ratio of overlap integrals we calculate 3.07 ± 0.46 .

By estimating the values of refractive index and phosphorescence yield, one can obtain from Eqs. (2), (3), and (4) a value of c_D and hence the volume per nucleotide, c_D^{-1} , in the compact structure. Assuming $n = 1.33$ and $\phi = 1$, we find $c_D^{-1} \approx 2000$ Å. For comparison, this value is about ten times the volume per nucleotide in completely stacked poly rA. If our estimate is anywhere near correct, we can conclude that the poly rA in our frozen solvent, while partially folded, is not as compact as is theoretically possible.

1. Consultant.
2. ORAU Summer Student Trainee.
3. See sect. 9.1 of this report.
4. *Chem. Div. Annu. Prog. Rep. Nov. 1, 1975*, ORNL-5111, p. 93; F. Van Nostrand and R. M. Pearlstein, *Chem. Phys. Lett.* 39, 269 (1976).
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10. Nuclear Chemistry

10.1 FRAGMENT MASS AND KINETIC-ENERGY DISTRIBUTIONS FROM THE SPONTANEOUS FISSION OF ^{252}No

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Pre-neutron-emission fragment mass and total-kinetic-energy distributions and the mass-energy correlations in the spontaneous fission (SF) decay of 2.30-sec ^{252}No have been deduced from measured energies of coincident fission fragment pairs, using silicon surface-barrier detectors. The ^{252}No for these measurements was produced in the $^{241}\text{Am}(^{15}\text{N},4n)$ reaction at the ORIC and deposited on 40- $\mu\text{g}/\text{cm}^2$ carbon foils, using a helium jet technique. Five such carbon foil collectors were located on the periphery of a remotely controlled wheel and stepping-motor unit and, following a 5-sec bombardment and reaction-product-collection period, the collection foil was rotated between a pair of 2- cm^2 surface-barrier detectors.

From an analysis of 154 correlated fission fragment events, pre-neutron-emission fission fragment kinetic energies and masses were deduced. The fission fragment mass distribution and average total-kinetic-energy distribution ($\langle\text{TKE}\rangle$) as a function of fragment mass are shown in Fig. 10.1. The fragment average total kinetic energy is 202.4 ± 1.2 MeV, and average light- and heavy-fragment masses (pre-neutron) are 110.1 ± 0.9 and 141.0 ± 0.9 amu respectively. The mass distribution, decidedly asymmetric, is similar to that observed for ^{252}Cf spontaneous fission, although a maximum in the $\langle\text{TKE}\rangle$ curve as a function of fragment mass occurs for near-symmetric mass divisions as it does for the heavier isotopes of fermium. The measured SF-decay branching fraction for ^{252}No is $26.9 \pm 1.9\%$, and the

Fig. 10.1. Pre-neutron-emission fragment-mass distribution (lower curve) and average total-kinetic-energy distribution ($\langle\text{TKE}\rangle$) as a function of fragment mass (upper curve) obtained for the spontaneous fission of 2.30-sec ^{252}No .

measured total half-life is 2.30 ± 0.22 sec. A complete description of these experiments, a comparison of measured and deduced fission characteristics for ^{252}No with those for the Cm, Cf, and Fm nuclides, and the implications of these results on the current theoretical understanding of the spontaneous fission process have recently been reported.³

1. Physics Division.

2. Physics Division, retired.

3. C. E. Bemis, Jr., R. L. Ferguson, Franz Plasil, R. J. Silva, Frances Pleasonton, and R. L. Hahn, *Phys. Rev. C* 15, 705 (1977).

10.2 PRODUCTION, IDENTIFICATION, AND THE ALPHA- AND SPONTANEOUS-FISSION DECAY CHARACTERISTICS OF THE NUCLIDE $^{262}\text{105}$

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The nuclide $^{262}\text{105}$, the second heaviest nuclide known, has been produced in the $^{249}\text{Bk}(^{18}\text{O},5n)$ reaction using 100-MeV ^{18}O ions at the ORIC. Separate but related experiments were performed in order to provide (1) an unambiguous elemental and mass identification via the x-ray and genetic-linkage techniques, (2) information on the alpha and spontaneous fission decay properties of $^{262}\text{105}$ as well as the possible electron-decay branching to the unknown nuclide $^{262}\text{104}$, and (3) details of the mass- and kinetic-energy distributions associated with the spontaneous fission of $^{262}\text{105}$ and/or $^{262}\text{104}$ via the coincident fragment double energy method.

The alpha-particle energy spectrum for reaction products produced in the $^{249}\text{Bk} + ^{18}\text{O}$ reaction at 100 MeV is shown in Fig. 10.2 for the time interval $0.2 \leq t(\text{sec}) \leq 80$ following bombardment and for the 8.44- and 8.66-MeV groups associated with the decay of $^{262}\text{105}$. The decay of these particular alpha-particle groups is shown in Fig. 10.3, and we have derived a half-life of 34.1 ± 4.6 sec for $^{262}\text{105}$ by least-squares fitting procedures. The half life, alpha-particle energies, and relative intensities are in agreement with previous determinations.³ A direct time-correlated genetic linkage with the alpha groups ascribed to $^{262}\text{105}$ and those of the alpha-decay daughter, 4.2-sec

Fig. 10.2. Alpha-particle energy spectrum for products produced in the reaction of 100-MeV ^{18}O ions with ^{249}Bk in the time interval $0.2 \leq t(\text{sec}) \leq 80$ following bombardment.

Fig. 10.3. Decay of alpha-particle events with energies in the range $8.40 \leq E(\text{MeV}) \leq 8.75$, that is, those ascribed to the decay of $^{262}\text{105}$.

^{258}Lr , was observed and provides the basis for the unambiguous mass and elemental identification.

Fission events arising in the decay of 2.6-hr ^{256}Fm , also a product of the $^{249}\text{Bk} + ^{18}\text{O}$ reaction, were a source of interference in our fission studies, but it was possible to discriminate against these events by selecting those time periods during the experiment when the interference was minimal. The decay of fission events for these selected experimental time periods is shown in Fig. 10.4, and a half-life of 32.6 ± 6.5 sec was derived. The spontaneous fission branching decay fraction for $^{262}\text{105}$ is $71 \pm 5\%$ with alpha decay the remainder. We have assigned the observed spontaneous fission events to the direct decay of $^{262}\text{105}$, although possible electron-capture decay of $^{262}\text{105}$ to $^{262}\text{104}$, which would decay via spontaneous fission, would be indistinguishable. However, we are able to place an upper limit of $\sim 5\%$ on the electron-capture branching decay of $^{262}\text{105}$ from the absence of L- or K-series x rays of $Z = 104$ preceding fission if the half-life of the daughter, $^{262}\text{104}$, is ≤ 200 μsec .

Fig. 10.4. Decay of fission activity observed in the $^{249}\text{Bk} + ^{18}\text{O}$ reaction at 100 MeV. The 32.6-sec component is ascribed to the decay of $^{262}\text{105}$.

Analyses of the kinetic-energy distributions from coincident fragment pairs are continuing, and a clear preference for mass asymmetric division is observed; no indications of the enhanced total-kinetic-energy effect for $^{262}\text{105}$ as previously predicted⁴ were observed, and the mass-energy distributions for $^{262}\text{105}$ are nearly indistinguishable from those of ^{256}Fm , also observed in these experiments. More definitive analyses designed to yield more detail regarding the fission fragment mass distributions are being performed.

1. Physics Division.
2. Radiochemistry Division, Lawrence Livermore Laboratory.
3. A. Ghiorso, M. Nurmiä, K. Eskola, and P. Eskola, *Phys. Rev. C* **4**, 1850 (1971).
4. H. W. Schmitt and U. Mosel, *Nucl. Phys. A* **186**, 1 (1972).

10.3 SEARCHES FOR SUPERHEAVY ELEMENTS IN NATURE

A systematic search for superheavy elements in nature and in accelerator targets has been carried out in the Chemistry Division in recent years.¹ During 1976, interest in this field increased greatly as the result of a report by Gentry et al.² of evidence for superheavy elements in giant halo inclusions found in biotite mica. The possible presence of several elements, $Z = 116, 124, 126$, and 127 , in enigmatic halos was indicated in the x-ray emission spectra induced by proton bombardment. Evidence for the presence of $Z = 126$ "generated a high level of confidence"² and seemed especially persuasive in light of theoretical predictions of stability of the doubly magic nucleus $^{310}_{184}126$.³ The concentration of stable superheavy elements seemed to be very high, some 100 pg or 10^{11} atoms in the roughly 10^{16} atoms constituting an average grain of monazite distinguished by a halo.

The following sections summarize our recent efforts to find superheavy elements in nature and, especially, to confirm the claims made in ref. 2.

10.3.1 Are There Superheavy Elements in Giant Halo Inclusions? A Search with Synchrotron Radiation

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H. L. Yakel ⁴	E. Ricci ⁷
S. Raman ⁵	D. L. Holcomb ⁸
R. V. Gentry ⁶	A. J. Millet ⁹

In further examination of giant and regular halo inclusions and other potentially promising samples, we excited characteristic x rays of the constituent

atoms with photons emitted by the Stanford electron storage ring. With this radiation source tuned with a broad-band x-ray monochromator, we had several advantages over the earlier experiment based on proton excitation.² Most significant among these advantages were (1) the possibility of a unique correlation between the observed x-ray emission line and its excitation energy (or binding energy of the level from which it originates) and (2) the large cross section for producing an $L\alpha$ x ray of $Z = 126$. As illustrated in Fig. 10.5, a line observed at 27.3 keV could be coming from $Z = 126$ or tellurium at an excitation energy of $h\nu = 37$ keV, but would have to be assigned to tellurium if the photon energy were dropped below the L_3 level energy of $Z = 126$. The x-ray production cross sections $\sigma_{L\alpha}$ of $Z = 126$ for 5.7-MeV protons as used in ref. 2 and for 37.5-keV photons are displayed in Table 10.1 and compared with those of thorium, a major constituent of the

Table 10.1. Extrapolated $L\alpha$ x-ray production cross sections (barns) for 5.7-MeV protons and 37.5-keV photons (see ref. 10)

Z	Protons	Photons
Th	57	1180
126	7.5	4180

inclusions.¹⁰ We see that photons are more effective than protons in producing 126 $L\alpha$, but more important, that the detectability of $Z = 126$ is much enhanced under photoexcitation compared with the built-in reference, thorium. For a given number of counts for thorium $L\alpha$, photoexcitation yields about 27 times as many events for $Z = 126$ as does proton excitation, assuming a given elemental concentration.

Eleven monazite giant-halo inclusions, different from but similar in origin to the ones investigated in ref. 2, were studied. In a first experiment,¹¹ in which the hard part of the synchrotron radiation was utilized, no characteristic x-ray lines that could be associated with $Z = 126$ or other superheavy elements in the range $105 \leq Z \leq 129$ were discernible in the spectra obtained from any of the samples; specifically, no evidence was found for $Z = 126$ at concentrations of about 5×10^9 atoms per inclusion or several ppm by weight.

Giant-halo inclusion 19-D, the lone survivor of the samples originally studied by the proton excitation technique,² was reexamined for superheavy elements in a second, improved experiment with synchrotron radiation. One of the spectra obtained from this halo, which proved by visual inspection under the microscope to be unimpaired by the previous proton bombardment, is shown in Fig. 10.6 and compared with the proton-excited spectrum (labeled FSU) of ref. 2. Although a detailed analysis of the data for sample 19-D and a variety of other terrestrial and meteorite samples has not been completed yet,¹² inspection of Fig. 10.6 provides a quick semiquantitative, postexperimental assessment of the investigation. Whereas there is a definite peak in the FSU data at the predicted position for 126 $L\alpha$, no structure is superimposed on the background of our data, suggesting the absence of the superheavy element with $Z = 126$ at a much lower level of concentration than indicated by the FSU data. As pointed out above, our experiment is 25 to 30 times more sensitive for 126 $L\alpha$

Fig. 10.5. Illustration of the relationship between the energies of x-ray emission lines and their excitation energies. Note the possibility of eliminating La $K\alpha$ by using 37- to 38-keV photons for excitation and the possibility of separating Te $K\alpha$ from 126 $L\alpha$ by varying the excitation energy across the 126 L_3 subshell.

Fig. 10.6. Comparison of x-ray spectra from sample 19-D excited by 5.7-MeV protons (FSU) or by 37.5-keV photons (our data).

relative to thorium $L\alpha$ than that of Gentry et al.;² and as seen in our data of Fig. 10.6, a higher count in thorium L and a lower background around 27 keV also favor the detectability of $Z = 126$. The question of the peak at 27.2 keV in the FSU data has been addressed in the meantime by some of the original researchers. They discovered on careful scrutiny¹³ that under proton bombardment a gamma ray of nearly identical energy as that predicted for 126 $L\alpha$ is produced by the $^{140}\text{Ce}(p, n\gamma)$ nuclear reaction.

10. Cross sections for protons extrapolated from C. V. Barros Leite, N. V. de Castro Faria, and A. G. de Pinho, *Phys. Rev. A* 15, 943 (1977); cross sections for photons taken from M. O. Krause, C. W. Nestor, Jr., C. J. Sparks, Jr. and E. Ricci (to be published).

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13. J. D. Fox, W. J. Courtney, K. W. Kemper, A. H. Lumpkin, N. R. Fletcher, and L. R. Medsker, *Phys. Rev. Lett.* 37, 629 (1976).

10.3.2 Separation of Superheavy Element Fractions from Madagascar Rock Samples

R. J. Silva J. H. Oliver

If the monazite inclusions in the giant halos contain superheavy elements at concentrations of about 100 ppm,¹ then one might expect, since the inclusions probably came from the surrounding material, to find similar concentrations in the bulk monazite-bearing rocks from the same region of Madagascar. Processing of 100-g samples of these rocks could then lead to microgram quantities of superheavy elements. Eleven rock samples of several hundred grams each, all from the Chaines Anosyen-

1. See, for example, *Chem. Div. Annu. Prog. Rep. Nov. 1, 1975*, ORNL-5111, pp. 73-75.

2. R. V. Gentry, T. A. Cahill, N. R. Flocchini, H. C. Kaufmann, L. R. Medsker, J. W. Nelson, and R. G. Flocchini, *Phys. Rev. Lett.* 37, 11 (1976).

3. A recent review on theoretical and experimental developments in the quest of extending the periodic chart has been given by C. E. Bemis and J. R. Nix, LA-UR-77-223 (1977), to be published in *Comments on Nuclear and Particle Physics*.

4. Metals and Ceramics Division.

5. Physics Division.

6. Columbia Union College, Takoma Park, Md.

7. Analytical Chemistry Division.

8. General Engineering Division.

9. Instrumentation and Controls Division.

nes region in southern Madagascar, were made available for processing by R. V. Gentry.

The elements starting with 121 belong to a long transition series resulting from the simultaneous filling of the 6f and 5g electron shells.² Estimates of oxidation potentials from relativistic Hartree-Fock and Dirac-Fock calculations of electron binding energies suggest that the $8s_{1/2}^2$, $8p_{1/2}^2$, and $6f_{3/2}^2$ electrons will be involved in the formation of ions in solution for the early "superactinides." There is some similarity with the early actinides where the $7s_{1/2}^2$, $6d_{3/2}^2$, and $5f_{3/2}^2$ electrons are involved, though the ionic radii of the superactinides are predicted to be appreciably larger. We might expect the chemistry of the early superactinides to be similar to that of the trivalent actinides, the tetravalent thorium or plutonium, or the hexavalent uranium, depending on conditions.

Crouse and Brown have reported a method for extracting thorium, uranium, and the rare earths from monazite sands, using sulfuric acid digestion followed by amine extraction.³ Figure 10.7 shows schematically the separation developed for the rock processing to lead to the three fractions U, Th + Pu, and R.E.

To date, two composite rock samples of 100 g each have been processed. Analysis of the samples before and after processing indicates an overall recovery of ~70% for U, Th, and R.E. Small portions of these processed samples have been counted for alpha and spontaneous fission events, but no activity over that from the products of the uranium and thorium natural decay chains has been detected.

Due to the relatively large amounts of Th, U, and R.E. in the present fractions, it is not possible to conduct a very sensitive test for the presence of superheavy elements. Further isolation of a pure superheavy element fraction is necessary. The predicted larger ionic radii for these elements seem well founded and could be the basis for an ion exchange column separation scheme.

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2. B. Fricke, *Structure and Bonding*, ed. J. D. Duntz et al., Springer-Verlag, Berlin, 1975, vol. 21, p. 89.

3. D. J. Crouse and K. B. Brown, *Recovery of Thorium, Uranium, and the Rare Earths from Monazite Sulfate Liquors by the Amine Extraction Process*, ORNL-2720 (July 1959).

ORNL - DWG. 77-8530

Fig. 10.7. Flow diagram for processing of Madagascan rock.

10.3.3 Search for Superheavy Element Neutron Emission in Monazites

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R. W. Stoughton J. Halperin

We have continued to examine natural samples with our neutron multiplicity counter,^{1,2} since high multiplicities ($\bar{\nu} \sim 10$ emitted neutrons per fission) would strongly suggest the existence of superheavy elements.^{3,4} We have recently been particularly interested in monazite minerals, since they are lanthanide ores which contain the actinides, thorium and uranium. Presumably they would contain any of the 15 superactinides, beginning with element 121, that might exist in nature and possibly those elements involving 5g electrons. Samples included monazite-bearing materials from Australia, Malaysia, South Africa, Madagascar, and the state of Georgia.⁵ The two samples of monazite-containing ore from Madagascar⁶ were from the same ore body as the giant halo inclusions of Gentry et al.⁷

We measured 500 g of each of the four monazite sands and the two samples from Madagascar in our improved neutron-multiplicity counter.² We then made a systematic study of the major corrections to the data due to the effects of uranium spontaneous fission, muon reactions with elements of high Z (largely rare earths and thorium), and neutron absorption by some of the rare earths (mainly Sm and Gd).

The discrete multiplicities through 7 and all ≥ 8 were recorded, but because of the small number of events with high multiplicity we have shown a single entry for those ≥ 5 . Because single-neutron events are

produced in large numbers by several processes [e.g., (γ, n) , (α, n)], it is not useful to evaluate multiplicities of one in terms of fission. Table 10.2 gives one an idea of the magnitudes of the corrections for Georgia monazite as a detailed example. The errors shown are standard deviations which result from propagating all counting errors and uncertainties in chemical analyses. Table 10.3 gives the gross counting rates and the corrected rates for the other five monazites. We conclude that the results are negative in all these cases, based on an uncertainty of twice the standard error.

Because the possible discovery of superheavy elements was reported⁷ for monazite inclusions from the same Madagascar ore body, we wanted to put the results of Table 10.3 in more quantitative terms. We felt that the errors were better determined than the limits on the counting rates, so we assumed that twice the standard errors were upper limits on any multiplicities shown by the samples. Then, on the assumption that the probability of emitting ν neutrons was a Gaussian function of ν , we obtained a relationship between the concentration of any superheavy element present, in grams/gram, and its half-life (see Fig. 10.8). We considered an upper limit on $\bar{\nu}$ of 10 and a lower limit on $\bar{\nu}$ of 3, since calculations of Kolb⁸ indicated a low value of $\bar{\nu}$ if superheavy element decay is by ternary fission. If the concentration were as high as indicated in the original announcement,⁷ 5×10^{-5} g/g, then $T_{1/2} \geq 8 \times 10^{14}$ and $\geq 3 \times 10^{16}$ years for $\bar{\nu} = 3$ and 10 respectively. If $T_{1/2} = 4.6 \times 10^9$ years (age of solar system), the corresponding values of C must be $\leq 3 \times 10^{-10}$ and 8×10^{-12} g/g. If $T_{1/2} = 4.6 \times 10^9$ years and $C = 5 \times 10^{-5}$, sample D 7187, which contained 103

Table 10.2. Georgian monazite (500 g, 31.22 live days)

	Neutron Multiplicities			
	2's	3's	4's	≥ 5 's
Counts/live day (gross)	274.3 $\pm$ 3.0	53.3 $\pm$ 1.3	5.5 $\pm$ 0.4	0.48 $\pm$ 0.12
Corrections				
Background	14.51 $\pm$ 0.52	1.11 $\pm$ 0.14	0.09 $\pm$ 0.04	0.04 $\pm$ 0.03
U, 2.285 g	271.5 $\pm$ 8.3	56.9 $\pm$ 1.9	5.7 $\pm$ 0.3	0.25 $\pm$ 0.06
Th, 17.6 g	0.62 $\pm$ 0.09	0.22 $\pm$ 0.03	0.07 $\pm$ 0.02	0.07 $\pm$ 0.02
R.E. μ effect, 135 g	0.47 $\pm$ 0.06	0.20 $\pm$ 0.02	0.05 $\pm$ 0.01	0.04 $\pm$ 0.01
Sm + Gd neutron absorption	12.2 $\pm$ 3.6	4.3 $\pm$ 1.3	0.63 $\pm$ 0.21	0.07 $\pm$ 0.01
Corrected counts/day	-0.6 $\pm$ 9.6	-0.8 $\pm$ 2.6	0.29 $\pm$ 0.54	0.15 $\pm$ 0.14

Table 10.3. Counts/live day on other monazites (500 g each)^a

Origin	Multiplicities			
	2's	3's	4's	≥5's
Australia (1.225 g U, 29.34 live days)				
Gross	159.6 ± 2.3	29.8 ± 1.0	3.14 ± 0.33	0.44 ± 0.12
Corrected	6.6 ± 5.6	0.66 ± 1.6	0.38 ± 0.39	0.26 ± 0.14
Malaysia (1.340 g U, 10.09 live days)				
Gross	174.9 ± 4.2	33.9 ± 1.8	2.87 ± 0.53	0.10 ± 0.10
Corrected	7.4 ± 6.8	1.6 ± 2.3	-0.38 ± 0.56	-0.24 ± 0.11
S. Africa (0.540 g U, 5.96 live days)				
Gross	81.0 ± 3.7	11.6 ± 1.4	0.17 ± 0.17	0.17 ± 0.17
Corrected	5.0 ± 4.7	-2.3 ± 1.5	-1.40 ± 0.19	-0.06 ± 0.18
Madagascar (D6356, 349 g, 0.265 g U, 15.64 live days)				
Gross	34.5 ± 1.5	5.6 ± 0.6	0.38 ± 0.62	0.00
Corrected	-0.34 ± 1.9	+0.12 ± 0.8	-0.41 ± 0.2	-0.19 ± 0.05
Madagascar (D7187, 232 g, 0.348 g U, 12.85 live days)				
Gross	68.8 ± 2.2	10.4 ± 0.9	1.48 ± 0.33	0.23 ± 0.13
Corrected	+0.95 ± 2.6	-0.08 ± 0.9	+0.12 ± 0.32	-0.04 ± 0.13

^aExcept for the Madagascar samples.

Fig. 10.8. Detection limits for the Madagascar monazite samples, for $\bar{\nu}$ values of 3 and 10. For a given value of C , the plot gives a minimum value for $T_{1/2}$. For a given $T_{1/2}$, a concentration greater than the corresponding value of C would be detected.

g of monazite, would have produced about 4×10^6 dis/day or 10^5 times our detection limit for $\bar{\nu} = 3$, and $\sim 10^7$ times our detection limit for $\bar{\nu} = 10$.

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5. We thank W. R. Fort of Kerr-McGee Chemical Corp., Oklahoma City, and Bruce Bennett of Kerr-McGee Chemical Corp., West Chicago, for sending us these four monazite samples free of charge.
6. We thank R. V. Gentry for making these pieces of ore available to us.
7. R. V. Gentry, T. A. Cahill, N. R. Fletcher, H. C. Kaufmann, L. R. Medsker, J. W. Nelson, and R. G. Flocchini, *Phys. Rev. Lett.* 37, 11 (1976).
8. D. Kolb, to be published.

10.3.4 Search for Superheavy Elements in Other Natural Samples

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R. V. Gentry¹

Recently, Forsling² indicated that he had observed 7.8-MeV alpha particles at mass position 292, following neutron irradiation and mass separation of radiogenic ²⁰⁶Pb; also, some fission tracks were observed. He suggested that the alpha emitter (and possibly the fissioning species) might indicate the presence of a superheavy element from which the alpha emitter was formed during neutron irradiation. If this were true the superheavy element or one of its decay products should fission. We assayed 2463 g of radiogenic lead (87.9% ²⁰⁶Pb),³ and a 4050-g brick of ordinary lead in our neutron multiplicity counter. The two samples showed no difference in multiplicity counts/kg-day within counting statistical errors.

Cherdyntsev et al.⁴ mentioned finding an alpha emitter (4.4 to 4.6 MeV) in nature which was volatile from hot nitric acid solutions; Meier⁵ stated that a 4.5-MeV alpha emitter was found in small samples of osmiridium. The implication was that this activity might be eka-Os (element 108). To check whether such a species might exist and might also give rise to fission, we obtained two 1-g samples of osmiridium⁶ for neutron multiplicity counting. The samples showed a count equivalent to background.

1. Columbia Union College, Takoma Park, Md.
2. Wilhelm Forsling, Research Institute for Physics, Stockholm; letter to R. V. Gentry, Sept. 7, 1976.
3. Courtesy of Eugene Newman and H. R. Gwinn, ORNL Isotopes Separations, Chemical Technology Division.
4. V. V. Cherdyntsev, V. L. Zvenev, V. M. Kuptsov, and G. I. Kisilitsina, *Geokhimiya*, No. 4, 395 (1968).
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6. We thank J. B. Payne of the Johnson Matthey Research Center, Reading, England, for lending us the samples of osmiridium.

10.3.5 Reexamination of Reported Anomalous Alpha Radioactivity in Conway Granite

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Several years ago Adams et al.³ reported some evidence for an unidentified 4.4-MeV alpha activity in certain core sections taken from the Conway

granite in New Hampshire. A similar alpha activity had also been reported by Cherdyntsev et al.⁴ and by Brukl et al.,⁵ but in neither case was the result confirmed. Our studies were made on several sections of the same core used by Adams et al.³ in an attempt to identify the source of the anomalous 4.4-MeV alpha activity.

The experimental treatment generally consisted in magnetic separation of the biotite from crushed granite cores. The small dense radioactive inclusions were then separated from the biotite by settling in a heavy liquid and were placed on (Eastman Kodak NTA 25 μ m) emulsion track plates for several weeks exposure to pick out the most active inclusions. These inclusions were assayed with a silicon surface-barrier alpha spectrometer for counting periods from about one day to a week.

About 50 different alpha spectra were obtained on the various cores. The alpha spectra generally showed evidence of both the ²³⁸U and ²³²Th alpha decay chains, though not always in the same ratio. Disequilibrium was also observed, but no attempt was made to determine the cause, since our purpose was to determine whether any 4.4-MeV alpha activity could be detected. With the possible exception of one spectrum, the experiments did not reveal any evidence of the 4.4-MeV alpha emitter reported by Adams et al.³ A rerun of that particular sample subsequently gave no evidence for the 4.4-MeV activity either.

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10.4 ATTEMPTED SYNTHESIS OF SUPERHEAVY ELEMENTS IN THE REACTION ⁴⁸Ca + ²⁴⁸Cm

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A 1.74-mg/cm² ²⁴⁸Cm target was irradiated with 255-MeV ⁴⁸Ca ions at the LBL SuperHILAC. Samples were obtained by directly catching recoil product atoms from the target in stacks of thin aluminum foils. Activity measurements as a function

of range could thus be obtained. Three irradiations were of 1 to 3 hr duration and a fourth was ~ 12 hr duration (1.2×10^{24} ^{48}Ca particles). The foils were counted for spontaneous fission activity for about one day in gas-flow proportional counters. No fission activity directly attributable to superheavy element decay was observed, and an upper limit on the production cross section was estimated. For a half-life between 15 min and 0.1 day, the upper limit for the cross section is between 2.2×10^{-33} and 2.6×10^{-34} cm^2 .

In addition, two irradiations of about one day were made, and group separations for superheavy elements were carried out on the recoil atom samples. One sample was subjected to separations based on ion exchange column techniques,³ and a thin source was prepared on a thin plastic foil. This sample has been continuously counted for coincident fission fragment events in a double silicon alpha-particle detector setup for about nine months. Only one coincident event has been observed. In the second, two samples containing those elements that coprecipitate with copper sulfide from either an acid or a basic solution were obtained and counted for spontaneous fission events for 60 and 90 days respectively. Again, no activity directly attributable to superheavy element decay was observed, and an upper limit on the formation cross section was set. For a half-life between 1 and 100 days, the upper limit for the cross section is between 3.3×10^{-35} and 5.5×10^{-35} cm^2 .

1. Lawrence Berkeley Laboratory, Berkeley, Calif.
2. Los Alamos Scientific Laboratory, Los Alamos, N.M.
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10.5 ABSOLUTE L-SERIES X-RAY AND LOW-ENERGY GAMMA-RAY YIELDS FOR MOST TRANSURANIUM NUCLIDES

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Radioactive-nuclide decay data, especially for the transuranium nuclides, have particular relevance to a number of applied areas in addition to being of intrinsic value in nuclear structure physics. Typical applications include management of reactor waste products, nuclear safeguards, and all other aspects of the nuclear fuel cycle, in assessing the impact of radioactivity on the environment, and in health

physics areas where quantitative estimates of absorbed dose and quantitative assays of the amount of a given radionuclide present require a knowledge of the absolute intensities of emitted radiations.

The transuranium nuclides of importance in applied health physics are, in general, alpha emitters and are difficult to detect "in vivo" using external detectors because of the absence of "hard" photonic radiations in sufficient abundance. Characteristic L-series x rays, and in a few cases low-energy gamma rays, do accompany the alpha decay of these nuclides, and it is usually these radiations that are detected externally.

To provide accurate L-series x-ray intensities, we have measured the characteristic L x-ray spectra arising in the decay of several actinide nuclides of importance in applied health physics. Isotopically pure point sources were prepared directly on thin carbon ($40 \mu\text{g}/\text{cm}^2$) or thin nickel foils ($0.9 \text{ mg}/\text{cm}^2$), using an isotope separator. Absolute disintegration rates were established by alpha counting, using standard 2π proportional counters operated with argon-methane. The low-energy photon spectra were measured using a $10 \text{ cm}^2 \times 1.2 \text{ cm}$ intrinsic planar germanium detector in fixed reproducible geometries. The germanium detector efficiency calibration was established using calibrated sources of ^{241}Am , ^{57}Co , ^{109}Cd , and ^{113}Sn and using the evaluated photon intensities of Campbell and McNelles.² In order to avoid difficulties that occur close to the K absorption edge in germanium ($\sim 11.1 \text{ keV}$), measurements were also made using an Si(Li) detector. These absolute intensity measurements for some of the nuclides studied are given in Table 10.4 and grouped for convenience into the readily identifiable L_I , L_{α} , L_{β} , and L_{γ} groups. The uncertainties in the intensities are the standard deviation and include uncertainties in source disintegration rate as well as the uncertainties in detector efficiency. Using these absolute L x-ray yields for the isotopically pure samples, yields for mixed isotopic samples, as is most often the case with the plutonium isotopes, may easily be constructed. Absolute yields and energies for some of the low-energy gamma-ray transitions are to be included in a future report.

1. ORAU Summer Student Trainee (1975) from Hood College.
2. J. L. Campbell and L. A. McNelles, *Nucl. Instrum. Methods* 125, 205 (1975).

Table 10.4. Absolute L x-ray intensities in the decay of several actinide nuclides

Parent nuclide	L_I	L_{II}	L_{III}	L_{IV}	ΣL
$^{234}\text{U}(\text{ThX})$	0.22 ± 0.01	3.66 ± 0.08	4.87 ± 0.10	1.05 ± 0.04	9.81 ± 0.13
$^{235}\text{U}(\text{ThX} + \text{PaX})$	2.01 ± 0.1	45.4 ± 2.0	94.3 ± 4.2	15.2 ± 0.7	157 ± 4
$^{237}\text{Pu}(\text{NpX})$	1.06 ± 0.05	16.3 ± 0.4	17.0 ± 0.5	3.83 ± 0.2	38.2 ± 0.7
$^{238}\text{Pu}(\text{UX})$	0.26 ± 0.01	4.15 ± 0.07	5.61 ± 0.07	1.36 ± 0.02	11.38 ± 0.10
$^{239}\text{Pu}(\text{UX})$	0.113 ± 0.005	1.82 ± 0.04	2.16 ± 0.04	0.53 ± 0.01	4.63 ± 0.06
$^{240}\text{Pu}(\text{UX})$	0.24 ± 0.01	3.78 ± 0.06	4.84 ± 0.07	1.20 ± 0.03	10.06 ± 0.10
$^{242}\text{Pu}(\text{UX})$	0.21 ± 0.02	3.10 ± 0.08	4.15 ± 0.10	1.08 ± 0.04	8.54 ± 0.14
$^{241}\text{Am}^a(\text{NpX})$	0.86 ± 0.03	13.2 ± 0.3	19.25 ± 0.60	4.85 ± 0.2	38.2 ± 0.7
$^{243}\text{Am}^a(^{239}\text{Np})$	1.8 ± 0.1	27.5 ± 0.6	30.6 ± 0.8	7.69 ± 0.21	67.6 ± 1.0
$^{244}\text{Cm}(\text{PuX})$	0.25 ± 0.01	3.86 ± 0.07	4.30 ± 0.07	1.03 ± 0.02	9.44 ± 0.10
$^{245}\text{Cm}(\text{PuX})$	3.2 ± 0.2	49.8 ± 2.2	47.6 ± 2.1	12.5 ± 0.6	113.1 ± 3.1
$^{246}\text{Cm}(\text{PuX})$	0.21 ± 0.01	3.33 ± 0.07	3.71 ± 0.07	0.86 ± 0.02	8.11 ± 0.10
$^{250}\text{Cf}(\text{CmX})$	0.21 ± 0.01	3.27 ± 0.08	3.85 ± 0.08	0.85 ± 0.03	8.18 ± 0.12
$^{252}\text{Cf}(\text{CmX})$	0.23 ± 0.02	3.09 ± 0.28	3.80 ± 0.34	0.93 ± 0.08	8.05 ± 0.45

^aFrom ref. 2.

10.6 TRANSFER REACTIONS STUDIES: THE PRODUCTION OF $^{245,244}\text{Cf}$ IN REACTIONS OF ^{239}Pu WITH ^{12}C , ^{16}O , ^{20}Ne , AND ^{14}N

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In our continuing study of the mechanisms of deep inelastic or multinucleon transfer reactions in the heavy elements, we have used recoil techniques in irradiations of ^{239}Pu with beams of ^{12}C , ^{16}O , ^{20}Ne , and ^{14}N to produce ^{245}Cf and ^{244}Cf . Because of the large Coulomb barriers for charged-particle emission and because Γ_n/Γ_f decreases rapidly with increasing Z in this region of the periodic table, one would expect that the production of californium nuclides from plutonium involves little or no contribution from the transfer from projectile to target of clusters containing more than four protons. Thus, these reactions may offer a way of selecting a particular transfer reaction path for investigation.

Our data strongly support this notion. Furthermore, they indicate that the same type of mechanism occurs in the transfer reactions induced by ^{12}C , ^{16}O , and ^{20}Ne , namely, a two-step process, such as (1) the transfer of a beryllium-like cluster from projectile (HI) to target, $^{239}\text{Pu} + \text{HI} \rightarrow ^{247}\text{Cf}^* + (\text{HI}-\text{Be})$, and (2) the evaporation of neutrons, in competition with fission, from the excited intermediate nucleus, $^{247}\text{Cf}^* \rightarrow ^{247-x}\text{Cf} + xn$. In particular, the experimental excitation functions obtained with ^{12}C , ^{16}O , and ^{20}Ne have similar maximum values, $\sim 10\mu\text{b}$, and have the

same energy dependence when plotted as a function of the excitation energy of $^{247}\text{Cf}^*$. Some 20 to 40 MeV of excitation energy is deposited in the intermediate nucleus as a result of the transfer. The average kinetic energies measured for the californium recoils are also in general agreement with the predictions of a model that describes the details of the transfer process, step 1 above. Preliminary analysis of the data obtained with ^{14}N indicates that the recoil energies are consistent with the proposed transfer mechanism, but that the cross sections obtained are much smaller than those obtained with alpha-particle-cluster projectiles, such as ^{12}C , ^{16}O , and ^{20}Ne .

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10.7 STRONGLY DAMPED REACTIONS FROM ^{20}Ne BOMBARDMENTS OF ^{48}Ti , Ni , AND ^{94}Zr

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Observation of products resulting from strongly damped collisions has been reported³ for heavy-ion-induced reactions over a broad range of target and projectile masses and energies. These products have an angular distribution which is forward peaked and

have kinetic energies corresponding to the Coulomb separation energies for two fragments.

At the ORIC we have been investigating the systematics of strongly damped reactions in ^{20}Ne bombardments of three targets: ^{48}Ti , ^{nat}Ni , and ^{94}Zr . The bombarding energy was chosen so that the center-of-mass energy was greater than the entrance channel Coulomb energy by approximately the same amount (~ 65 MeV) for all three projectile-target systems. The nuclear charge and kinetic energy of reaction products were determined, as a function of angle, with a ΔE - E telescope consisting of an ionization chamber and a surface-barrier detector.

Strongly damped reaction products were observed with significant yield in all three systems investigated. The charge distribution, summed over all angles and energies, that was obtained with the nickel target is shown in Fig. 10.9. Elastically scattered $Z = 10$ fragments were excluded in these results. The marked odd-even effect in this distribution is apparently due to preferential formation of even Z nuclei in the initial reaction as well as in the evaporation process. For products with $6 \leq Z \leq 14$ the angular distributions are forward peaked. Products with $Z \geq 15$ exhibit an

Fig. 10.9. Total production cross section for products of the reaction 164-MeV $^{20}\text{Ne} + \text{Ni}$, as a function of product nuclear charge.

isotropic angular distribution in the center-of-mass frame. Products with $8 \leq Z \leq 12$, particularly at angles forward of the grazing angle, appear to have two components in their energy spectra, a relatively sharp peak at an energy corresponding to the beam velocity and a broader distribution peaked at the Coulomb separation energy. These have been interpreted, respectively, as due to quasi-elastic events (decay of a projectile-like fragment, for example) and to strongly damped events.

Results obtained with the ^{48}Ti target are quite similar to those obtained with nickel. However, preliminary analysis of the zirconium target data indicates that yields of products with Z from one to several units larger than that of the neon projectile are reduced markedly, compared with the nickel and titanium target systems.

Analysis of our results on these three heavy-ion reactions will attempt to relate the observed trends to macroscopic nuclear properties through comparison with various theoretical models. For example, Fig. 10.10 shows average kinetic energies, as a function of

Fig. 10.10. Average fragment kinetic energies, in the center of mass, for the reaction 164-MeV $^{20}\text{Ne} + \text{Ni}$, as a function of fragment nuclear charge. Filled points are experiment results, the curve is from a liquid-drop fission calculation, and open points represent a correction to the calculation for the effects of particle evaporation.

product charge, for both quasi-elastic and strongly damped events from our Ne + Ni system. The filled points are experimental points; the curve is obtained from a liquid-drop dynamical calculation for fission and includes effects of nuclear viscosity.⁴ The open points are the result of correcting the theoretical values for the effects of particle evaporation from the fragments.⁵ The disagreement between theory and experiment for lower Z values could be taken to indicate that these products have not become fully damped with respect to the kinetic-energy degree of freedom.

1. Physics Division.
2. Tokyo Metropolitan University.
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10.8 OBSERVED DIFFERENCES IN ^{200}Po COMPOUND NUCLEI PRODUCED BY ^{40}Ar AND ^{84}Kr PROJECTILES

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As part of our program to study compound nuclei produced in reactions with very heavy ions, we have produced ^{200}Po compound nuclei with beams of ^{40}Ar and ^{84}Kr . The experiments were done at the SuperHILAC, Lawrence Berkeley Laboratory, with a gas-jet system used to collect and assay the alpha-radioactive polonium isotopes. Our data for the reactions $^{40}\text{Ar}(^{160}\text{Dy}, xn)^{200-x}\text{Po}$ have been discussed previously.^{4,5}

Recently, we obtained data for the reactions $^{84}\text{Kr}(^{116}\text{Cd}, xn)^{200-x}\text{Po}$. These results, along with the earlier data for ^{40}Ar , are plotted in Fig. 10.11 as excitation functions. It is seen for a given (heavy ion, xn) reaction that the cross sections for krypton-induced reactions are smaller than those obtained with argon, and the peaks of the krypton excitation functions are shifted to higher excitation energies with respect to the argon curves. These observations are qualitatively consistent with our earlier results for erbium compound nuclei produced with argon and krypton beams⁶ and indicate that the decay of compound nuclei produced by such heavy

Fig. 10.11. Excitation functions for polonium nuclides produced in the reactions $^{40}\text{Ar} + ^{160}\text{Dy}$ and $^{84}\text{Kr} + ^{116}\text{Cd}$. The curves of part a are from ref. 5, while part b shows data for the krypton reactions as a function of excitation energy, E^* , and of ^{84}Kr bombarding energy.

beams does depend upon the specific mode of formation.

1. Physics Division.
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3. Lawrence Berkeley Laboratory.
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10.9 STUDY OF EVAPORATION RESIDUES FROM ^{86}Kr BOMBARDMENT OF ^{65}Cu , ^{90}Zr , AND ^{109}Ag

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We have continued our study of heavy-ion fusion reactions at the LBL SuperHILAC by measuring both cross sections and mass and charge distributions of evaporation residues in ^{86}Kr bombardments of ^{65}Cu , ^{90}Zr , and ^{109}Ag . In interpreting the results of these experiments, we have utilized a nuclear de-excitation calculation that includes fission competition.⁵

Our earlier results on evaporation residue cross sections from the $^{40}\text{Ar} + ^{109}\text{Ag}$ reaction were in good agreement with the theoretical calculation⁶ and encouraged us to make similar comparisons using krypton ions. With a 1.5-m time-of-flight apparatus, we have obtained evaporation residue cross sections at three bombarding energies for $^{86}\text{Kr} + ^{65}\text{Cu}$, at two energies for $^{86}\text{Kr} + ^{90}\text{Zr}$, and at one energy for $^{86}\text{Kr} + ^{109}\text{Ag}$.⁷ The data for $^{86}\text{Kr} + ^{65}\text{Cu}$ are shown in Fig. 10.12. The experimental points are bracketed by two options of the theoretical calculation, and the agreement is satisfactory. However, the theoretical value for the evaporation residue cross section for 720-MeV $^{86}\text{Kr} + ^{109}\text{Ag}$ is 135 mb, as contrasted with our experimental value of 28 ± 8 mb. In this case the theoretical value is very sensitive to the quantity a_f/a_v used in the calculation (a_f is the level density parameter for fission; a_v , for particle emission). This difficulty apparently arises only in systems where the fission barrier at zero angular momentum is not considerably larger than the smallest particle binding energy. In other systems, with a higher barrier, the theoretical calculation is apparently reliable.

For 716- and 366-MeV $^{86}\text{Kr} + ^{65}\text{Cu}$, we have determined mass and charge distributions of evaporation residues using the time-of-flight apparatus and the ΔE - E telescope. The mass distribution from the 716-MeV experiment is given in Fig. 10.13 by the points. The histogram indicates the result of a theoretical calculation⁵ of the type mentioned above. Except for the shift in scales, which may be due to inadequate calibration of the time-of-flight apparatus, the agreement is excellent. The measured charge distribution was found to be broader than that calculated, but the broadening could be accounted for by the relatively poor resolution of the ΔE counter

Fig. 10.12. Cross section for evaporation residue products as a function of laboratory bombarding energy for $^{86}\text{Kr} + ^{65}\text{Cu}$. The dashed curves represent theoretical calculations; $\Delta J = \text{NO}$ indicates that particles do not remove angular momentum; σ_R is the total reaction cross section calculated with an optical model.

Fig. 10.13. Calculated and experimental mass distributions of evaporation residue products from 716-MeV ^{86}Kr bombardments of ^{65}Cu . The absolute experimental mass scale is subject to some uncertainty.

used. Both the time-of-flight calibration and the ΔE detector resolution have been improved recently, and our experiments at the SuperHILAC are continuing.

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10.10 GAMMA-RAY MULTIPLICITIES IN EVAPORATION RESIDUES FORMED IN BOMBARDMENTS OF ^{150}Nd BY $^{20}\text{Ne}^1$

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The first three moments of the multiplicity distribution were deduced for the gamma-ray cascades in the evaporation residues produced in bombardments of ^{150}Nd with ^{20}Ne at four energies from 127.7 to 172.4 MeV by means of measurements of the first- and higher-order coincidence rates between a Ge(Li) spectrometer and eight NaI(Tl) detectors. The cross sections for the production of $^{160-165}\text{Yb}$ and $^{156-161}\text{Er}$ were also measured.

Average multiplicity $\langle M_J \rangle$ and the width of the multiplicity distribution σ_{M_J} for cascades via a state of spin J were found to be independent of J . The results are summarized in Table 10.5. For a given product, $\langle M \rangle$ and σ_M increase with bombardment energy, but for fixed energy they decrease with increasing number of emitted neutrons. The observed values of $\langle M \rangle$ and σ_M range from 11 to 32 and 6 to 9 respectively (see Fig. 10.14). The multiplicities $\langle M \rangle$ in the $(^{20}\text{Ne}, xn\alpha)$ products are considerably lower than those for $(^{20}\text{Ne}, xn)$, but the widths σ_M are the same for a given value of x . The skewness of the multiplicity distribution is negative, approaching zero as the number of emitted neutrons increases.

Angular momentum distributions were deduced (1) for each product prior to gamma decay and (2) for the initial compound nuclei which lead to each product. In each case these were found to overlap extensively for several neighboring neutron numbers. The J distribution in ^{163}Yb extends up to $J \approx 85$ prior to gamma decay. At the higher energies, alpha emission plays an important role in the de-excitation process by removing on the average an angular momentum of $\sim 10\hbar$. The present results suggest that alpha emission follows neutron evaporation. The J distributions obtained are compared with the predictions of the Bass model for fusing collisions.

Table 10.5. Values of the multiplicity $\langle M \rangle$, multiplicity width σ_M , and skewness $s_M = \mu_3/\sigma_M^3$ obtained as weighted averages of the corresponding values for levels with different J^π values in the various identified evaporation residues following reactions of ^{150}Nd with ^{20}Ne at the indicated bombardment energies

The underlined numbers are estimates of the statistical errors and refer to the least significant figures indicated

E_{lab}	Identified evaporation residue										
	^{165}Yb	$^{164}\text{Yb} + ^{160}\text{Er}$	^{163}Yb	^{162}Yb	^{161}Yb	^{160}Yb	^{161}Er	^{159}Er	^{158}Er	^{157}Er	^{156}Er
127.7 MeV											
$\langle M \rangle$	27.1 <u>23</u>	23.2 <u>2</u>	16.60 <u>23</u>	11.2 <u>3</u>			18.2 <u>16</u>				
σ_M		6.87 <u>80</u>	5.8 <u>7</u>	5.9 <u>8</u>							
s_M		-1.25 <u>152</u>	-0.54 <u>126</u>	0.09 <u>131</u>							
144.0 MeV											
$\langle M \rangle$		26.1 <u>4</u>	22.7 <u>4</u>	20.1 <u>2</u>	11.2 <u>12</u>			15.4 <u>8</u>	11.7 <u>11</u>		
σ_M		7.2 <u>31</u>	6.9 <u>14</u>	6.0 <u>11</u>	3.7 <u>45</u>			7.7 <u>19</u>	3.1 <u>46</u>		
s_M		-2.1 <u>67</u>	-3.1 <u>38</u>	-1.1 <u>27</u>				-1.0 <u>26</u>			
163.5 MeV											
$\langle M \rangle$			28.8 <u>28</u>	25.3 <u>4</u>	20.9 <u>7</u>	17.2 <u>5</u>		22.9 <u>12</u>	21.0 <u>4</u>	13.1 <u>11</u>	
σ_M			14.6 <u>143</u>	7.5 <u>16</u>	8.4 <u>20</u>	5.2 <u>21</u>		8.2 <u>43</u>	9.3 <u>16</u>	5.3 <u>32</u>	
s_M			-2.0 <u>117</u>	-1.2 <u>43</u>	1.4 <u>31</u>	-1.5 <u>68</u>		-1.7 <u>66</u>	-2.0 <u>19</u>	-0.1 <u>88</u>	
172.4 MeV											
$\langle M \rangle$			32.2 <u>30</u>	30.8 <u>15</u>	23.3 <u>11</u>	18.6 <u>6</u>		25.5 <u>17</u>	22.3 <u>15</u>	15.2 <u>8</u>	12.9 <u>15</u>
σ_M			11.2 <u>50</u>		6.7 <u>44</u>	8.4 <u>16</u>		9.6 <u>55</u>	8.2 <u>14</u>	6.5 <u>24</u>	8.6 <u>30</u>
s_M			-1.8 <u>100</u>		-2.4 <u>123</u>	-1.1 <u>18</u>		-1.7 <u>73</u>	-1.4 <u>23</u>	-2.2 <u>47</u>	0.4 <u>26</u>

Fig. 10.15. Systematics trend of the $h_{9/2}$ band in thallium nuclei. The $A = 195, 197$ results come from ref. 4; the $A = 191, 193$ results are from the present experiments. Very qualitative comparisons are made with the even- A mercury cores.

Fig. 10.16. Trend of positive parity states in thallium nuclei. The $A = 195, 197$ results come from ref. 4; the $A = 191, 193$ results are from the present experiments. The positions of the 5^- band in $^{190,192,194}\text{Hg}$ are shown as hatched lines.

Fig. 10.14. Average multiplicity (M) of the gamma cascades in the various reaction products formed in bombardments of ^{150}Nd by ^{20}Ne as a function of bombardment energy. It is seen that (M) increases with energy and that the highest (M) values are associated with the products emitting the fewest neutrons at a given bombardment energy.

For the lower energies, excellent agreement is observed. For the higher energies the Bass model prediction exceeds the measured xn and $xn\alpha$ cross sections at all J , indicating that other exit channels account for an appreciable fraction of the fusion cross section.

1. Paper published in *Phys. Rev. C* 14, 2138 (1976).
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10.11 BANDS IN ODD- A THALLIUM ISOTOPES

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In the past year, experiments at the ORIC on $^{191,193}\text{Tl}$ have been completed. In addition, work on ^{189}Tl has been initiated at the Berkeley 88-in. cyclotron, using an $(^{28}\text{Si}, 4n\gamma)$ reaction. A primary purpose of these measurements is to follow the systematic trends of odd- A proton bands in this transitional region immediately below lead. This region is quite interesting in that it displays a variety of nuclear shapes and coupling schemes.

The $h_{9/2}$ and $i_{13/2}$ bands observed in thallium nuclei can be viewed as rather strongly coupled particles on slightly oblate mercury cores. Both of these Nilsson orbitals intrude across the $Z=82$ shell model gap into the low-energy level schemes of thallium nuclei. The $h_{9/2}$ band is observed also in ^{185}Au , but there is an aligned band rather weakly coupled to the prolate ^{184}Pt core. By studying the spacings in these bands, we hope to learn much about the details of the couplings of these particles to their respective cores.

The yrast structure in the odd- A thallium nuclei is the $h_{9/2}$ band. The systematics of this band in the thallium nuclei are shown in Fig. 10.15. The work on $^{195,197}\text{Tl}$ has been performed in a Stockholm-Jülich collaboration,⁴ while the $^{191,193}\text{Tl}$ results are from our experiments. In each case, the $^{21/2}_-$ member of the band breaks the trend established by the lower members. Furthermore, compressed levels are observed at higher spins in $^{195,197}\text{Tl}$. The cause of this change in the $h_{9/2}$ band is not really understood. Lieder et al.⁵ have proposed that the higher-spin states reflect the $10^+ \rightarrow 8^+$ compression in this core, as illustrated in Fig. 10.15. Work is continuing on the theoretical explanation of these changes in the $h_{9/2}$ band.

Positive parity bands are also observed in these thallium nuclei, as shown in Fig. 10.16. However, it seems that we observe a vastly different structure in $^{191,193}\text{Tl}$ compared with that seen in $^{195,197}\text{Tl}$. Our in-beam work, our UNISOR measurements on ^{193}Pb decay, and the earlier work of Newton et al.⁶ lead to

the placement of an $i_{13/2}$ band in ^{193}Tl . We observe in ^{191}Tl a similar band at a slightly lower energy. This band is evidently not the same as that observed in $^{195,197}\text{Tl}$; it begins with a $^{15/2}^+$ level and is explained as a three-quasi-particle structure. The rapidly falling $i_{13/2}$ band evidently absorbs reaction strength in $^{191,193}\text{Tl}$, although we have candidates for an analogous $^{15/2}^+$ state in these nuclei.

1. University of Tennessee, Knoxville.
2. Deceased.
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10.12 PROPERTIES OF ^{164}Er IN THE BAND CROSSING REGION

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Erbium-164 belongs to the class of nuclei termed "backbenders," so-named because of the abrupt increase in the moment of inertia at about spin 14^+ in the ground-state rotational band. In an extensive experimental investigation of the high-spin states in this nucleus completed recently, we made some significant new findings.

Normally, the behavior of backbending nuclei is established from the gamma-ray cascade down through the yrast sequence following a compound-nucleus reaction. During the past year, however, in a collaborative effort carried out at the Berkeley SuperHILAC, we⁶ showed for the first time that it is possible to excite up the ground band of ^{164}Er through the backbend, and up to the 18^+ level in the yrast sequence by the Coulomb excitation mechanism. In addition, we saw good evidence for excita-

tion of the 16^+ and 18^+ members of the ground-state band.

In order to get information on still higher spin states in ^{164}Er , and hopefully to find the 14^+ member of the excited band, we carried out extensive gamma-gamma coincidence measurements at the ORIC, utilizing the reaction $^{150}\text{Nd}(^{18}\text{O}, 4n\gamma)^{164}\text{Er}$. These experiments were quite successful, as the deduced level scheme of Fig. 10.17 illustrates. As seen, above the band crossing point we now have several states in both the yrast sequence and the ground band. Additionally, we obtained the necessary gamma-ray branching ratio from the 16^+ state which makes it possible to calculate the important interaction matrix element between the two bands. This matrix element turns out to be 54 keV, a small value which is completely compatible with interpreting the backbending here in terms of the rotation-alignment model.⁷

ORNL-DWG. 77-8485

Fig. 10.17. Level scheme of ^{164}Er deduced from both Coulomb excitation and compound-nucleus reaction experiments. The intensities of the 560.6- and 388.2-keV transitions are shown in parentheses.

Fig. 10.18. Conventional plot of $2J/h^2$ vs $(h\omega)^2$ for ^{164}Er to illustrate the backbending effect.

A conventional backbending plot of these data is shown in Fig. 10.18. Note that at the 16^+ state of the ground band there is a discontinuity which may indicate the intersection of this band with a second excited band.

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10.13 LIFETIMES OF GROUND BAND STATES IN ^{150}Nd

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Recent measurements of reduced transition probabilities of high-spin states in strongly deformed nuclei have shown that these nuclei are well understood in

terms of the rotational model. However, pronounced deviations from the rotational description have been observed for $B(E2)$ values of ground-band states in transitional nuclei and are often interpreted as due to band mixing between the ground band and low-lying beta (and gamma) vibrational bands. The observed increase in $B(E2)$ for such nuclei has been taken³ to be of the form

$$B(E2; I \rightarrow I-2) = B_0(E2; I \rightarrow I-2) \times \{1 + (\alpha/2)[I(I+1) + (I-2)(I-1)]\}^2,$$

where $B_0(E2)$ is the unmixed rigid rotor value, and α is a mixing (or stretching) parameter. While previous work has accounted for deviations in terms of the single parameter α , it may well be that other explanations such as fourth-order cranking, centrifugal stretching, and Coriolis antipairing can also account for nonrotational behavior.

In a further study of the problem with these nuclei just at the boundary of the strongly deformed region, the ground-state rotational band of ^{150}Nd has been investigated by using the Doppler-shift recoil distance technique. Recoil distance measurements are preferred, since no other method is believed to be of comparable accuracy in the half-life range under study. In addition, this method involves fewer assumptions than are employed in other measurements such as multiple Coulomb excitation yields.

An isotopically enriched 2.8-mg/cm² ^{150}Nd foil was bombarded with 149-MeV $^{40}\text{Ar}^{8+}$ ions from the ORIC. Following Coulomb excitation of the target nuclei, the backscattered ^{40}Ar ions were detected in an annular surface-barrier detector. Spectra of gamma rays in coincidence with the backscattered ions were taken at several target-stopper separations. A plot of the ratio of the unshifted gamma-ray intensity divided by the total gamma-ray intensity as a function of the target-stopper separation is shown in Fig. 10.19, and the resulting half-lives and $B(E2)$ values are summarized in Table 10.6. The details of the method of data analysis are given elsewhere, for example, see refs. 4 and 5. While the 10^+ rotational state is clearly excited in the Coulomb excitation process, an unfortunate degeneracy between its gamma ray and another gamma ray from a known vibrational level prevents our obtaining a half-life value for this state.

It is clear from the $B(E2)$ ratios in Table 10.6 that there is enhancement in the transition strength as one goes to higher spin. The enhancements are very similar to those found⁶ in the case of ^{152}Sm . An informative method of comparing these experimental

Fig. 10.19. Plot of the ratio of the unshifted gamma-ray intensity to the unshifted plus shifted intensity as a function of the target-stopper separation for three of the transitions in ¹⁵⁰Nd.

Table 10.6. Summary of half-life and $B(E2)$ data for ¹⁵⁰Nd

Transition	E_γ (keV)	$T_{1/2}$ (psec)	$B(E2)$ (e^2b^2)	$\frac{B(E2)_{\text{expt}}}{B(E2)_{\text{theory}}}$
2 ⁺ → 0 ⁺	130.3	1440 ± 70	0.56 ± 0.03	(1.00) ^a
4 ⁺ → 2 ⁺	251.2	63.0 ± 3.2	0.82 ± 0.04	1.03 ± 0.05
6 ⁺ → 4 ⁺	339.0	12.4 ± 1.1	0.98 ± 0.09	1.13 ± 0.09
8 ⁺ → 6 ⁺	409.3	4.0 ± 0.4	1.21 ± 0.12	1.33 ± 0.13

^a All ratios are normalized to this ratio as unity.

Fig. 10.20. Plot of $\sqrt{B(E2, I \rightarrow I-2) / B(E2, I \rightarrow I-1)} \langle 2200 | 00 \rangle / \langle 1200 | 1-2 \rangle$ vs $\frac{1}{2} [I(I+1) + (I-2)(I-1)]$ for ¹⁵⁰Nd. The part in bracket notation is a ratio of Clebsch-Gordan coefficients.

results with the single parameter prescription is by a plot as shown in Fig. 10.20. A plot of this type should yield a straight line, the slope of which is α and the intercept is $B_0(E2)$. A weighted least-squares fit to the data indicates a constant value for $\alpha = (2.6 \pm 0.5) \times 10^{-3}$ and $B_0(E2) = 0.542 \pm 0.008$. It is of interest to note that these values are nearly identical to values of the mixing parameter determined for the other $N=90$ isotones, ¹⁵²Sm and ¹⁵⁴Gd, indicating only small changes in the nuclear structure with increasing proton number in this region.

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10.14 LEVELS IN ^{195,197}Tl FROM LEAD DECAY

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Studies of the levels in ¹⁹⁵Tl populated by decay of ¹⁹⁵Pb have been completed since our preliminary report.³ Systematics of the single-particle states in the light thallium nuclei have been extended further by our studies of the levels in ¹⁹⁷Tl from the decay of ¹⁹⁷Pb. The lead isotopes for these measurements were produced in (¹⁶O, xn) reactions on natural tungsten or rhenium targets and were continuously separated using the UNISOR isotope separator on-line to the ORIC.

A study of the high- j shell-model states and the band structure of levels associated with them is important to the understanding of nuclei in this mass region. In ¹⁹⁵Tl we have been able to identify tentatively the $h_{11/2}$ hole state at 1360.8 keV. Thirteen levels have been assigned to the band structure built on the $h_{9/2}$ state. Four of these levels are members of the yrast band; additionally, the other levels have been assigned to two related bands which gamma decay into the yrast band. Although seven excited states of ¹⁹⁵Tl are associated with the decay of the $3/2^-$ ground state of ¹⁹⁵Pb, we still have not been able to determine the half-life of the ¹⁹⁵Pb ground state.

Gamma-gamma coincidence, time-multiscaled gamma-ray singles spectra, and internal-conversion electron spectrometry were employed to study the complex decay of ^{197}Pb . Decay of $^{197}\text{Pb}^m$ (44.6 min) populates 39 high-spin levels in ^{195}Tl , and decay of $^{197}\text{Pb}^g$ (68.5 min) populates 23 low-spin levels in ^{197}Tl . The multiplet structure built on the $h_{11/2}$ hole state seen for $^{193,195,197}\text{Tl}$ is believed to arise from coupling with phonon vibrations of the lead core. The well-defined, nonyrast bands built on the $h_{9/2}$ states of $^{195,197}\text{Tl}$ can be interpreted rather successfully in terms of the triaxial rotor model of Meyer-ter-Vehn.⁴ Although more refined calculations will be performed, triaxiality appears essential to the interpretation of the $h_{9/2}$ structure observed.

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10.15 THERMAL-NEUTRON CAPTURE AND FISSION CROSS SECTIONS AND RESONANCE INTEGRALS FOR ^{243}Cm

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Neutron cross sections for capture and fission for the transactinium nuclides are required to quantitatively account for the buildup and destruction of these nuclides in the fuel of nuclear power reactors. These nuclides affect the reactivity and core power distribution of reactor systems via neutron absorption and via spontaneous and/or neutron-induced fission. The requirements of fuel management, reprocessing and actinide waste isolation, and storage and/or disposal also depend on the quantities of these nuclides in spent reactor fuel. Of particular interest is the nuclide ~ 30 -year ^{243}Cm , which occurs in the production path of reactors fueled with ^{235}U , ^{238}U and ^{239}Pu , since only limited cross-section data for ^{243}Cm have previously been reported and/or are available with unknown or poorly established accuracy. According to recommendations of the IAEA Advisory Group Meeting on Transactinium Isotope Nuclear Data,^{1,2} we have measured the thermal-neutron cross sections for capture and fission together with the corresponding resonance integrals for ^{243}Cm .

Cross sections for ^{243}Cm were established using cadmium filter techniques in conjunction with carefully monitored irradiations with cobalt in the Oak Ridge Research Reactor. Using the TRL isotope separator, nearly isotopically pure ^{243}Cm (99.939%) was prepared and was available for these experiments; two separate reactor irradiations, each with multiple samples, were performed. The first experiment, designed to establish the capture cross sections, consisted of a relatively short irradiation period, thus minimizing second-order reactions. The second experiment was designed to provide information on the absorption cross section (capture + fission) by measuring the depletion of ^{243}Cm relative to an internal monitor of ^{248}Cm spiked into the samples.

The quantities of ^{244}Cm produced in the $^{243}\text{Cm}(n,\gamma)^{244}\text{Cm}$ reaction were determined mass spectrometrically (relative to ^{243}Cm) and were used to deduce the capture cross sections $\sigma_{\text{th}}(n,\gamma)$ and $\text{RI}(n,\gamma)$ for ^{243}Cm . The changes in the mass ratios, $^{243}\text{Cm}/^{248}\text{Cm}$, in the samples of the second experiment were also established mass spectrometrically and used to deduce the absorption cross sections.

Cross-section values and resonance integrals of $\sigma_{2200}(n,\gamma) = 130.7 \pm 9.6$ b, $\sigma_{2200}(n,f) = 609.6 \pm 25.9$ b, $\text{RI}(n,\gamma) = 214.7 \pm 20.3$ b, and $\text{RI}(n,f) = 1575 \pm 136$ b were deduced. A complete description of these experiments and results is the topic of a forthcoming publication,³ to which the reader is referred.

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10.16 DIFFERENTIAL FISSION CROSS-SECTION MEASUREMENTS AT THE ORELA FOR ^{243}Cm ¹

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The differential fission cross-section measurements previously reported for ^{245}Cm at the ORELA⁴ have been extended to include ~ 30 -year ^{243}Cm . The

Fig. 10.21. Portion of the experimental time-of-flight fission data for ^{243}Cm together with data for ^{235}U and ^{239}Pu also measured in the same chamber. The ^6Li beam-flux monitor data are also shown.

quantity of ^{243}Cm required for these determinations was prepared using the TRL Isotope Separator, and approximately 60 μg of 99.939% isotopically pure ^{243}Cm was obtained. Approximately 10 μg of this material was incorporated into a hemispherical-plate ionization chamber developed by us¹ for use in the time-of-flight cross-section determinations. Target plates of ^{235}U , ^{239}Pu , and ^{252}Cf were also included in the chamber to provide cross-section normalizations and/or a continual check on the proper operation of the counter. Neutron flux monitoring was also provided by a specially constructed counter based on the $^6\text{Li}(n,\alpha)$ reaction.

Measurements at a 9.5-m flight path station at the ORELA began in December 1975, were continued through 1976, and are now complete. A portion of some of the time-of-flight data is given in Fig. 10.21 for ^{243}Cm and the internal monitors of ^{235}U and ^{239}Pu as well as for the ^6Li beam-flux monitor.

A thorough analysis of the response of the ^6Li beam-flux monitor counter is in progress prior to the actual conversion of our ^{243}Cm data to cross-section values as a function of neutron energy. Newly selected cross-section sets from ENDF/B-V for ^{235}U and ^6Li will be used in the ^{243}Cm cross-section conversion.

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10.17 $^{232}\text{Th}(n,\gamma)$ CROSS SECTIONS FROM 2.6 TO 800 keV¹

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The $^{232}\text{Th}(n,\gamma)$ reaction has assumed special significance as the basis of an alternative nuclear reactor cycle following the current de-emphasis of the ^{238}U - ^{239}Pu cycle. Yet its cross section above a few kilovolts remains rather poorly known despite requests by various groups for cross-section accuracies of 3 to 10%.^{3,4}

Thorium is a particularly difficult target for capture cross-section studies because of its low binding energy (~ 4.8 MeV) and natural radioactive decay chain. The nuclear resonance structure up to ~ 10 keV neutron energy requires neutron time-of-flight methods, yet the prompt-gamma detectors applicable

to this technique must remain quite sensitive to the ^{208}Tl 2.6-MeV decay-chain gamma. This problem has been successfully overcome by isotope separation followed by timely (30- to 60-day cycle) chemical purification. The decay sequence for ^{232}Th involves a rate-determining transition [Eq. (1)] through the 5.7-year ^{228}Ra and a holdup at the ^{228}Th step:

All other daughter decays are short in comparison. By interrupting the decay chain at the radium step, the growth of the 2.61-MeV gamma in ^{208}Tl can be prevented.

The ^{232}Th was separated from natural thorium electromagnetically, achieving a 300-fold reduction in gamma radioactivity. The ^{232}Th was maintained by periodically passing the thorium through an ion absorption column to remove the radium. The purification factor remained better than 250 during our experiments. A thin metal foil (8.22×10^{-4} atom/b) was fabricated and mounted between two C_6F_6 liquid scintillators, with the sample subtending the ORELA pulsed neutron beam some 40 m from the source. An average energy resolution of $\sim 1.5 \times 10^{-3}$ was realized up to 10 keV neutron energy. Experimental details have been previously described.^{5,6}

Resonance energies and neutron widths to 4 keV have been measured by neutron transmission.⁷ We have measured capture areas for some 113 resonances (three apparent multiplets) in the region between 2.6 and 4.0 keV. Since the radiative widths are narrowly distributed near 20 meV, both experiments should determine the narrower neutron widths; with few exceptions, agreement is good. The sensitivity of the present work in this energy range seems to be about 0.5 meV, compared with about 2 meV for the transmission results.

The parameterization of the cross sections in terms of level parameters has been continued from 4 to 10.4 keV, in which region some 328 levels (49 apparent multiplets) have been measured. Some examples of the data are shown in Fig. 10.22. As the p -wave neutron penetrability increases rapidly over this energy range, the capture areas must include increasingly greater contributions from small unresolved resonances. Over the range 2.6 to 105 keV, the capture cross-section data averaged in 250-eV intervals were fitted quite well by four strength functions ($10^4 S_0 = 0.365 \pm 0.024$, $10^4 S_1 = 1.078 \pm 0.057$ with

Fig. 10.22. Samples of the capture yield data showing the fitted curves generated from least-squares adjusted parameters.

inelastic competition above 50 keV, $10^4 S_2 > 0.842 \pm 0.084$, and $\bar{\Gamma}_\gamma/D_0 = 0.0203/13.58$). However, this least-squares parameterization should not be considered as measurements of these quantities, since they exhibit correlation (see Figure 10.23). Additional structure in the data was examined with the distribution free-runs test.⁸ In the present fit to the

data, no evidence for additional structure was found.

The $^{232}\text{Th}(n, \gamma)$ cross section has been measured to good accuracy in the 2.6- to 800-keV range. Resonance parameters have been derived to 10 keV, and strength functions fit the data well to 105 keV. As is evident from Fig. 10.23, the data disagree signifi-

Fig. 10.23. Average data to 800 keV shown as histograms. The four-strength-function fit adjusted by least squares is shown with and without inelastic competition by the ^{232}Th 2⁺ state near 50 keV. Also shown is a representation of recent evaluations.

cantly from current evaluations of the average cross section and could have a significant impact on future reactor evaluations.

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10.18 RESONANCE NEUTRON CAPTURE BY ^{209}Bi

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Bismuth-209 with a weakly bound proton in the $1h_{9/2}$ shell beyond the closed 82-proton and 126-neutron core lies at the terminus of the slow-neutron

capture path (*s* process) in nucleosynthesis. Short-lived alpha-decay processes effectively terminate further mass accretion by this mechanism. We have measured the capture cross section of ^{209}Bi from 2.6 to 900 keV, at which point the threshold to inelastic scattering is reached. The measurements have been carried out at the ORELA with 5-nsec pulses on a 40-m flight path,³ using metallic samples of bismuth (0.00204 and 0.0113₃ atoms/b). Peaks seen in the capture yield have been fitted with single-level resonance parameters. In the present work, resonance capture identification (for $l = 0, 1$) appears to be complete to ~30 keV. Of the 34 peaks seen below 30 keV, 22 have been reported in neutron transmission experiments.^{4,5} Above 30 keV our data were not adequate to isolate all resonances, particularly those formed with $l \geq 2$ neutrons. Since a number of resonances have been fitted in transmission work up to 70 keV, we have elected to fit those in the capture data also. The capture areas are listed in Table 10.7. Table 10.8 lists averaged capture cross sections from 25 to 900 keV in histogram form (with increasing bin size). Table 10.9 lists average capture cross sections for a range of Maxwellian temperatures appropriate to stellar interiors. There is some disagreement at the

Table 10.7. Capture parameters for resolved resonances in $^{209}\text{Bi}(n,\gamma)$

Many resonances above 30 keV were not fitted individually, and those analyzed correspond to those reported in neutron transmission measurements (refs. 4 and 5)

Energy (keV) ^a	$g\Gamma_n\Gamma_\gamma/\Gamma$ (meV)	Energy (keV) ^a	$g\Gamma_n\Gamma_\gamma/\Gamma$ (meV)
0.8000 ^b	25.0 ± 3.0^b	27.45 ^e	156.5 ± 21.6
2.310 ^b	20.0 ± 10.0^c	28.79	11.5 ± 2.0
3.351	10.9 ± 0.1^d	29.01	8.9 ± 1.9
4.458	10.8 ± 0.2	29.20	12.7 ± 2.2
5.113	40.8 ± 0.6	29.52	10.5 ± 2.0
6.289	6.4 ± 0.2	30.48	18.0 ± 4.0
6.527	9.1 ± 0.2	32.73	5.1 ± 2.7
9.018	10.6 ± 0.4	32.90	16.0 ± 6.5
9.159	9.6 ± 0.4	33.31	243.0 ± 18.0
9.375	0.8 ± 0.3	34.68	29.0 ± 4.0
9.718	21.7 ± 0.6	37.25	11.2 ± 3.9
9.766	21.2 ± 0.6	38.10	38.1 ± 3.9
12.09	7.7 ± 0.9	39.17	22.5 ± 4.1
12.10	49.0 ± 7.8	42.40	19.2 ± 4.5
12.24	3.6 ± 0.7	43.60	13.7 ± 4.0
14.88	10.1 ± 0.9	44.09	5.1 ± 3.8
15.51	68.0 ± 9.3	44.60	30.2 ± 4.2
15.65	21.8 ± 1.3	45.18	28.8 ± 5.0
17.44	16.7 ± 1.0	45.56	129.0 ± 12.2
17.83	21.7 ± 1.0	46.49	17.8 ± 5.0
20.86	12.8 ± 0.9	49.85	28.6 ± 5.2
21.06	15.8 ± 1.2	51.74	8.4 ± 5.4
22.27	18.2 ± 1.1	52.77	5.1 ± 5.6
23.13	11.2 ± 1.1	53.70	33.2 ± 7.3
23.85	5.0 ± 1.9	54.22	23.4 ± 5.8
24.20	5.0 ± 1.1	55.42	15.1 ± 5.8
25.27	30.7 ± 2.2	57.76	5.1 ± 5.8
27.05	70.4 ± 3.7	61.57	64.4 ± 9.1
27.29	12.8 ± 2.2	69.14	216.0 ± 25.1

^aEnergies are believed accurate to about 0.1% except for the broad resonances.

^bFrom S. F. Mughabghab and D. I. Garber, *Neutron Cross Sections*, BNL-325, 3d ed., vol. 1 (1973).

^cEstimated.

^dStatistical standard deviation combined with uncertainty in scattered neutron sensitivity correction. Additional normalization errors are estimated at $\pm 3\%$.

^eProbable multiplet.

lower temperatures with earlier low-resolution Van de Graaff data.⁶

Average radiation widths have been evaluated. Twelve *s*-wave resonances yield $\bar{\Gamma}_\gamma = 164 \pm 45$ meV. The distribution of widths, however, leads to only 2.2 "degrees of freedom," implying relatively few strong primary gamma transitions from the capturing nega-

tive parity states in the ($^{209}\text{Bi} + n$) compound nucleus. The 41 levels ($l > 0$) for which $g\Gamma_\gamma$ could be evaluated yield $\bar{\Gamma}_\gamma = 33.7 \pm 3.0$ meV. The distribution of widths for these primarily positive parity states leads to some 6.3 "degrees of freedom," or a significantly larger number of primary gamma transitions than for the *s*-wave levels. We further deduce an average level

Table 10.8. Residual average ^{209}Bi neutron capture cross sections for unanalyzed resonances up to 900 keV, just below the onset of inelastic scattering

$\bar{E}$ (keV)	ΔE	$\bar{\sigma}_{n\gamma}$ (^{209}Bi) (mb)
30	10	4.7 ± 3.1^a
40	10	18.5 ± 3.1
50	10	10.9 ± 1.7
60	10	9.8 ± 1.7
70	10	9.1 ± 1.7
87.5	25	4.4 ± 1.7
112.5	25	1.0 ± 1.8
137.5	25	3.6 ± 1.8
175	50	4.7 ± 0.9
225	50	3.5 ± 0.9
275	50	2.4 ± 0.9
350	100	3.9 ± 0.6
450	100	4.4 ± 0.6
550	100	2.6 ± 0.6
650	100	2.8 ± 0.6
750	100	2.6 ± 0.4
850	100	2.7 ± 0.4

^aIndicated error is predominantly the 10% uncertainty in the scattered neutron sensitivity correction.

Table 10.9. Average ^{209}Bi neutron capture cross sections at stellar interior temperatures

The thermal velocity v_T is defined as $(2kT/m)^{1/2}$, with m the reduced mass

kT (keV)	$\frac{\langle \sigma v \rangle}{v_T}$ (mb)	$\bar{\sigma}(n, \gamma)$ (mb)
5	$16.4, 35^a$	
10	$12.4, 29^a$	
20	$12.1, 17^a$	
30	$10.7, 12 \pm 4^a$	7.8 ± 2.5^b
40	$9.3, 9^a$	
50	$8.2, 7.5^a$	
60	7.4	
80	6.3	
100	5.7	

^aFrom ref. 6.

^bFrom J. A. Holmes, S. E. Woolsey, W. A. Fowler, and B. A. Zimmerman, "Tables of Thermonuclear Reaction Rate Data for Neutron-Induced Reactions on Heavy Nuclei," *At. Data Nucl. Data Tables* 18(4), 305 (1976).

spacing of 1.14 ± 0.25 keV for $l > 0$ levels in the energy interval to 30 keV and calculate a resonance integral of $\int \sigma dE/E = 200 \pm 10$ mb.

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10.19 HIGH-RESOLUTION NEUTRON CAPTURE CROSS SECTIONS IN $^{63,65}\text{Cu}$ ¹

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The measurement of the neutron capture cross sections in nuclei provides valuable data for reactor design, nucleosynthesis of elements, and an improved understanding of the neutron interaction with nuclei. The copper isotopes were chosen for study because of their interest to reactor design and because detailed measurements of total cross sections in these isotopes have been made in a separate experiment.⁵

A comprehensive evaluation of capture cross sections has been carried out for isotopically enriched samples of copper from approximately 3 to 50 keV at the ORELA time-of-flight facility. A detailed description of experimental conditions was previously documented.⁶⁻⁸ Some 167 resonances in ^{63}Cu and 108 resonances in ^{65}Cu have been characterized.¹ For ^{63}Cu , a value of $\langle \Gamma_\gamma \rangle = 490 \pm 30$ meV has been measured. The average p -wave level spacing $\langle D \rangle_{l=1} = 0.495 \pm 0.026$ keV and a p -wave strength function $S_1 = (0.44 \pm 0.07) \times 10^{-4} \text{ eV}^{-1/2}$ have been determined. For ^{65}Cu , $\langle \Gamma_\gamma \rangle = 385 \pm 20$ meV, $\langle D \rangle_{l=1} = 0.685 \pm 0.060$ keV, and $S_1 = (0.47 \pm 0.08) \times 10^{-4} \text{ eV}^{-1/2}$. The corresponding s -wave mean level spacings for ^{63}Cu and ^{65}Cu are 1.04 ± 0.11 and 1.47 ± 0.19 keV respectively.

The current high-resolution experiment has yielded numerous previously unreported resonances. It has served to remove some ambiguities in level assignments (spins, resolution of doublets, etc.) and provided an accurate determination of some average s -wave and p -wave properties. These measured

values are consistent with optical-model⁹ calculations under the assumption of a spherical potential. In fact, these optical-model parameters will reproduce reasonable strength function values for other mass numbers in this region. The calculated values of the strength function were found to depend more sensitively on the incident neutron energy, the real part of the potential V_0 , and the diffuseness parameter rather than on other parameters in the optical-model calculation.

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2. College of William and Mary, Williamsburg, Va.
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10.20 THE 292.4-eV NEUTRON RESONANCE PARAMETERS OF $^{91}\text{Zr}^1$

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Because of the role of zirconium as a constituent of fuel elements as well as of structural components of nuclear reactors, there is an especial interest in the evaluation of neutronic effects for this element. The lowest strong s -wave neutron resonance in zirconium (the 292.36-eV resonance in ^{91}Zr) has a major influence on the magnitude and change in neutron absorption with zirconium thickness. Yet the experimental

determination of the radiative capture width for this resonance has been uncertain to at least 20%. Further, the resonance spin assignment and neutron width have been changed in recent years.^{4,5} An analysis has been carried out for both neutron capture and transmission with data taken at the ORELA time-of-flight facility for the 292.36-eV resonance parameters.

A neutron transmission measurement of a thin metal disk (0.00701 atom/b) of high-purity natural zirconium was cycled in and out of a 5-nsec pulsed beam. The neutrons were detected and timed with a lithium glass scintillator located 78 m from the source. The thin sample transmission measurement is most sensitive to the quantity $g\Gamma_n$. Our result, $2g\Gamma_n = 722 \pm 9$ meV, compares with earlier values of 788 ± 40 ,⁶ 741 ± 47 ,⁷ and 655 ± 82 (ref. 8) meV and provides a good fit to the capture yield. A $J = 2^+$ level assignment can be made from the analysis, leading to a value of $\Gamma_n = 866 \pm 11$ meV.

A high-purity natural zirconium metal sample (0.0124₄ atom/b) was used for the neutron capture measurements. The capture gamma-ray yield was detected in a pair of C_6F_6 liquid scintillators viewing the sample some 40 m from the pulsed source. By means of an on-line pulse-height weighting procedure, the total gamma-ray energy as a function of time of flight was measured and converted to capture cross section with appropriate attention to backgrounds and normalization.⁹ Our radiative width $\Gamma_\gamma = 86.8 \pm 2.2$ meV (evaluated with $J = 2$, $\Gamma_n = 866$ meV) is substantially smaller than many of the earlier results [e.g., 100 ± 50 ,⁶ 120 ± 30 ,⁷ and 180 ± 30 (ref. 8) meV]. The differences are even greater than indicated, since these earlier results were based on a $J = 3$ ($g = 7/12$) assignment for the resonance. An analysis by Steen⁴ of thick-sample resonance integrals, in fact, supports the lower radiative width that we report. The level properties are summarized as follows:

E_0 (eV)	J^π	Γ_n (meV)	Γ_γ (meV)	$(\Delta\sigma_\gamma)_{\text{th}}$ (mb)	ΔI_γ (b)
292.36 $\pm$ 0.10	2 ⁺	866 $\pm$ 11	86.8 $\pm$ 2.2	80 $\pm$ 2	1.61 $\pm$ 0.03

$\Delta\sigma_\gamma$ and ΔI_γ are the partial contributions to the capture thermal cross section and dilute resonance integral attributable to the resonance.

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10.21 MONTE-CARLO MODELING OF X-RAY TRANSPORT IN A HETEROGENEOUS PHANTOM— APPLICATIONS TO THE DETECTION OF RESPIRED ACTINIDE NUCLIDES¹

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In an effort to investigate some of the variables which affect detection of respired actinides, using external detectors, Monte-Carlo photon transport techniques have been used in conjunction with a

mathematical heterogeneous phantom⁴ to determine the spatial distribution of uncollided photons which exit the body from various distributions of plutonium and other actinide nuclides in the lung. The photon transport is considered through three different media: lung tissue, soft tissue, and bone. The calculations have been carried out for the L_α , L_β , and L_γ lines of the L x-ray spectrum and for different assumed isotropic point-source locations within the volume of the lung and also for the uniform distribution. Those photons that exit the body unattenuated, that is, those that have not undergone any collisions, are counted in 0.7- by 0.7-cm grids. The distance 0.7 cm matches the half distances between ribs, and the grid structure is aligned to coincide with the ribs for ease in orientation. The calibration factors appropriate for various external detectors in whole-body counting situations have been derived for $^{238,239,240}\text{Pu}$, ^{241}Am , ^{243}Am , and ^{244}Cm . Although the detector calibration factors are strongly dependent on assumed distributions of the respired nuclides in the lung due to the severe attenuation of these photons by the intervening tissue and bone structure, our calculated calibration factors span those currently used at ORNL. The calculations have been used to optimize the geometrical design of germanium detector arrays for use in whole-body counting applications.

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11. Chemical Physics

11.1 STRUCTURAL CHEMISTRY

11.1.1 Crystal Structure of the Mushroom Toxin β -Amanitin¹

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β -Amanitin, $C_{39}H_{53}SO_{15}N_9$, was isolated from the deadly poisonous American mushroom *Amanita phalloides* and crystallized from 95% ethanol. The space group is orthorhombic $P2_12_12_1$ with $a = 14.004(3)$, $b = 14.943(3)$, and $c = 30.794(7)$ Å.

The structure was solved by direct methods, and a structural model containing ethanol and water of crystallization as well as the octapeptide is now being refined. Hydrogen atoms have not yet been included, and $R(F)$ on 3395 unique reflections is currently 0.11. A structural formula is shown in Fig. 11.1, and a stereoscopic view of the molecule as observed in the crystal is shown in Fig. 11.2. The terminal hydroxy group of the dihydroxyisoleucine is shown to have two positions because of disorder.

All amino acid residues have the *L* configuration, and all peptide bonds are in the *trans* conformation. The C^β atom of isoleucine is *S* as expected. The C^β

Fig. 11.1. Structural formula of β -amanitin.

Fig. 11.2. Stereoscopic view of β -amanitin. The dark atoms represent disordered position of the terminal hydroxy group.

and C γ of the dihydroxyisoleucine, the cysteine S, and the C γ atom of the hydroxyproline all have the *R* configuration.

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2. Gibbs Chemical Laboratory, Harvard University, Cambridge, Mass.

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11.1.2 Crystal Structure of 5,6-Dihydrocytidine-6-sulfonate, an Intermediate in the Bisulfite Ion-Catalyzed Conversion of Cytidine to Uridine

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5,6-Dihydrocytidine-6-sulfonate, C₉H₁₅O₈N₃S, crystallizes in a triclinic cell with twinned habit. Cell dimensions are: *a* = 6.805(3), *b* = 8.497(6), *c* = 12.301(5) Å; α = 115.35(4), β = 89.90(3), and γ = 97.93(3)°. The structure analysis was based on 2232

unique intensities measured on the Oak Ridge computer-controlled diffractometer, using niobium-filtered Mo *K* α radiation. Estimates of individual ("untwinned") intensities were made for those data composed of contributions from both lattices.

Correct orientations for both dihydrocytosine rings were found using program ORTRAN² when the sulfonate group was placed in the initially unexpected pseudoaxial position. The translation between the two rings was determined from a sharpened three-dimensional Patterson function. The complete structure was then developed by three cycles of structure-factor calculation and $(2|F_o| - |F_c|) \exp(i\phi_c)$ synthesis. Hydrogen atoms have not yet been included, and the current *R*(*F*) is 0.09.

The conformation adopted by both molecules (Fig. 11.3) indicates that bisulfite addition to pyrimidines can be accommodated with a minimum of conformational rearrangement. The *anti* configuration³ found in guanylyl-3',5'-cytidine⁴ and adenosyl-3',5'-uridine⁵ is preserved, although the ribose does adopt the 2'-

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Fig. 11.3. Perspective view of the 5,6-dihydrocytidine-6-sulfonate molecule. The two independent but nearly identical molecules have been averaged.

endo conformation⁶ rather than the 3'-*endo* found in those molecules. It should be noted that the *anti* configuration is possible only because the sulfonate is pseudoaxial; in 6-methyluracil⁷ the methyl forces a *syn* conformation with O2 in close proximity to the ribose.

11.1.3 Crystal Structure and Conformation of the Cyclic Hexapeptide cyclo-(Gly-L-Pro-D-Ala)₂

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W. E. Thiessen

The L-proline residue is known to be a conformational determinant in both structural and globular proteins, and there has been considerable recent interest² in conformational analysis of cyclic hexapeptides of the type cyclo-(X-L-Pro-Y)₂. A recent crystal structure analysis³ of hydrated cyclo-(L-Ala-L-Pro-D-Phe)₂ shows that the C₂ symmetry possible for the molecule is rigidly maintained in the crystal. We have undertaken crystallographic analyses of cyclo-(Gly-L-Pro-D-Ala)₂, cyclo-(Gly-L-Pro-Gly)₂·4H₂O, and cyclo-(D-Ala-L-Pro-D-Ala)₂·5H₂O, crystals of which were kindly provided by Prof. E. R. Blout. We report here the crystal structure of cyclo-(Gly-L-Pro-D-Ala)₂, in which the molecule shows significant deviation from twofold symmetry.

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ORNL-DWG. 77-10257

Fig. 11.4. Perspective view of the cyclo-(Gly-L-Pro-D-Ala)₂ molecule. The large circles represent oxygen atoms, intermediate-sized circles represent nitrogen atoms, and small circles represent carbon atoms. The darkened atoms represent a disordered carbon.

This cyclic peptide, $C_{20}H_{30}N_6O_6$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.389(6)$, $b = 10.379(8)$, and $c = 22.006(16)$ Å. The structure was solved by direct methods and refined to a final $R(F)$ of 0.055 on 1575 unique reflections having $|F| > 3\sigma(|F|)$.

Fig. 11.4 depicts the molecule as observed in the crystal and makes clear the reason for the departure from twofold symmetry. Just as in cyclo-(L-Ala-L-Pro-D-Phe)₂, there is a very short contact (2.82 Å) between the two carbonyl oxygens inside the ring. This contact prevents effective hydrogen bond formation if twofold symmetry is maintained,³ but breakdown of the symmetry permits formation of one H bond ($O \cdots N$ distance: 3.02 Å) at the minimal expense in energy of lengthening the other $O \cdots N$ distance to 3.42 Å. The factors which decide between these alternative geometries are not yet clear, but it is worth noting that while the cyclo-(L-Ala-L-Pro-D-Phe)₂ molecule "literally lies in a sea of solvent,"³ cyclo-(Gly-L-Pro-D-Ala)₂ is unhydrated, and there are only two intermolecular H bonds. The intermediate cases of cyclo-(Gly-L-Pro-Gly)₂·4H₂O and cyclo-(D-Ala-L-Pro-D-Ala)₂·5H₂O should prove interesting.

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11.1.4 Structure of an Epoxide from Permanganate Oxidation of Butylated Hydroxy Toluene

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Controlled permanganate oxidation² of 2,6-di-*t*-butyl-4-methyl phenol (butylated hydroxy toluene) by B. M. Benjamin and V. F. Raaen produced a crystalline compound with an NMR spectrum atypical for oxidation products in this series. An x-ray diffraction crystal structure analysis of the unknown product was undertaken as an undergraduate project in a research participation program with the Southern College University Union. An application of direct methods implemented by the MULTAN program showed the structure to be 5,6-oxido-2,6-di-*t*-butyl-4-methylcyclohexan-1,3-dione-2,4-diol as illustrated in Fig. 11.5. Least-squares refinement of the 3413 unique diffraction data from the triclinic crystal ($a = 8.901$, $b = 12.387$, $c = 7.302$ Å; $\alpha = 100.8$, $\beta = 94.0$, $\gamma = 99.1^\circ$; $Z = 2$, space group $P1$) produced an R on F^2 of 0.061.

Fig. 11.5. Stereoscopic illustration showing the molecular geometry, packing, and hydrogen bonding for 5,6-oxido-2,6-di-*t*-butyl-4-methylcyclohexan-1,3-dione-2,4-diol.

The unusual boat configuration of the cyclohexane ring is stabilized by an internal hydrogen bond. The bond lengths and angles, including those involving hydrogen atoms, are all quite normal for an x-ray structure. The epoxide distances are 1.471 Å for C-C and 1.457 Å, 1.433 Å for C-O-C, with the asymmetry attributable to carbonyl group conjugation.

1. Research Participant with Southern College University Union from Centre College, Kentucky.
2. See Sect. 1.1.6 of this report.

11.1.5 Neutron Crystal-Structure Analysis of *o*-Terphenyl: Conformational and Packing Data for Testing Potential Energy Functions for Hydrocarbons

G. M. Brown H. A. Levy

Data on molecular conformations and packing from crystal-structure determinations provide the basis for evaluating the parameters of potential energy functions required for predictions of conformations, packing, and energy.¹⁻⁴ We have determined the crystal structure of *o*-terphenyl by the neutron-diffraction method to obtain data for testing potential functions¹ for hydrocarbons. The overcrowding in *o*-terphenyl resulting from the presence of the two bulky phenyl groups in ortho positions on the central ring makes the molecule a particularly useful one for study. The neutron technique is advantageous for such hydrogenous compounds because it, in contrast to the x-ray technique, allows precise, accurate location of the hydrogen atoms, which are involved in a large fraction of the nonbonded intra- and intermolecular contacts in these compounds.

Bond lengths, valence angles, and other details of the molecular structure are shown in the drawings of Fig. 11.6. The angles ϕ in the figure are twists about the inter-ring bonds from the theoretical conformation (not physically possible) in which all three rings are coplanar. The deviation of each carbon and hydrogen atom from the least-squares best plane through its own ring of six carbon atoms is shown. For each of the four axial carbon and two axial hydrogen atoms of each of the two biphenyl moieties of the molecule, a second out-of-plane deviation is also shown, marked with an asterisk. This is in each case the deviation from the best ring plane for the half of the biphenyl moiety to which the atom does not belong. Positive deviations are outward from the

Fig. 11.6. Molecular structure of *o*-terphenyl. Top: View perpendicular to the least-squares best plane through the middle ring, showing the twist angles ϕ (deg) about the inter-ring bonds and the deviations (in units of 10^{-3} Å) of atoms from the least-squares best planes through the rings, with estimated standard errors of the deviations (in parentheses). The carbon atoms are numbered. See text for further explanation. Middle: Skeletal drawing of the molecule in the same orientation as in top drawing, showing all bond lengths (Å) and valence angles (deg) and their standard errors. Bottom: View in a direction perpendicular to that of top drawing, showing the intramolecular nonbonded distances (Å) of interest in relation to the molecular conformation, with standard errors.

sides of the planes visible to the viewer of the top drawing of the figure.

The consequences of overcrowding in the molecule demonstrated in Fig. 11.6 are: the large twist angles, 42 and 62° in the same sense, about the bonds C(1)–C(1') and C(1'')–C(2'); the significant enlargement of the angles C(1)–C(1')–C(2') and C(1'')–C(2')–C(1') at the expense of C(1)–C(1')–C(6') and C(1'')–C(2')–C(3'), respectively; the rather large deviations in opposite directions from the central ring plane of the axial atoms of the two terminal rings.

We plan to use the molecular structural and crystal packing data from this study in potential energy calculations for the *o*-terphenyl molecule and crystal.

The general features of the molecular structure and the molecular orientation are consistent with predictions from measurements of the diamagnetic susceptibility of the crystal;⁵ the details will be useful in interpreting results of a current diamagnetic study.⁶

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11.1.6 Crystal Packing in Substituted Biphenyls: Structure of 4,4'-Dichlorobiphenyl

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The structures of the 4,4'-dihalobiphenyls have been investigated as part of a project to study the effects of crystal packing forces on molecular geometries. When X = F, the space group is $P2_1/a$ with $Z = 2$, the same as for biphenyl itself.³ When X = Cl or Br the space group remains the same (although indexed in these cases as $P2_1/n$), while Z increases to 8. The molecular volumes in the two structures are quite different: 217(1) and 224(3) Å³ for biphenyl itself and for X = F; 261(1) and 272(3) Å³ for X = Cl and Br. Bitolyl,⁴ X = CH₃, also crystallizes in $P2_1/n$ with $Z = 8$ and has a molecular volume of 267(1) Å³. The differences in molecular volumes do not closely parallel changes in radii for X = H, F, Cl, and Br, indicating that the two structures differ in packing density.

A full crystal structure analysis has been performed for 4,4'-dichlorobiphenyl. A data set was collected using Mo $K\alpha$ radiation; cell constants were found to be 9.682(3), 13.740(4), and 15.780(4) Å for a , b , and c respectively, and $\beta = 96.23(3)^\circ$. The structure was solved and refined by standard methods to a final R of 4.2% for the 1653 reflections having $I \geq 3\sigma(I)$. The dihedral angles between the phenyl rings are 38.6 and 42.1° for the two independent molecules; the same angles take values of 36 and 40° in bitolyl. There are small but significant discrepancies between the C–C–C angles in the X = Cl and C = CH₃ compounds. Since packing is very similar in the two cases, electronic effects⁵ may well account for the differences.

1. Visiting scientist with ORAU support from Department of Chemistry, University of Kentucky, Lexington.

2. Graduate student at University of Kentucky, Lexington.

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11.1.7 Analysis of Crystallographic Density Maps Using Critical-Point Topology

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In 3-space there are four types of critical points (zero gradient points) classified by the signs of the second-derivative eigenvalues. These may be designated peak (---), pass (+--), pale (++-), and pit (+++), where pass and pale are saddle points. The network of critical points and connecting paths provides a global characterization for a crystallographic density map and is particularly useful for complicated low-resolution maps. Suppose we have a pair of adjacent atoms with variable Gaussian width. The density at the pass where the Gaussian functions overlap increases with the width variable until the two original peaks and the pass merge to form a single new peak. Similarly, a chain of atoms transforms into a bumpy ridge with an orderly reduction of critical points as the resolution becomes poorer. An elegant, but abstract, mathematical description is provided by the Morse theory.¹

A computer program ORCRIT is being developed in FORTRAN to provide a graph representation of the critical-point network in a density map. There are three main steps to the calculation: (1) find the critical points, their density, and second derivatives using a 3-D interpolation polynomial; (2) connect the critical

points in a weighted minimal spanning tree (modulo the space-group symmetry); (3) prune, correct, verify, and extend the connectivity suggested by the spanning-tree calculation. This is done using multiple sources of knowledge in an artificial intelligence framework.²

The program should be useful for several crystallographic problems, including interpretation of macromolecule density maps and anisotropic Fourier refinement of small molecules.

1. M. Morse and S. S. Cairns, *Critical Point Theory in Global Analysis and Differential Topology*, Academic Press, New York, 1969.

2. See Sect. 11.1.8 of this report.

11.1.8 Methodology of Artificial Intelligence for Crystallography

C. K. Johnson

Artificial intelligence is a computer science methodology concerned with symbolic manipulation processes related to intelligent action. By "intelligent action" is meant an act or decision arrived at by an understandable chain of symbolic analysis and reasoning steps based on knowledge about the problem domain. Some better known artificial intelligence projects include integrated robotic systems, visual scene interpretation, and speech understanding.

The application of this methodology to applied sciences such as crystallography¹ appears useful, and the author spent a year on detached assignment at Stanford University working in this area. A collaborative project under way with Stanford involves the interpretation of crystallographic electron density maps. The basic model for the three-dimensional density function is a critical-point network, a graphlike representation portraying global topological features.² Various abstractions for the molecular model also are represented as graphs, and the molecular and density models are manipulated until appropriate mapping of one onto the other is achieved.

The mapping manipulations can be done manually through interactive computer graphics, with the operator supplying the domain knowledge, or through computer programs which implement a system of rules containing a simplified interpretation of the domain knowledge. The system of rules (production rules) to be developed will be based on experiences obtained from the interactive graphics

mode of operation. As techniques develop and are encoded into computer programs, the computer graphics display will serve as a monitor for the calculation. The start of the interactive graphics system will be a graphics terminal interacting with a PDP-10 host computer. As the program system develops, a satellite minicomputer will be added to improve responsiveness.

1. E. A. Feigenbaum, R. S. Englemore, and C. K. Johnson, *Acta Crystallogr., Sect. A* 33, 13 (1977).

2. See Sect. 11.1.7 of this report.

11.1.9 Holography in Crystallography

C. K. Johnson

Several news items¹ have appeared recently concerning a holographic technique and its postulated impact on crystallography. An analysis² showed the claims for the technique to be inaccurate, but in the process of making the analysis, a perspective was developed on areas where holography and crystallography can interact productively.

Optical techniques, such as the optical transform,³ have had a small but enthusiastic group of crystallographic supporters since the 1940s. The optical transform allows one to obtain an image for the square of the complex Fourier transform of a two-dimensional real function without a mathematical formulation for the function or its transform. Holographic techniques provide a mechanism whereby a real 2-D function can be synthesized optically from its complex Fourier coefficients encoded into a computer-drawn hologram.⁴

Holograms are capable of synthesizing 3-D objects (actually 2-D surfaces embedded in 3-D space), but the complex wave front for a nonplanar object is extremely difficult to formulate and compute.⁴ The hidden-line problem and its ramifications make the situation even more difficult when several objects are present. An alternative approach⁵ utilizes holograms of 2-D projections of the objects to produce multiple stereopairs creating the impression of three-dimensionality. This procedure⁵ has proven useful in the display of computer-drawn molecular models of the sort produced by the ORTEP program. In this approach the holograms are made optically, but the possibility exists for producing computer-drawn holograms directly from the calculated projections.⁶

Another area where holography and crystallography may interact involves the postulated 1-Å x-ray laser.⁷ Holographic recording and reconstruction schemes for the x-ray region will be difficult to develop, but the payoff could be a new experimental procedure for solving the crystallographic phase problem.

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2. C. K. Johnson, *Science* 196, 478 (1977).
3. C. A. Taylor and H. Lipson, *Optical Transforms, Their Preparation and Applications to X-Ray Diffraction Problems*, Bell, London, 1964.
4. T. S. Huang, *Proc. IEEE* 59, 1335 (1971).
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6. T. Yatagai, *Appl. Opt.* 15, 2722 (1976).
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11.1.10 Experiments in Least-Squares Crystal Structure Refinement of Large Molecules Using Rigid Groups Coupled with Slack Constraints

G. M. Brown

These experiments have been done to develop the capability of refining crystal structures of macromolecular catalysts to the degree that sufficiently accurate atomic coordinates can be derived to elucidate catalytic mechanisms. The least-squares calculations are being made with RAELS,¹ a computer program written at ORNL with some specific features desirable for refining large structures.

After some testing of the program, using data for a small known structure, most of the work has been done on the structure of *Peptococcus aerogenes* ferredoxin, which had already been refined² by use of difference syntheses, differential-difference syntheses, and idealization procedures to the value 0.208 for the usual crystallographic reliability factor R (to 0.188 if the final idealization is omitted). Ferredoxins are of interest in connection with proposals for photosynthetic production of hydrogen. This particular ferredoxin molecule has 389 atoms distributed among 54 amino acid residues and a molecular weight of about 6000. The ~3000 intensity data extend to 2.0 Å resolution.

The rigid-body refinement feature available in program RAELS is particularly appropriate for this problem, where the resolution is not at the atomic level. In general, each of the amino acid residues has been treated as made up of rigid groups coupled by slack constraints on the bond lengths and angles depending on the positions and orientations of two

different rigid groups. The amino acid residues are also linked together by slack constraints. For the specification of the geometries of various rigid groups and of the ideal bond length and angle values for the slack constraints, the most reliable recent structural data on amino acids and peptides from the literature were used. The ferredoxin molecule was described as made up of 17 single atoms and 115 rigid groups (of which a few were also single atoms represented as groups for convenience), and 499 bond length and angle slack constraints were used. For each of these constraints the chosen ideal bond length or angle value enters the least-squares calculations as an observation with an assigned weight. Part of the weighted residual sum comes from the slack constraints and the rest from the real observations, the structure factors.

The procedure seems to be working properly for ferredoxin; however, in a practical sense the improvement of the structure so far as chemical sense is concerned is probably only marginal. This is not surprising, since the structure was already extensively refined. The usual discrepancy index R first increased to 0.2245 because of the very tight constraints implied by replacing individual atoms by rigid groups. Subsequently, R increased slightly to 0.227, but the weighted index R_w went down slightly from 0.243 to 0.231. Some questions remain about the appropriate weighting scheme for this kind of least-squares procedure, and more experimenting with adjustments of thermal parameters is required. Further experiments are in progress. It seems likely that the program will prove most useful in refinements with data at 1.5 Å resolution or better, rather than in a refinement with 2-Å data.

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11.1.11 Dynamic Corrections for Neutron Scattering from Molecular Liquids

L. Blum¹ A. H. Narten

The application of neutron diffraction to liquid materials has been hampered by inelastic and recoil effects that introduce a sizable and unwanted background signal, which must be subtracted from the measured cross section to obtain the desired structural information. In 1952, Placzek² provided a

prescription for computing these "dynamic corrections" to neutron scattering from monatomic fluids, and the resulting correction term is of a simple parabolic form (Fig. 11.7, dashed curves). In all neutron diffraction studies of molecular liquids it has been assumed that the dynamic corrections are also of a simple parabolic form. We have shown^{3,4} that this assumption is erroneous, because the molecular structure leads to significant modulation in the dynamic correction terms (see Fig. 11.7, which shows the computed correction terms for neutron scattering from CCl_4). The dashed curves describe the "self" part due to recoil from individual uncorrelated atoms. In addition, there is a "distinct" contribution due to recoil from different atoms in the same molecule which depends on the mean intramolecular distances and their vibrational amplitudes. As a consequence, the total corrections (solid lines) are modulated by coherence effects.

Since the molecular structure must be known⁵ for the evaluation of the dynamic corrections, it is not clear that the independent determination of molecu-

lar structure parameters from neutron diffraction is feasible with good precision. One solution, adopted by us, is the combination of neutron and x-ray diffraction studies. The molecular structure is determined from the x-ray data, and this information is used to compute the dynamic corrections for neutron scattering from the same fluid. In this way we have, for the first time, derived structure and correlation functions for a molecular fluid (CCl_4) without using disposable parameters in the neutron data reduction.

1. Department of Physics, University of Puerto Rico, Rio Piedras.
2. G. Placzek, *Phys. Rev.* 86, 377 (1952).
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4. L. Blum and A. H. Narten, *J. Chem. Phys.* 64, 2804 (1976).
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Fig. 11.7. Dynamic corrections for neutron scattering from CCl_4 molecules. The points have been computed for rigid and the solid lines for vibrating molecules. The dashed curves describe the "self" part of the corrections.

11.1.12 Diffraction Pattern and Models of van der Waals Fluids

A. H. Narten S. I. Sandler¹

Increasingly, predictions of the thermodynamic and transport properties of liquids for engineering applications are being based on statistical mechanical methods.²⁻⁴ One such method is the reference interaction site model (RISM),⁵ which assumes that the correlations between molecules are determined primarily by the short-range, repulsive portions of the intermolecular potential. These repulsive interactions are modeled as hard-core interactions by assuming molecules as composed of overlapping hard spheres rigidly fused together. The pair correlations $g_{\alpha\gamma}(r)$ produced by these interactions are determined from an approximate integral equation which is solved in a computationally convenient variational form. To solve the RISM equation, the molecular structure and density must be specified. The only adjustable parameters of the model are the sphere diameters $\sigma_{\alpha\gamma}$ for the interaction $u_{\alpha\gamma}(r)$ between site α on one molecule and site γ on another,

$$u_{\alpha\gamma} = \infty, \quad r < \sigma_{\alpha\gamma},$$

$$u_{\alpha\gamma} = 0, \quad r \geq \sigma_{\alpha\gamma}.$$

We have used the RISM theory to interpret x-ray diffraction data for two liquids with weakly interacting molecules, namely, CS_2 and C_6H_6 . The experimental data were used to find the dimensions of the "best" RISM molecule, in the sense that the computed x-ray structure function for this RISM fluid gave the best agreement with the curve derived from experiment. We found the agreement between the results from the RISM theory and experiment excellent for liquid CS_2 and fair for liquid C_6H_6 . Even in the latter case, however, the agreement is good enough to warrant the following more detailed examination of results predicted by this model.

Liquid CS_2 . We have modeled the linear CS_2 molecule by three spheres with a C-S separation of 1.57 Å, determined from the high-angle part of the measured x-ray structure function. The "best" carbon and sulfur diameters were found to be $\sigma_{\text{CC}} = 3.0$ Å and $\sigma_{\text{SS}} = 3.5$ Å. Intermolecular atom-atom pair correlation functions computed for this RISM fluid are shown in Fig. 11.8. The most obvious conclusion from this figure is that while the S-S correlation is sharply peaked at $r = \sigma_{\text{SS}}$, the C-S and C-C correlations are quite diffuse, indicating that even though

Fig. 11.8. The sulfur-sulfur (—), carbon-sulfur (---), and carbon-carbon (-·-) intermolecular atom pair correlation functions for liquid CS_2 calculated from RISM theory.

there is a strongly preferred sulfur-sulfur nearest-neighbor distance, the C-S tails of adjacent molecules are much less ordered. This suggests that no single orientational model (i.e., neighbors in only parallel or crossed orientations) will be able to account for the structure of liquid carbon disulfide.⁶

Liquid C_6H_6 . The "best" RISM molecule for this fluid consists of 12 overlapping hard spheres, 6 of which are located at the carbon positions with a diameter $\sigma_{\text{CC}} = 3.4$ Å and another 6 at the hydrogen positions with a diameter $\sigma_{\text{HH}} = 2.58$ Å. The intermolecular atom pair correlation functions for H-H and C-H interactions (Fig. 11.9) are sharply peaked at $r = \sigma_{\text{HH}}$ and $r = \sigma_{\text{CH}}$ respectively. This means that the predominant configuration in the liquid is one in which at least one hydrogen atom from an origin molecule is in contact with both a hydrogen and a carbon atom from a neighboring molecule. The only arrangement with both H-H and C-H contacts is one in which pairs of molecules fit together like six-toothed bevel gear wheels whose axes are almost at right angles. Such an *L* configuration is consistent with a C-C distance of ~4 Å (Fig. 11.9, bottom), an X-H distance of ~4.5 Å (Fig. 11.10, top), an X-C distance of ~5.5 Å (Fig. 11.10, center), and an X-X distance of ~6 Å (Fig. 11.10, bottom), where X denotes the ring center.⁷

We conclude that the RISM theory predicts the structure of van der Waals fluids in agreement with

Fig. 11.9. Interatomic pair correlation functions computed for an RISM fluid with 12 sites in the benzene molecule (solid lines). The dashed curve at the bottom is for an RISM fluid with continuous repulsive interactions between carbon atoms, and the circles are for the experimental function $g_{cc}(r)$.

diffraction data. The theory can be extended to include attractive forces necessary to predict thermodynamic properties.

Fig. 11.10. Ring center (X-X) and atom-center (X-C, X-H) correlation functions for the 12-site model of liquid benzene predicted by the RISM theory (solid lines), and center-center correlation functions $g_{xx}(r)$ predicted by the 6-site Lennard-Jones model of Evans and Watts (+ + +) [Mol. Phys. 32, 93 (1976)]. These authors report molecular dynamics results for a 6-site model of liquid benzene. The pair potential is represented as a sum of Lennard-Jones interactions.] The vertical bars indicate the ring center separations in crystalline benzene at -30°C .

1. Department of Chemical Engineering, University of Delaware, Newark.

2. See, for example, *Proceedings of the Engineering Foundation Conference on the Correlation and Prediction of Thermodynamic Properties and Phase Equilibria in the Chemical Industry*, ed. S. I. Sandler and T. S. Storvick, American Chemical Society (to appear, summer 1977).

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6. For a detailed discussion, see S. I. Sandler and A. H. Narten, *Mol. Phys.* 32, 1543 (1976).

7. A detailed report has been submitted to *J. Chem. Phys.*

11.2 ATOMIC AND MOLECULAR COLLISIONS

11.2.1 Crossed Molecular Beam Studies of Excited Atom Reactions

H. F. Krause S. Datz

Numerous experimental methods have been employed to study neutral-neutral reactions involving atoms in ground and excited states, but there are few reports of single-collision experiments where detailed reaction energy disposal has been studied. The marriage of molecular spectroscopy to molecular beams is ideally suited to this end; consequently, we have applied our previously reported chemiluminescent techniques¹ to a state-selected study of near-resonant electronic energy transfer involving $\text{Hg}^*(6^3P_2)$ with ground-state NO. We have extended our capabilities

in this field by the acquisition of a pulsed tunable-dye-laser, and we are applying a laser-induced fluorescence technique in the study of elementary combustion reactions.

Role of kinetic and molecular rotational energy in near resonant electronic excitation transfer:

The energy available for transfer from the metastable $\text{Hg}(6^3P_2)$ state is 44043 cm^{-1} . The first excited state of $\text{NO}(A^2\Sigma^+, v' = 0, K' = 0)$ lies 44200 cm^{-1} above the $X^2\Pi_{1/2}$ ground state; hence pure electronic excitation is endoergic by 156 cm^{-1} . For the $X^2\Pi_{3/2}$ reactant, the endoergicity is only 31 cm^{-1} , so that almost resonant conditions for energy transfer exist. In these studies the excited atom beam was formed by passing a ground-state mercury beam through an intersecting electron beam whose energy was variable. Excited atoms having lifetimes shorter than 10^{-4} sec decayed before colliding with a molecular beam. Photons emitted from the beam intersection volume were dispersed by a grating monochromator and detected as pulses by a photomultiplier. In our initial studies the $\text{NO}(X^2\Pi)$ reactant was a thermal beam with Maxwell-Boltzmann velocity and rotational energy distributions ($T = 100$ to 400 K), and rotational distributions of the $\text{NO}(A^2\Sigma^+)$ were found to be hotter than the initial NO temperature by $\sim 200 \text{ K}$. Now, velocity and rotational state-selected studies have been performed. These were accomplished by expanding the NO through a nozzle whose temperature was variable ($T = 150$ to 400 K). The initial rotational state distribution was very narrow (2 or 3 rotational levels, $T_{\text{rot}} \lesssim 10 \text{ K}$), and the velocity distribution was greatly narrowed at fixed temperature ($\Delta v/v \approx 0.1$). Under these conditions, highly resolved emission spectra of $\text{NO}(A^2\Sigma^+, v' = 0)$ over the collision energy range 0.036 to 0.080 eV were obtained and indicate that the rotational energy distribution did not vary, but the cross-section velocity dependence increased monotonically with energy ($\sim$ factor of 2). The fraction of the total available energy in product rotation near threshold (0.036 eV) approached $\sim 100\%$, but it was only $\sim 50\%$ at twice this collision energy. Evidently, the product rotational energy distribution (similar to a thermal distribution at $T \approx 300 \text{ K}$) is much hotter than that of the reactant because of the conversion of kinetic collision energy into product rotational energy, and the broad product rotational distribution ($2 \leq K' \leq 10$) is indicative of the wide range of torques exerted on NO during the collision.

Study of elementary combustion processes. Studies of ground and excited carbon reactions have been initiated. Our goal is to study reactions such as $\text{C}(2^3P \text{ or } 1D_2) + \text{NO}(X^2\Pi) \rightarrow \text{CN}(X^2\Sigma^+ \text{ or } A^2\Pi) + \text{O}(2^3P_1)$, and $\text{C}(2^1D_2) + \text{H}_2 \rightarrow \text{CH}(X^2\Pi) + \text{H}$. These elementary reactions are of particular interest, since there are numerous potential energy surfaces that correlate (adiabatically) reactants and products so that large cross sections for chemical reaction are expected, and the systems are simple and amenable to theoretical calculations. Carbon atoms in the 2^3P ground state and the 2^1D_2 first excited state (1.26 eV) are produced by evaporating pure graphite at high temperature ($T \approx 2600 \text{ K}$). Detection of the ground-state product radicals such as $\text{CN}(X^2\Sigma^+)$ and $\text{CH}(X^2\Pi)$ will be achieved using the laser-induced-fluorescence technique. Radicals formed in excited states such as $\text{CN}(A^2\Pi)$ will be detected via chemiluminescence. Of interest for these systems are (1) reaction cross sections for each initial and final electronic state and (2) partitioning of the energy released in the reaction into each (v, J) state of the final electronic state.

A nitrogen-pumped, tunable-dye-laser system has been acquired, interfaced, and tested in a laser-induced-fluorescence setup. We have also developed a dynode gating technique that reduces the ever-present scattered laser light intensity by at least a factor of 10^4 over conventional setups. Our approach is also considerably faster (risetime, 50 nsec) than the fastest previously reported dynode gating technique³ (risetime, 250 nsec). This improvement coupled with efficient photon collection indicates that detection of 10^4 molecules/ cm^3 [e.g., $\text{CH}(X^2\Pi)$] should now be routine.

In the course of characterizing the carbon atom source (for beam intensity and impurity fractions C_2 , C_3 , etc.), we have preliminarily identified the crossed-beam chemiluminescent reaction $\text{C}^*(2^1S) + \text{NO} \rightarrow \text{CN}^*(B^2\Sigma, v' = 0, 1) + \text{O}$. Although the beam impurity fraction of the metastable $\text{C}^*(2^1S)$ state (2.68 eV) is low [10^{-4} of $\text{C}(2^3P)$], high reaction probability is expected due to adiabatic correlation of reaction and product states. Detailed vibrational energy disposal in the reaction as well as $\text{CN}^*(B^2\Sigma)$ production vs C_2 , C_3 beam population is being studied.

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11.2.2 Inelastic Scattering and Electron Detachment in Collisions of Cl^- Ions with Atoms and Diatomic Molecules

J. T. Cheung S. Datz

Although rate constants for the process of electron loss from negative ions in collision with atoms or molecules have been investigated, no information on the mechanism of this process (electron detachment) has yet been reported. In our work we find that, rather than simple mechanical removal, all detachment proceeds via the formation of a negative ion state of the target atom or molecule.

In our experiments we use the technique of time-of-flight translational spectroscopy. The apparatus consists of three sections (Fig. 11.11): a Cl^- ion source, a scattering cell, and a detector. Negative atomic Cl^- are generated by surface ionizing HCl on a hot thoriated iridium ribbon to which a variable negative potential is applied. The grounded grid and apertures subsequently accelerate and collimate the beam. Thermal electrons are removed by applying a weak magnetic field perpendicular to the beam direction. The ions then pass through a parallel-plate energy analyzer and are bent 127° before being focused into a pair of modulating plates by einzel lenses. Under optimum conditions, the beam intensity at a distance 1 in. from the last aperture ranges from $\sim 1 \times 10^{-8}$ A for $E = 20$ to $> 5 \times 10^{-7}$ A for $E = 100$ eV. Time-of-flight analysis showed the energy resolution, $\Delta E/E$, to be $\leq 0.6\%$ for $E > 100$ eV and $\approx 1\%$ for $60 < E < 100$ eV. The scattering chamber is 2 cm long with circular

entrance and exit apertures 2 mm in diameter. It can be cooled to 120 K. A pair of deflecting plates located after the scattering chamber are used to remove ions for electron detachment studies. A channeltron multiplier is mounted in the beam line to detect both the ions and the fast ($E > 150$ eV) neutrals.

Electron detachment of Cl^- in collision with atoms and diatomic molecules. The energy loss spectra of neutral Cl atoms formed in the scattering of fast Cl^- (300 to 500 eV) from several diatomic molecules (Cl_2 , HCl , NO , N_2) and rare gases (Ar , Ne) have been measured. All measurements were made in the forward scattering direction. For direct stripping of the electron from Cl^- ion, an inelastic energy loss of 3.6 eV is required. However, in the case of NO and Ne targets, the only observable inelastic peaks were at 6.6 and 9.2 eV, respectively, and were constant over the range of the initial energies. For Cl_2 , N_2 , HCl , and Ar , the primary energy losses were 4.1, 6.6, 6.0, and 7.5 eV; a second higher peak at 7.1, 14.0, 10.6, and 15.0 eV was also observed. An example is given in Fig. 11.12. To explain these energy losses, a detachment mechanism via temporary negative ion formation of the target is proposed; the two peaks correspond respectively to the formation of the ground state and the first-excited-state negative ions.

Inelastic scattering and electron detachment in collisions of Cl^- with H_2 and D_2 . Because of the large mass difference between the projectile and the targets in these systems, we were able to lower the relative collisional energy and to measure scattering events both in the forward and the backward directions.

Fig. 11.11. Schematic diagram of the apparatus.

Fig. 11.12. Energy loss spectrum for $\text{Cl}^- + \text{N}_2 \rightarrow \text{Cl}^- + \text{N}_2^+$. The scale is the energy loss (eV) of the center-of-mass motion.

Collisional electron detachment. Three detachment channels were observed and their excitation functions were measured.

1. Energy loss of this process is not constant. Instead it shows direct proportionality ($\sim 0.1 E_{\text{beam}}$) to the beam energy and is reminiscent of the "spectator" peak reported previously^{1,2} for the $\text{K}-\text{H}_2$ and $\text{Na}-\text{H}_2$ systems. The spectator peak was explained by the elastic backscattering from a single atom of the target molecule, accompanied by electron detachment. This channel is dominant at low relative energy ($E_{\text{CM}} < 12$ eV). It reaches a maximum at $E_{\text{CM}} \approx 20$ eV and decreases rapidly.
2. Energy loss of this process is constant at 13.3 eV (± 0.7). This suggests temporary formation of H_2^- in its first excited state ($^2\Sigma_g^+$). The excitation function reaches a maximum at $E_{\text{CM}} = 25$ eV, declines gradually at higher energies, and extrapolates down to a threshold at about 14 eV.
3. This process has a constant energy loss of 8.1 eV (± 0.8), corresponding to the formation of H_2^- in its ground state ($^2\Sigma_u^+$). The excitation function shows a monotonic increase with energy. At high collisional energy ($E_{\text{CM}} > 30$ eV), this becomes the dominant process. Preliminary data also showed that channel 3 is more favorable than 2 at larger scattering angles.

Inelastic scattering in collisions of Cl^- with H_2 . At very low relative collisional energy ($3.4 \text{ eV} < E_{\text{CM}} < 11 \text{ eV}$), we measured the time of flight of the Cl^- ions backscattered from H_2 and hence deduced the effi-

ciency for trans $\rightarrow$ vib energy transfer of the process

For any collisional energy in this range, about 50% of the translational energy was converted to the vibrational energy of the H_2 molecule. This is approximately six times more inelastic than the case of its isoelectronic analog, that is, K^+ backscattered from H_2 .^{1,2} The result of the K^+-H_2 system is in good agreement with an exact classical calculation involving only the K^+-H_2 repulsive potential and H-H potential. The high efficiency for trans $\rightarrow$ vib energy transfer for the $\text{Cl}^- - \text{H}_2$ system is thus attributable to crossing of potential energy surfaces.

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11.2.3 Ion Pair Formation and Atom Abstraction in Collisions of Alkali Atoms with High-Electron-Affinity Hexafluorides

B. K. Annis S. Datz

It has recently been reported that the electron affinities of several hexafluoride molecules (e.g., MoF_6 , WF_6 , PtF_6 , and UF_6) are ~ 4.5 eV, and hence the reaction of K or Cs with these molecules to form $\text{AF}_6^- + \text{M}^+$ is exothermic at thermal energy. In several experiments the energy threshold for ion pair formation has been taken as a measure of molecular electron affinities, and in some cases ion pairs have been reported to occur at extremely low translational energies. However, a true assessment of these collision processes must include a study of alternate reaction channels.

The reactions of K and Cs with WF_6 , UF_6 , MoF_6 , TeF_6 , SeF_6 , and SF_6 were studied at thermal energies, using crossed molecular beams. By using seeded nozzle beams of UF_6 in He, the velocity dependence of the reaction $\text{Cs} + \text{UF}_6 \rightarrow \text{Cs}^+ + \text{UF}_6^-$ has been measured in the energy region 1 to 5 eV ($E_{\text{CM}} = 0.4$ to 1.4 eV).

At thermal energies no significant ($\sigma < 10^{-18} \text{ cm}^2$) ion pair formation was observed in any case. Instead, the even more exothermic abstraction reactions to form MF (and possibly MAF_5) occurred with large cross sections. The measured product angular distributions were in all cases found to be consistent

Fig. 11.13. Angular distribution of CsF from Cs + UF_6 fitted with the "complex" model of Marcus.

Fig. 11.14. Energy dependence of the $\text{Cs} + \text{UF}_6 \rightarrow \text{Cs}^+ + \text{UF}_6^-$ reaction.

with complex formation. However, substantial differences in the mode of complex disintegration were noted. For example, the CsF angular distribution from $\text{Cs} + \text{UF}_6$ is shown in Fig. 11.13; note the forward-backward peaking characteristic of complex disintegration. For TeF_6 , however, the distribution is better fitted by the formation of MTeF_5 . Since the abstraction reaction paths are more exothermic than ion pair formation, complex formation would demand the predominance of abstraction. However, as energy is added to the system the lifetime of the complex is shortened to the point where this mechanism can no longer be valid. The results obtained with accelerated beams for $\text{Cs} + \text{UF}_6 \rightarrow \text{Cs}^+ + \text{UF}_6^-$ are shown in Fig. 11.14. Both the magnitude and the energy dependence of this cross section are in strong disagreement with complex formation and indicate a binding energy of the CsUF_6 complex to be ≤ 1 eV.

11.2.4 Negative Molecular Surface Ionization of UF_6

P. F. Dittner S. Datz

Investigations have been carried out to elucidate the surface ionization process of UF_6 molecules (electron affinity ≈ 5 eV)^{1,2} by measuring the UF_6^- ion current obtained when a molecular beam impinged upon heated surfaces. In order to measure the absolute flux of UF_6 striking the wire, the beam was condensed in a liquid-nitrogen-cooled trap for a fixed time period, dissolved in HDEHP, added to a liquid scintillator, and counted in a scintillation spectrometer. For several metals the efficiency was orders of magnitude lower than Saha-Langmuir predictions. However, on a Pt-C surface an absolute efficiency of $96 \pm 4\%$ is obtained at $T = 500$ to 1500 K. Below 500 K a precipitous decrease attributable to surface coverage is observed. Modulating the molecular beam and measuring the decay times of the ion signal allowed us to determine the residence times of the UF_6 as a function of wire temperature. From this data we derive that the heat of adsorption of $\text{UF}_6 = 33.6$ kcal/mole on this surface. The differences in behavior observed on pure metal and carbon-covered surfaces are ascribed to the differences in dissociation equilibrium on the surface,

the lower electron affinity of the UF_5 and F products yielding a lowered surface ionization efficiency.

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2. R. N. Compton (submitted to *J. Chem. Phys.*).

11.2.5 Hydrogen Recycle Chemistry: Interaction of Low-Energy Proton Beams with Carbon

S. Datz P. F. Dittner
S. Overbury

A system has been constructed for the study of energy exchange, chemical reactivity, and chemical "sputtering" of first wall materials with charge-exchanged hydrogen from the plasma. The initial study is on pyrolytic carbon interacting with 10- to 1000-eV beams of H and D. The system, consisting of mass-analyzed ion beam, heatable sample, mass filter, and electrostatic analyzer, all contained in a 10^{-10} torr vacuum, has been completed. A low-energy ion backscattering system for surface analysis was developed and was used to measure surface composition of high-purity pyrolytic graphite. Significant concentrations of O and Si are measured which decrease with argon sputter cleaning and are reestablished, presumably by diffusion, upon heating to $\sim 1500^\circ\text{C}$. The mass spectrometer system has been installed, and background pressures of CH_4 of $\sim 10^{-12}$ torr are found in the vacuum system. This should allow detection of $\sim 10^{-14}$ to 10^{-15} torr CH_4 from "chemical" sputtering.

For the low energy (<200 eV H^0) anticipated from the plasma, a considerable amount of reflection is anticipated. The electrostatic analyzer system has been employed for initial measurements of the energy spectra of H^+ and H^- backscattered from the carbon target and checked as a function of energy and as a function of surface impurity composition for both surface conditions. To do this, a method has been devised to determine the neutral H^0 component in the reflected beam which will allow a complete determination of the reflected energy spectrum, which can then be compared with results of the "Marlowe" computer program for this system. The method involves measurement of charge fractions transmitted through thin carbon foils at known exit energies. This experiment, which has been initiated, also yields the stopping power for low-energy hydrogen atoms in carbon.

11.2.6 Higher-Order Z_1 Effects and Effects of Screening by Bound K Electrons on the Electronic Stopping of Channeled Ions

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P. F. Dittner P. D. Miller¹
J. A. Biggerstaff¹

For swift ions totally stripped of electrons in a random medium, the first-order theory predicts that the electronic stopping power, S , at a given velocity,

v , should be strictly proportional to the square of the ionic charge $Z_1 e$. Observations on the differences in π^+ and π^- stopping led to theories which demonstrated an additive Z_1^3 contribution to the stopping due to polarization. The theory seemed to explain the differences in S/Z_1^2 observed for He and H in various media, but Lindhard² later pointed out that a subtractive Z_1^4 term must be considered. Hence the expression

$$S = -dE/dx = NZ_2 \frac{4Z_1^2 e^4}{mv^2} \times (L_0 + Z_1 L_1 + Z_1^2 L_2), \quad (1)$$

where m is the electron mass, and N is the density of target atoms Z_2 . A true test of these contributions requires extension to higher values of Z_1 . However, for higher Z_1 (and to some extent for lithium at the energies in question, <4 MeV/amu), determination of higher-order Z_1 effects is obscured by fluctuations of ionic charge, q , occurring in a random solid. Hence the effect of screening by bound electrons also comes into question.

In this work we use a technique of ion channeling wherein ions may pass through solids with no charge-changing collisions, and we report the stopping powers in gold {111} channels for totally stripped nuclei of $Z_1 = 1$ to 9 at 2.0 MeV/amu and $Z_1 = 1$ to 5 at 3.5 MeV/amu. The effects of screening were measured at 2 MeV/amu from a comparison of the stopping of totally stripped ions with ions having a single bound electron for $Z_1 = 6$ to 9 and ions having two bound electrons for $Z_1 = 7$ to 9.

At 2 MeV/amu the stopping powers for bare nuclei from $Z = 5$ to 9 are found to scale exactly as Z_1^2 . If the bound electrons screened the nuclear charge perfectly, then S/q^2 for B^{5+} , C^{5+} , and N^{5+} should be identical. Higher values of S/q^2 for the clad ions reflect imperfect screening, and an "effective" charge $q' = (SZ_1^2/S_z)^{1/2}$ can be obtained by comparison with the stopping power, S_z , of the bare nucleus with the same charge. Center-channeled ions interact directly only with conduction ($6s$ and $5d$) electrons of the gold ($E_b < 10$ eV) and at longer range with $5p$, $5s$ and $4f$ electrons. The reduction in screening arises from contributions to stopping from conduction electrons which penetrate within the radius of the bound projectile K electron.

For the channeled totally stripped ions at 2 MeV/amu, a rise of 3.5% is seen between H and He, 3.5% between H and Li, only 2% between Li and B, and thereafter no significant change is seen up to fluorine. It is clear that no set of additive corrections of the form given in Eq. (1) can account for this behavior.

At higher velocities (3.5 MeV/amu) the higher-order Z_1 effect is considerably greater. Here an almost linear increase of about 20% per unit Z_1 is seen from $Z_1 = 1$ to 5. The linearity is in accord with a Z_1^3 correction, but the magnitude is 6 to 7 times greater than that for random stopping; this is also in contradiction to the expected decrease in polarization effect with increased velocity.

No theories of higher-order Z_1 effects have been specifically compounded for the case of channeled ions. Theories developed are for random collisions, and the analysis for valence electrons has not yet been completed; but it is difficult to see how polarization and Bloch corrections for valence electrons alone can be responsible for the observed effects. Increasing the ion velocity will increase the contribution of inner shells to the total stopping power. To first order this contribution is expected to scale as Z_1^2 , but polarization terms for large impact parameter collisions of channeled ions with 5p, 5s, and 4f electrons could be large and may be responsible for the increasing Z_1^3 effect at high velocities. The effects of dynamical screening, which have not been considered in detail thus far, also appear to scale only with Z_1^2 ; however, since the magnitude of this effect which tends to nullify charge differences is larger at lower velocities, deviations from Z_1^2 scaling may tend to suppress the Z_1^3 term for higher Z_1 at lower velocities.

1. Physics Division.

2. J. Lindhard, *Nucl. Instrum. Methods* 132, 1 (1976).

11.2.7 Electron Capture to K Vacancies in Chlorine Ions (≈ 1.5 MeV/amu); Relation to Emergent Charge States

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Recently a number of experiments have been directed toward the determination of the contribution of electron capture to K -shell ionization in heavy-ion collisions. In one such experiment reported by Hopkins et al.² the fraction of K vacancies in chlorine ions (~ 2 MeV/amu) passing through targets of varying Z_2 were correlated with the scaled Brinkman-Kramers cross sections for electron transfer from the target atoms to the chlorine K shell. In this work the authors determined the chlorine K -shell vacancy fractions by measuring the

Cu K x-ray yield from a thin layer of copper affixed to the exit surface of the target, the sensitivity of this yield to projectile vacancy fraction having been previously determined.

In the present work we measured the charge-state distributions of chlorine ions after emergence and relaxation and correlated these values with K -vacancy fraction. Beams of 45-, 54-, and 62-MeV chlorine from the Oak Ridge Tandem Van de Graaff were passed through targets of C, Al, KCl, Ni, Ag, and Au, and the emergent charge-state distributions and exit energies were measured. The mean charge states $\bar{q} = \sum \psi_i(q_i)q_i$ for all emergent energies were obtained and are plotted for an emergent energy of 50 MeV in Fig. 11.15 vs target atom Z_2 . The dashed curve shows a comparison with the effect predicted based on the chlorine K -vacancy fraction $\phi(K)$ reported in ref. 2 and a simple model relating the number of bound electrons ($\bar{n}_e = \bar{q} - Z$) to $\phi(K)$.

Because of the level matching of the chlorine projectile K shell with those in the KCl target, a maximum in the charge transfer cross section is expected, and Hopkins et al. report $\sim$ zero K vacancy fraction for chlorine ions in this target. We assumed this value and assess the effect on $\bar{n}_e$ of a single K vacancy. First, of course, the K vacancy will reduce $\bar{n}_e$ by one unit. Second, the presence of a K vacancy in an emergent ion with L electrons present will lead

Fig. 11.15. Mean bound electron number $\bar{n}_e$ and charge state $\bar{q}$ for chlorine ions emerging from targets Z_2 at 50 MeV. Error bars refer to K vacancy fraction (ref. 2).

to loss of a second electron by an Auger event with a probability that $1 - \omega_q$ is the fluorescence yield for Cl^{q+} . Here we estimate ω_q as ~ 0.2 based upon computed values³ of ω_q for the various configurations of highly ionized Ar^{q+} . Finally, since the equilibrium charge state is principally determined by capture and loss to the chlorine L shell, we consider the effect of a K vacancy on the processes occurring in the L shell. The effect should appear as an increase in the effective Z at the L shell radius by one unit. Using the semiempirical formulation of Nicolaev and Dmitriev,⁴ we obtain $\bar{q}'/Z$ for $Z = 17$ and for $Z = 18$ at the same velocity (1.5 MeV/amu); the result is $\bar{q}'/Z = 0.738$ for $Z = 17$ and $\bar{q}'/Z = 0.731$ for $Z = 18$, from which a change in n_e for a given K electron vacancy fraction $\phi(K)$ is

$$\bar{n}_e = \phi(K)[1 + (1 - \omega_q) - (\bar{n}'_{e(Z+1)})] = 1.4\phi(K).$$

Using the values of $\phi(K)$ from ref. 2 we obtained the dashed curve shown in Fig. 11.15. With the exception of the point at the lowest value of Z_2 (carbon), the agreement with the expectations of the model appears quite good. The discrepancy at this point is not clearly understood, but it may be related to maxima in the L -shell electron transfer cross sections.

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2. F. Hopkins, J. Sokolov, and A. Little (to be published).
3. C. P. Bhalla, *Phys. Rev. A* 8, 2877 (1973).
4. V. S. Nicolaev and I. S. Dmitriev, *Phys. Lett. A* 28, 277 (1968).

11.3 REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE

11.3.1 Electron Spin Resonance Studies of Radicals from Peptides

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D. G. Doherty¹

Work has continued on the study of radicals made from simple peptides by abstraction of hydrogen through attack of $\dot{\text{O}}\text{H}$. The peptide as the zwitterion in aqueous solution containing about 1% hydrogen peroxide is photolyzed. The peroxide gives $\dot{\text{O}}\text{H}$ which then abstracts hydrogen from the peptide to give the observed, short-lived radical. As pointed out in the last annual report² the simplest dipeptides

and tripeptides containing only L-alanine, β -alanine, and glycine give predominantly radicals resulting from hydrogen abstraction at the carboxylate end of the peptide. With other amino acids such as L-valine and sarcosine, radicals are seen that result predominantly from side-chain attack.

Further examples of side-chain attack are illustrated by the aspartates, Fig. 11.16. Greater detail on these as well as other cases described in the last annual report² has appeared elsewhere.³ Glycyl-L-aspartate and β -alanyl-L-aspartate behave similarly. Excellently resolved spectra were obtained, and in both cases a pair of radicals were observed that resulted from $\dot{\text{O}}\text{H}$ attack at the aspartate residue. One kind of radical (1 and 3 in Fig. 11.16 and the corresponding radicals in D_2O solution) was easily identified as resulting from simple hydrogen abstraction from the aspartate side chain. The other kind of radical (2 and 4 and the corresponding radicals in D_2O solution) has not been completely identified, but much can be said about the structure. In 2, for example, it is known that the region of high electron density is on the main peptide chain as illustrated with the main features of the chain remaining intact. It is likely that the group R remains as the carboxylate group. The side chain, however, contains only a single hydrogen (22.4-G coupling) in the position β to the region of high spin density. This implies that a chemical change has taken place in the aspartate side chain, the details of which are not yet established.

Partly to give more information on the radicals from aspartates, kinetic studies of radical growth and decay were started. A rotating sector was used on the photolytic source which interrupts the light in square-wave fashion and allows growth and decay data to be accumulated. The pair of radicals formed from β -alanyl-L-aspartate were examined. One notion was that 1 (Fig. 11.16) might be initially formed, with 2 subsequently forming from 1 by a chemical change in the side chain. This implies that the growth of 2 would resemble the decay of 1, and an induction effect might be seen. The kinetic data show identical behavior for 1 and 2. Both radicals increase in concentration quite rapidly when photolysis starts, and both decay relatively slowly (several msec) when photolysis ceases. Radicals 1 and 2 cannot be related by simple consecutive steps. Additional sector work was done on the radical from β -alanylglycine.⁴ In all cases the decay curves are second order, and consideration is now being given to the measurement of absolute concentrations so

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that second-order reaction rate constants may be evaluated.

Fig. 11.16. Formulas of radicals studied in photolyzed solutions containing the indicated aspartate and hydrogen peroxide in H_2O and D_2O solution. Numbers with arrows are hyperfine coupling constants in gauss.

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2. *Chem. Div. Annu. Prog. Rep. Nov. 1, 1975*, ORNL-5111, p. 110.
3. D. G. Doherty, R. Livingston, and H. Zeldes, *J. Am. Chem. Soc.* 98, 7717 (1976).
4. *Chem. Div. Annu. Prog. Rep. May 20, 1974*, ORNL-4976, p. 177.

11.3.2 Electron Spin Resonance Studies of Radicals from Aromatic Hydrocarbons in Molten $SbCl_3$

R. Livingston A. S. Dworkin
G. P. Smith H. Zeldes

An ESR study of polycyclic aromatic hydrocarbons dissolved in molten antimony trichloride has been started in support of the study of the general chemistry of these systems described in Sect. 1.2.1. The hydrocarbons here described are in the order of decreasing ease of oxidation.

Perylene in molten antimony trichloride at $80^\circ C$ (air free) gives an exceedingly strong free-radical spectrum, with the main problem that of obtaining a solution sufficiently dilute to give sharp, well-resolved lines. Solutions of approximate molarities of 0.033, 0.018, 0.002, and 0.0005 were examined, the latter two being sufficiently dilute. The radical is perylene cation. Approximate couplings for the three sets of four equivalent protons are 0.44, 3.04, and 3.99 G, which are very close to values (0.45, 3.03, and 4.04 G) reported by Möbius¹ for $10^{-4} M$ perylene in sulfuric acid at $25^\circ C$. These solutions were colored green. When air was added to the 0.0005 M solution the color became dark purple, and the perylene cation concentration increased by over a factor of 10.

Upon melting and maintaining a solution of anthracene in antimony trichloride at $80^\circ C$, a very weak spectrum of about a dozen components, only partially resolved, may be observed. Subsequent work strongly indicates the species is the anthracene cation. The intensity of this spectrum shows a time dependence, and the results have not been reproducible. The first solution examined was 0.2 M but, unfortunately, was not homogeneously mixed. The spectrum seen upon melting disappeared after 1 hr. Another solution of 0.045 M did not show the spectrum, whereas an 0.008 M solution showed an

extremely weak spectrum upon melting which became noticeably stronger during the next 2 hr. These solutions were green, but upon heating to 125°C the solutions become opaque and black with the development of a very strong ESR signal consisting of a single broad line. This signal was observed over a period of a few hours and progressively grew in intensity. After cooling the sample to room temperature (solid), a single, intense, broad line without structure was present. The species cannot be identified from these observations. Possibilities include a mixture of radicals or the formation of finely divided solid particles containing unpaired electrons somewhat resembling the signal seen from pitch samples. Upon adding air to an 0.008 *M* solution of anthracene in antimony trichloride at 80°C, a very intense, moderately well resolved spectrum of anthracene cation was observed. After an hour the spectrum had disappeared. An approximate measure of the smallest coupling gave 1.38 G, which agrees perfectly with the value¹ for the radical in sulfuric acid at 25°C. A 0.01 *M* solution in a melt of SbCl₃-8.5 mole % AlCl₃ at 80°C gave a very intense, very-well-resolved spectrum of the cation which did not change in intensity over a period of 2 hr. Increasing the temperature to 126°C gave an immediate enhancement in intensity by 50%, with moderate additional enhancement over the next 1.5 hr.

No spectrum was obtained from air-free solutions of pyrene in SbCl₃ at 80°C. Upon adding air a strong but only moderately-well-resolved spectrum was obtained which has been identified as pyrene cation. The pyrene cation spectrum persists over a period of several hours. A solution of pyrene (0.004 *M*) in a melt of SbCl₃-AlCl₃ gave an extremely intense and very-well-resolved spectrum of the cation. Upon further heating to 126°C the same spectrum was observed, and it appeared to be quite stable over a period of a few hours.

Air-free solutions of naphthalene (0.09 and 0.04 *M*) in SbCl₃ showed no spectrum at 80°C. The 0.04 *M* solution with added air at 80°C also showed no spectrum, and the melt remained clear and colorless. A 0.03 *M* solution of naphthalene in a melt of SbCl₃-5 mole % AlCl₃ at 80°C gave an intense, beautifully resolved spectrum which was clearly identified as the perylene cation. This almost surely is a condensation product of the naphthalene. Approximate values of the three coupling parameters are 0.44, 3.1, and 4.05 G, which compare favorably with the values¹ for perylene cation in sulfuric acid at

25°C. The melt was black and opaque. Further heating to 128°C gave an increase in intensity by approximately a factor of 4; the intensity remained unchanged for 2 hr at that temperature. This study will be extended to include other hydrocarbons.

I. K. Möbius, *Z. Naturforsch.* 20a, 1102 (1965).

11.3.3 Electron Spin Resonance Studies of Radicals from Cyclic and Acyclic Carbonate Esters¹

H. Zeldes R. Livingston

Transient free radicals (see Fig. 11.17 for structures) have been formed by the removal of a

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Fig. 11.17. Radicals produced in photolyzed solutions containing the indicated carbonate ester and hydrogen peroxide. Absolute values of hyperfine couplings in gauss are shown for indicated nuclei by numbers below the formulas; g values are also shown. Pi-electron spin densities ρ_α at the site of the unpaired electron (site α) and absolute values of McConnell's constant Q in gauss estimated from the couplings are also given for some of the radicals.

single hydrogen atom from dimethyl carbonate, diethyl carbonate, ethylene carbonate (1,3-dioxolan-2-one), and propylene carbonate (4-methyl-1,3-dioxolan-2-one). Electron spin resonance spectra were observed during photolysis near room temperature of solutions containing 1% H_2O_2 and resulted from hydrogen atom abstraction by $\dot{\text{O}}\text{H}$ formed by photolysis of H_2O_2 . The spectra were of very good quality, leaving no uncertainty as to the nature of the hyperfine splittings. In most cases the assignment of the couplings was indicated unambiguously by the splitting pattern, but in the cases of radicals I and IV it was necessary to rely on comparisons with other radicals. The measured couplings and g values are shown in Fig. 11.17. It was possible to estimate the pi-electron spin density ρ_α at the site of the unpaired electron (site α) for some of the radicals from the couplings. These values as well as absolute values of McConnell's constant Q are also shown (Fig. 11.17), where Q is defined by $a_\alpha^{\text{H}} = Q\rho_\alpha$, and a_α^{H} is the hydrogen coupling at the site of the unpaired pi electron. The Q values for the similar cyclic radicals (I and III) were both found to be 18.0 G, and those for the similar acyclic radicals (V and VI) were both found to be 22.7 G. The close agreement for the two cyclic radicals is quite reasonable. However, the close agreement for the two acyclic radicals is surprising, since the α carbon in one case is a primary carbon and in the other case a secondary carbon. Beta-hydrogen couplings are dependent upon spin density at the α position and upon the orientation of the C-H bond to the β -hydrogen. The β -hydrogen couplings of II and III are consistent with a rigid planar structure for the ring atoms, and that for I suggests a small distortion from planarity.

1. Expanded abstract of a paper in *J. Magn. Reson.* 21, 109 (1976).

11.3.4 Electron Spin Resonance Studies of Radicals from Nitrogen Heterocyclic Compounds

H. Zeldes R. Livingston

Electron spin resonance is being used to study photolytically produced short-lived radicals formed from nitrogen heterocyclic compounds in solutions near room temperature. The studies are aimed at radical identification, the measurement of g values and hyperfine couplings, and establishing mechanisms of their formation. In some cases acid-base

equilibria and rate constants can be determined. Radicals have been produced from substituted pyridines by reactions which lead to the addition of a hydrogen atom to the ring nitrogen. Two mechanisms are clearly involved. In one, excited acetone abstracts the α -hydrogen of an alcohol, say, isopropyl alcohol, to form two molecules of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$. The latter radical donates an electron to the nitrogen heterocycle, and this is followed by protonation to form the observed radical. In the other mechanism an excited heterocycle abstracts a hydrogen atom from an alcohol to form the heterocyclic radical. Thus the former mechanism requires the presence of both acetone and an alcohol, and the latter mechanism requires the presence of an alcohol.

A study of three 1-hydropyridinyl radicals made by the photolytic reduction of nicotinic acid (3-pyridinecarboxylic acid), nicotinamide, and methyl nicotinate has been completed. The radicals were studied near room temperature in solutions containing both acetone and isopropyl alcohol. Our main interest was to determine the hyperfine couplings for the radical derived from nicotinamide (vitamin B_3). The nitrogen couplings and the couplings of hydrogens attached to ring atoms were very similar for the three radicals and similar to those of the 1-hydro-3-pyridinecarboxylate anion radical. The coupling of the hydrogen attached to the ring nitrogen for the radicals from nicotinic acid and nicotinamide was assigned by also analyzing spectra produced in solutions containing D_2O . It was found that only one of the two amide hydrogens of the radical from nicotinamide gives a measurable splitting. Undoubtedly the nonequivalence results from the hindered rotation about the C-NH₂ bond.

A study of the 1-hydro-2,5-pyridinedicarboxylate anion radical in basic aqueous solutions has been completed.² The radical, produced by the photolytic reduction of the 2,5-pyridinedicarboxylate anion radical in aqueous solutions containing a small amount of alcohol, was studied as it underwent a reversible, base-catalyzed dissociation of the NH hydrogen:

where R^{-2} is the 2,5-pyridinedicarboxylate anion. At low enough concentrations of NaOH, equilibrium (1) is displaced far to the left. Under this condition, line shape effects arising from the dynamics of the equilibrium involve only the spectral parameters of

nonexchanging RH^{-2} , a parameter T_2 for the line width in the absence of exchange, and the mean value of the exchange-limited lifetime τ_S of the NH-hydrogen spin state. The interpretation of the line shape effects is greatly simplified, since it does not depend upon the spectral parameters of $\dot{\text{R}}^{-3}$ and upon the relative concentrations of RH^{-2} and $\dot{\text{R}}^{-3}$. Fortunately, in this case the more significant line shape effects occurred in this region. A computer program was written to produce simulations of spectra recorded for a range of concentrations of NaOH. All of the required parameters except for τ_S were obtained from the nonexchanging spectrum in nearly neutral solutions, and τ_S was determined from the simulations. From τ_S and the sodium hydroxide concentration, the forward rate constant k was calculated using

$$\tau_S = 2/k[\text{OH}^-] \quad (2)$$

Thus, values of k were obtained from a range of values of ionic strength, and these were extrapolated to obtain the value $(2.2 \pm 0.6) \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ for k at infinite ionic dilution at 32°C .

At higher concentrations of NaOH, there was a very rapid interconversion of the dissociated and undissociated radicals, resulting in a single sharp-lined spectrum whose NH-hydrogen coupling was absent, and whose remaining couplings represented average values for the two forms of the radical weighted by their relative concentrations. From the measurement of couplings in this region the couplings for the dissociated form of the radical were determined as well as the degree of dissociation for NaOH concentrations spanning the region from 0 to 100% dissociation. From these data and published values of the water activity in NaOH solutions, the thermodynamic equilibrium constant for Eq. (1) was determined. By combining this and the known ionization constant of water, the ionization constant of $\dot{\text{R}}\text{H}^{-2}$ in aqueous solution at 32°C , expressed in pK units, was determined to be 16.64 ± 0.1 .

A study of the 1-hydro-3,5-pyridinedicarboxylate anion radical in basic aqueous solutions is under way. In this case the spectra are rather weak for the purpose of studying line shape effects. In order to have reasonable signal-to-noise ratios it was necessary to use amplitudes of modulation high enough to make a significant contribution to the width. This difficulty has been overcome for this problem by developing a computer program to plot the

modulation-corrected spectrum for comparison with the experimental spectrum.

1. Expanded abstract of a paper scheduled to appear in the March 1977 issue of *J. Magn. Reson.*
2. Expanded abstract of a paper in *J. Magn. Reson.* 25, 67 (1977).

11.4 PHOTOCHEMISTRY AND RADIATION CHEMISTRY

11.4.1 Kinetics of Formation and Decay of the Methyl Radical in the Flash Photolysis of Gaseous $\text{H}_2\text{O} + \text{CH}_4$

C. J. Hochanadel T. J. Sworski
P. J. Ogren¹

This system was studied primarily as an actinometer to determine the amount of water dissociated by the flash, so that absolute rate constants and the molar extinction coefficient of HCO could be determined in the $\text{H}_2\text{O} + \text{CO}$ system.² Time-resolved kinetic spectrophotometry indicates that most of the CH_3 radicals are formed by fast processes during the flash and decay by complex kinetics involving reactions of both CH_3 and H radicals. The formation and decay of the CH_3 are explicable by the following reaction mechanism:

The absolute rate constant $k_3 = (3.1 \pm 0.6) \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and the molar extinction coefficient for CH_3 at $2160 \text{ \AA}$ of 9000 ± 800 were previously determined.³ We used a literature value⁴ of $k_2 = 5.1 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. We determined by the method of least squares, using numerical modeling, both the amount of water dissociated by the flash and the absolute rate constant $k_4 = (1.6 \pm 0.1) \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ for the important reaction of CH_3 with H at 1 atm of CH_4 . This is a very fast reaction, and our second-order rate constant is in good agreement with recent estimates of the second-order limit.

An attempt was made to determine the molar extinction coefficient of HCO by comparison of the absorptions due to CH_3 and HCO in the flash photolysis of CH_3CHO . Although the predominant modes of dissociation of CH_3CHO yield $\text{CH}_3 + \text{HCO}$ and $\text{CH}_4 + \text{CO}$, there is a minor mode that yields $\text{CH}_3\text{CO} + \text{H}$. This attempt was unsuccessful, since the CH_3CO spectrum was found to overlap both the CH_3 and HCO spectra. The production of $\text{CH}_3 + \text{CH}_3\text{CO}$ in the flash photolysis of acetone was used to determine the CH_3CO spectrum.

1. Department of Chemistry, Central College, Pella, Iowa.
2. See sect. 11.4.2 of this report.
3. C. J. Hochanadel, J. A. Ghormley, J. W. Boyle, and P. J. Ogren, *J. Phys. Chem.* 81, 3 (1977).
4. R. Zellner and W. Steinert, *Int. J. Chem. Kinet.* 8, 397 (1976).

11.4.2 Absorption Spectrum and Kinetics of Formation and Decay of the Formyl Radical in the Flash Photolysis of Gaseous $\text{H}_2\text{O} + \text{CO}$

C. J. Hochanadel T. J. Sworski
P. J. Ogren¹

Flash photolysis of water vapor in an atmosphere of CO produces a transient absorption centered at 2300 Å that we attribute to the formyl radical, HCO . Time-resolved kinetic spectrophotometry indicates that much of the HCO is produced by fast processes during the flash and, after production is complete, decays by a second-order process. The formation and decay of the HCO radical is explicable by the following reaction mechanism:

The flash photolysis of water vapor in an atmosphere of CH_4 was used as an actinometer to determine the amount of water dissociated by the flash.² We used the following literature values: $k_2 = 9.2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ (ref. 3) and $k_5 = 2.0 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ (ref. 4). The following parameters were determined by the method

of least squares, using numerical modeling: the absolute rate constants $k_3 = (3.8 \pm 0.4) \times 10^7 \text{ M}^{-2} \text{ sec}^{-1}$ with CO as the third body and $k_4 = (1.4 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, and the molar extinction coefficient for HCO at 2300 Å of $790 \pm 30 \text{ M}^{-1} \text{ cm}^{-1}$.

The formyl radical is an important intermediate in many kinetic systems, especially in combustion kinetics and atmospheric chemistry. The need for accurate rate constants of the elementary reactions of HCO has assumed increased urgency as a result of current problems associated with the production, conversion, and usage of energy.

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3. R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., *Chem. Phys. Lett.* 44, 204 (1976).
4. W. G. Broune, R. P. Porter, J. D. Verlin, and A. H. Clark, p. 1035 in *Twelfth Symposium (International) on Combustion*, The Combustion Institute, 1967.

11.4.3 Reaction Mechanism and Absolute Rate Constant for Bromine Hydrolysis in the Flash Photolysis of Aqueous Bromide Ion Solutions

T. J. Sworski C. J. Hochanadel
P. J. Ogren¹

There is a marked influence of pH on bromine formation in the flash photolysis of nitrous oxide-saturated aqueous sodium bromide solutions. The bromine concentration increases and asymptotically approaches a maximum when Br_2^- decays in acidic solutions with $\text{pH} = 4$. The bromine concentration increases, reaches a maximum, then decreases and asymptotically approaches a lower value when Br_2^- decays in unbuffered solutions. Time-resolved kinetic spectrophotometry, using the Br_2^- absorption centered at $\sim 3600 \text{ Å}$ and the Br_3^- absorption centered at $\sim 2700 \text{ Å}$, indicates that all of the Br_2^- is formed by fast processes during the flash and then decays by a second-order process to form bromine:

We attribute our observations to significant base-catalyzed hydrolysis of bromine in unbuffered solutions:

For 0.1 M sodium bromide solutions, the following parameters were determined by the method of least squares, using numerical modeling: $k_3 = (1.36 \pm 0.02) \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and $k_{-3} = (2.94 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$. The equilibrium constant $K = k_3/k_{-3} = 4.6 \times 10^5$ is in good agreement with the thermodynamic literature value.²

Our results are also consistent with an acid-catalyzed equilibrium for bromine hydrolysis:

However, we do not favor this mechanism, since the first-order rate constant k_4 for bromine hydrolysis would be $1.8 \times 10^4 \text{ sec}^{-1}$, much greater than the value of $1.1 \times 10^2 \text{ sec}^{-1}$ previously determined.³

1. Department of Chemistry, Central College, Pella, Iowa.

2. H. A. Liebhafsky, *J. Am. Chem. Soc.* **61**, 3513 (1939).

3. M. Eigen and K. Kustin, *J. Am. Chem. Soc.* **84**, 1355 (1962).

11.4.4 New Reaction Mechanism for the Radiation Chemistry of Deaerated Aqueous Bromide Ion Solutions⁽¹⁾

T. J. Sworski F. T. Jones²

Both hydrogen peroxide and bromine are initial products in the ⁶⁰Co gamma radiolysis of deaerated 0.4 M sulfuric acid solutions containing 0.1 M sodium bromide. The bromine concentration increases, reaches a maximum, and then decreases, while the instantaneous hydrogen peroxide yield decreases slightly with increase in time of irradiation. We presume that material balance is maintained by production of oxygen as a secondary product with $G(\text{H}_2) = G(\text{H}_2\text{O}_2) + G(\text{Br}_2) + 0.5G(\text{O}_2)$.

A reaction mechanism was quantitatively established with theoretical curves, obtained by the method of least squares, using numerical modeling, that well represent the experimental dependence of hydrogen peroxide and bromine concentrations on time of irradiation. The initial hydrogen peroxide yield is given by

$$G(\text{H}_2\text{O}_2) = G_{\text{H}_2\text{O}_2} + G_{\text{H}}/(1 + k_1[\text{Br}_2]/k_2[\text{H}_2\text{O}_2]) \quad (1)$$

Bromine scavenges H atoms with surprising efficiency to protect some of the molecular hydrogen peroxide from being decomposed by H atoms with k_1

$= (7.7 \pm 1.0) \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ relative to a literature value of $k_2 = 1.6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. Computer simulation of long irradiation times indicates that the instantaneous hydrogen peroxide yield asymptotically approaches a limiting value given by

$$G(\text{H}_2\text{O}_2) = G_{\text{H}_2\text{O}_2} + (G_{\text{H}} - G_{\text{OH}})/2 - 2G_{\text{H}}/(1 + k_1[\text{Br}_2]/k_2[\text{H}_2\text{O}_2]) \quad (2)$$

as the bromine concentration asymptotically approaches zero. The most surprising result to be drawn from our reaction mechanism is that the hydrogen peroxide yields given by Eqs. (1) and (2) are markedly dependent on bromide ion concentration.

1. Abstract of paper presented at the 24th Annual Meeting of the Radiation Research Society, San Francisco, Calif., June 27-July 2, 1976.

2. Stevens Institute of Technology, Hoboken, N. J.

11.5 PHOTOCHEMICAL ENERGY STORAGE BY PHOTODIMERS

W. B. Whitten

We are studying the potential storage of solar energy, for subsequent controlled release as heat, by dimerization reactions of linear polyacenes with four or more benzene rings. The dimerization reaction and the reverse (depolymerization) have been well studied for anthracene, which has only three rings and thus absorbs very little at wavelengths longer than those of the uv region of the spectrum. This makes anthracene dimerization impractical for solar energy conversion, although the reaction otherwise has several desirable characteristics. Dimerization reactions have the disadvantage that quantum yield depends on concentration, but this can be overcome by tying pairs of polyacenes together with propane bridges as has already been done for naphthalene and anthracene.

So far, we have been working with tetracene (four rings), which absorbs to wavelengths beyond 475 nm. It has been known for some time that tetracene photodimer can be formed and that the dimer can be depolymerized by exposure to uv wavelengths shorter than 300 nm. We are attempting to find out whether the dimer can be depolymerized thermally and to determine the activation energy for thermal depolymerization, the amount of energy stored, and the quantum yield for dimer formation. We have prepared tetracene photodimer by exposing deoxy-

generated solutions of tetracene monomer in *o*-xylene to incandescent light. That the photoproduct formed was indeed the photodimer was verified by photodepolymerization in cyclohexane solution, using an Aminco spectrophotofluorimeter. The characteristic monomer fluorescence grew from an initially almost negligible level to a very strong emission after several minutes exposure to 250-nm excitation. Initial thermal depolymerization experiments show that upon slow heating ($10^{\circ}\text{C}/\text{min}$), the dimer powder starts to discolor at a noticeable rate at $\sim 230^{\circ}\text{C}$. The depolymerization is about half completed between 290 and 300°C , with accompanying sublimation of the tetracene monomer commencing near 300°C at atmospheric pressure.

11.6 THEORY OF OPTICAL SPECTRA OF MOLECULAR AGGREGATES

R. P. Hemenger

There are a number of systems of interacting chromophores whose optical absorption and circular dichroism (CD) spectra are substantially altered from the spectra of the isolated chromophores. One oft-cited example is the polymer of pseudoisocyanine, whose absorption and CD spectra show a very narrow band well separated from the monomer spectrum. Another well-studied system is that of dye dimers in solution. Also of interest are those systems containing photosynthetic pigments, primarily chlorophyll or bacteriochlorophyll, which have either been isolated from photosynthetic organisms or have been constructed as models of photosynthetic systems. Examples of these are chlorophyll-containing proteins, bacterial photoreaction centers, and monomolecular films. Each of these systems has well-resolved spectral features which are not seen in the spectra of the isolated pigments.

If optical spectra are to be used to resolve questions about the structure and function of these systems, it is necessary to understand the properties of aggregate electronic-excited states. One especially challenging problem has been that of correctly taking into account molecular vibrations for all molecular-excited-state interaction strengths from "weak" through "intermediate" to "strong." With few exceptions, theoretical treatments have been restricted to either the weak-coupling or the strong-coupling limit. The essential feature of the former treatments is to allow only the zero vibrational level of each electronic ground state to take part in excited-state interactions. The results obtained with this

restriction are essentially the same as those from the time-dependent Hartree method, which has elsewhere been called the classical dipole method or the decorrelation approximation. This approach has attractive features: it is simple conceptually and is readily applicable to molecular aggregates of arbitrary size and geometry. However, this approximation is not valid for coupling strengths in the intermediate or strong range. The strong-coupling approximation, or exciton model, on the other hand, while being very simple, has an obvious deficiency. Since each electronic transition is treated as a sharp line in this approximation, all information is lost about shifts and band shape changes in absorption and CD spectra of the aggregate due to vibrational structure. Those theoretical calculations of optical spectra which fall into neither of these two categories, weak-coupling model or exciton model, have been restricted to aggregates whose monomers have vibrational structure consisting of a single vibronic progression. For the case of a dimer this problem has been solved exactly, while approximate methods have been developed for polymers and lattices.

Using very general considerations, we have deduced five explicit relations (sum rules) connecting moments of the absorption and CD spectra of the aggregate with those of the individual chromophores.¹ These hold for all coupling strengths. Furthermore, in the vicinity of the strong-coupling limit, three more sum rules hold for individual exciton transitions.² One of these latter sum rules gives an explicit expression for the width of individual exciton peaks in the strong-coupling limit. It accounts quantitatively for the well-known narrowing of these peaks relative to the absorption bands of the constituent monomers.

We have also developed a new theory¹ that makes no restriction as to aggregate size, but requires the monomers to have many vibrational degrees of freedom that are poorly resolved in optical spectra. In this theory, called the "degenerate-ground-state" (DGS) model, all vibrational levels, of both the electronic ground and excited states, are included, but those of the ground state are treated as though all were of equal energy. The DGS model is a generalization of the weak- and strong-coupling exciton models in the sense that it contains each as a limiting case. It is clearly superior to either of the latter models for intermediate coupling, as we have shown by comparing the results of a DGS calculation to an exact calculation on an idealized dimer (Fig. 11.18). In fact, agreement between these two

Fig. 11.18. Comparison of normalized absorption spectra calculated in three different ways for a model dimer having a single vibronic progression. Exact solution, —; DGS model, ---; weak-coupling model, - · -. The abscissa is in units of the vibrational quantum in the monomer; J is the intermolecular excited-state interaction energy in the same units.

calculations is so good we believe it demonstrates that knowledge of nonoptically accessible transitions (the only ones *not* included in DGS) is unnecessary for accurate calculation of the optical spectra of large molecules.

The DGS model satisfies all eight sum rules. The fact that it satisfies the three strong-coupling rules proves that the model gives correct intensities, positions, and widths of individual exciton peaks near the strong-coupling limit. These rules constitute very strong constraints on the DGS model, which appears to be much better than all previous exciton calculational models outside of the weak-coupling limit.

The DGS model has been used in the development of a computer program (called "A9") that calculates aggregate optical absorption, CD, and linear dichroism spectra from the optical absorption spectra of the monomers for a specified set of exciton interactions among them. For the aggregate of M molecules the A9 program uses Monte Carlo techniques to evaluate the $(M-1)$ -fold multiple integrals that occur in the spectral algorithms derived from the DGS model. The A9 program has so far been tested on aggregates of up to seven molecules, for which central processor running times of several minutes on an IBM 360/91 computer are required to obtain reasonably good statistics in the calculated absorption or CD spectrum.

11.7 EXCITON STATES OF BACTERIOCHLOROPHYLL-PROTEIN

11.7.1 Calculation of Optical Spectra

R. P. Hemenger R. M. Pearlstein

We have begun an analysis of the exciton-state structure of the lowest excited (Q_y) singlet state of the bacteriochlorophyll (BChl) in the water-soluble BChl-protein of molecular weight ≈ 140 kilodaltons extracted from the green photosynthetic bacterium *P. aestuarii*. We have chosen to concentrate initially on this chlorophyll-protein because it is the only one so far in which the spatial arrangement and orientations of the chlorophylls have been precisely determined by single-crystal x-ray crystallography. The protein structure, as determined by Fenna and Matthews,¹ is a trimer consisting of three identical protein subunits each containing seven BChl molecules. These chlorophylls are contained within the subunit protein structure, are tightly though not covalently bound to the protein, and have an average center-center nearest-neighbor separation of 12 Å. No two are in van der Waals contact. The porphyrin rings are confined to a flattened disk-shaped region of dimensions $45 \times 35 \times 15$ Å and lie between 10 and 40° of the average plane (that plane most nearly parallel to those of the seven porphyrin rings). The chlorophylls otherwise form no obviously regular pattern.

Accurate absorption and CD spectra of the same protein in solution at 77 K, obtained prior to the structural determination, display several partially resolved features in the BChl Q_y absorption band, compared with a single peak in the monomer spectrum. These features were interpreted in terms of exciton interactions among the chlorophylls in the protein by assuming a particular structure and strong coupling. However, a calculation using standard strong-coupling exciton theory applied to the Q_y transition monopoles of the seven BChls in one subunit of the protein produces spectra with fewer and less distinct features than those observed and a much smaller overall red shift. This lack of agreement with experiment should not be taken as an indication of the inapplicability of exciton theory to the spectra of chlorophyll-proteins, but rather as a signal that a more comprehensive analysis is required. Such an analysis must include treatment of vibrational energy levels and environmental effects. The inclusion of the vibrational energy levels of the individual chlorophyll molecules is the single most important factor in determining the shape of the calculated absorption and CD spectra. The vibrational levels substantially affect not only the overall red shift and the number of

1. R. P. Hemenger, *J. Chem. Phys.* 66, 1795 (1977).
2. R. P. Hemenger, *J. Chem. Phys.* (in press).

spectral features but even the sharpness of the latter. The protein environment of the bacteriochlorophylls may produce intensity borrowing among vibronic transitions as well as overall spectral shifts.

If all of the pairwise exciton interactions are weak, compared with the width of the spectral envelope, the effects of the vibrational levels can easily be included. Unfortunately, the exciton interaction energies for the bacteriochlorophyll in the protein are comparable to the width of the spectral envelope. Therefore, a correct treatment of the effect of the vibrational energy levels on the spectra requires a more elaborate calculation such as one based on the DGS model.² The geometry of the protein is such that to a good approximation, interactions between BChls not in the same subunit can be neglected, and we have therefore focused our attention on the 7-BChl aggregate. We are using A9 (ref. 2) and two other, simpler, computer programs developed at ORNL to aid in the analysis of this aggregate. Although we are experiencing some difficulty because of the sparsity of available information on the BChl wave function and on the interactions of the BChl with its host protein, we have already come close to fitting the known absorption (though not yet the CD) spectrum of the BChl-protein in the BChl Q_y transition region at 77 K. Early indications are that the highest peak in the spectrum is due to an almost dimeric state having roughly equal amplitudes on the two BChls closest to the protein's three-fold symmetry axis.

1. R. E. Fenna and B. W. Matthews, *Nature* 258, 573 (1975); R. E. Fenna, L. F. Ten Eyck, and B. W. Matthews, *Biochem. Biophys. Res. Commun.* (in press).

2. See sect. 11.6 of this report.

11.7.2 Electric-Field-Oriented Linear Dichroism

R. M. Pearlstein N. E. Geacintov¹
W. B. Whitten E. F. Phares²

Linear dichroism (LD) spectroscopy of purified chlorophyll-proteins oriented in pulsed electric fields is a new experimental technique (ours is only the second laboratory to apply it) for obtaining information about chlorophyll interactions in situ. It consists of measuring the difference in absorbance of light polarized respectively parallel and perpendicular to the direction of a uniform electric field.

We have designed and assembled our own instrument for doing this spectroscopy by modifying an existing Cary 14 absorption spectrophotometer. A new cuvette carriage has been installed in the Cary sample chamber that holds, in addition to the water-cooled cuvette, a prism to polarize the incident light beam, an electronically driven motor that controls the prism orientation, and the supports for the platinum electrodes that provide the electric field. (The field is pulsed to minimize heating effects.) The Cary photomultiplier has been replaced by a cooled tube, with fiber-optic coupling, that is sensitive to the near infrared. Both sample and reference signals are obtained by photon counting either in synchrony with the millisecond-duration field pulses or out of synchrony (for zero-field reference measurements). The completed instrument performed quite satisfactorily when tested with suitable small fragments of spinach chloroplasts, whose field-oriented LD spectrum is known, supplied by W. A. Arnold of the ORNL Biology Division.

Because of the great current interest in the BChl-protein from *P. aestuarii* and in the hope of providing additional verification of our own ongoing theoretical calculations, we are measuring the field-oriented LD spectrum of that molecule in high-resistance solutions. The purified protein was obtained with the collaborative assistance of the ORNL Biology Division. An inoculum of a mixed culture containing *P. aestuarii* was provided by J. M. Olson of Brookhaven National Laboratory. The culture was grown in 20-liter batches, harvested, and cells were ruptured by sonication. Extraction and purification of the chlorophyll-protein was done with column chromatography and other standard techniques; tests performed on the final material indicated that it is of very high quality.

Results of measurements performed so far show a single peak in the field-oriented LD spectrum, taken at about 10°C, of BChl-protein in the BChl Q_y transition region. The peak is narrow—about half the width of the unresolved room-temperature Q_y absorption peak—and apparently coincides in energy with the strongest low-temperature (77 K) resolved absorption peak at 814 nm. The LD peak is positive; that is, absorbance increases when the electric vector of the incident light is parallel to the direction of the pulsed field. It shows no sign of saturation up to a field strength of ~13kV/cm. Preliminary exciton-theoretical analysis gives correctly the energy, sign, and relative strength of the observed LD peak, provided that the resolved absorption peak at 814 nm

is in fact due to a dimeric state³ and that the protein aligns in the field along its axis of rotational symmetry. We tentatively conclude that our observed LD peak provides strong corroboration of the persistence of chlorophyll-protein exciton-state structure at physiological temperatures.

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1. New York University
 2. Biology Division.
 3. See sect. 11.7.1 of this report.

12. Thermal Energy Storage

12.1 PHYSICAL CHEMISTRY OF PHASE-CHANGE MATERIALS

S. Cantor D. E. Heatherly

During the past year a new program of research into the physical chemistry of low-temperature (up to $\sim 250^\circ\text{C}$) thermal energy storage was initiated. Most of the program in the Chemistry Division involves the study of phase-change materials, that is, compounds and mixtures that store and discharge energy isothermally in enthalpy of transition and that are suitable for applications (residential, commercial, industrial, agricultural) other than central-station power generation.

Since several quantities of significance to thermal energy storage can be determined readily by differential scanning calorimetry (DSC), this instrumentation is used extensively in our studies. Endothermic (heat-storing) and exothermic (heat-releasing)

changes can both be measured, and by appropriate calibration and integration, enthalpy of transition and heat capacity can be quantitatively determined from the data. In exothermic measurements, the onset of crystallization is usually seen as a sharp break in the thermal spectrum; therefore, the extent of supercooling can be easily determined. The linear heating and cooling capabilities of the instrument can also be used to accelerate, on a micro scale, the daily thermal cycle of phase-change materials; by this procedure, thermal decomposition or other chemical changes can be monitored by comparing thermal spectra obtained during a cycling run.

12.1.1 Behavior of Paraffin Waxes

Five paraffin waxes were examined by means of differential scanning calorimetry; most of the results are summarized in Table 12.1. A typical thermal spec-

Table 12.1. DSC studies of paraffin wax

Wax	Transition maxima		ΔH of transition (cal/g)		Thermal cycling
	Solid-solid	Solid-liquid	Solid-solid	Solid-liquid	
Pennzoil 112/118 white scale wax	24, 30°C shallow peaks, peak at 24°C is larger	49°C	~ 10 (combined)	33	Several samples cycled between 10 and 70°C several hundred times; one sample cycled 1743 times; <i>no changes observed</i> in melting temperature or in profile of transitions
Gulf alpha olefins 24-28	24, 28°C shallow peaks, peak at 24°C is larger	50°C	~ 6 (combined)	29	<i>No changes observed</i> after 62 cycles between 10 and 60°C
Gulf wax 20	38°C	58°C	~ 10	31	<i>No changes observed</i> after 48 cycles between 10 and 65°C
Sunoco wax 3420	40°C	58°C	~ 7.5	34.6	<i>No changes observed</i> after 232 cycles between 15 and 65°C
Shellwax 100	46°C	62°C	~ 10	36.3	

trum for one of the waxes is presented in Fig. 12.1. In no case did we observe supercooling of liquefied wax. Nor were there any indications of thermal decomposition, isomerization, or other chemical change occurring as a result of thermal cycling within the specified temperature range. The waxes that were studied (commercial designation given in the first column of Table 12.1) are essentially mixtures of normal alkanes with chain lengths C_{18} to C_{35} and for which the average value of the combined heat of fusion and heat of transition is 57 cal/g.¹ This value is at least 23% greater than the combined heats of fusion and transition obtained for the five waxes studied. Nonetheless, because of high thermal stability and self-nucleation properties, paraffin waxes are considered attractive heat storage media.

However, the low thermal conductivity of paraffin waxes is a drawback to their use as heat storage media. The effect of this property was examined

preliminarily by measuring the time for complete melting of Pennzoil 112/118 white scale wax. Four samples contained in Pyrex cylinders of different volumes (10, 25, 50, 500 ml), but of equal depth, were simultaneously immersed in water baths fixed at 48.9, 51.7, and 54.4°C—all above the freezing temperature of the wax. The 12 experimental results fit the empirical equation

$$\tau = aD^n \Delta T,$$

where τ is the time for complete melting, D is the inner diameter of the cylinder, and ΔT is the temperature difference between the water bath and the median of the melting range (45.5°C) for this wax.

To support heat transfer studies (in other divisions of ORNL) associated with the use of paraffin wax in thermal energy storage, we determined the kinematic viscosity of the Pennzoil wax. By means of a capillary flow viscometer (Ubbelohde suspended level type) previously calibrated with water, it was found that the kinematic viscosity of the wax is 6.30 cSt at 49.0°C and 4.96 cSt at 59.95°C.

1. A. A. Schaerer et al., *J. Am. Chem. Soc.* 77, 2017 (1955).

Fig. 12.1. DSC endotherm of Sunoco 3420 paraffin wax heated at 5°C/min. The area under each curve is proportional to the enthalpy change associated with the transition. The left-hand peak represents a solid-state transition; the right-hand peak is the melting transition.

12.1.2 Behavior of Salt Hydrates

The melting and the freezing behavior of three salt hydrates were studied by means of differential scanning calorimetry.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Five samples were studied, three containing 3 to 6 wt % borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), the nucleating agent for this hydrate. Samples were thermally cycled as many as ten times, and the heat of transition was measured both endothermically (from a heating scan) and exothermically (from a cooling scan). During the first heating of a sample, 53 to 57 cal/g was absorbed at about 32°C; subsequent endotherms showed absorption of 22 to 39 cal/g at this temperature. Exotherms of samples with borax released 25 to 34 cal/g at 22 to 25°C; samples without borax released the same amount of heat at -10 to -13°C. The extent of energy absorption or release did not seem to depend on heating or cooling rates, which, in these experiments, varied between 0.31 and 10°C/min. The results clearly show that borax reduces the extent of supercooling but does not entirely eliminate it.

The loss in the enthalpy of transition—from about 60 to 30 cal/g—is almost certainly due to the inability

of anhydrous Na_2SO_4 to recombine with its saturated solution. When $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{c})$ is heated above 32.4°C , it is transformed to a saturated aqueous solution. Upon cooling, the reverse of the transformation does not readily go to completion. In the DSC experiments, despite favorable size and geometry in which anhydrous Na_2SO_4 was always very close to any aqueous solution present, only half of the stored energy was released isothermally. The results obtained are consistent with the suggestion¹ that the rate of recombination of water and $\text{Na}_2\text{SO}_4(\text{c})$ is limited by the diffusion rate of water through the solid layer of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ that forms around the anhydrous sulfate.

$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$. Thermograms of sodium acetate trihydrate exhibited maxima at -13 , 32 , 45 , and 58°C , the last being the melting point and the other three appearing to be solid-state transitions. The heat of fusion, determined from the area under the melting peak, seems to depend on heating and cooling rates and on the time and temperature at which the sample is maintained between scans. The sum of the transition enthalpies at 32 , 45 , and 58°C seldom exceeded 10 cal/g . On the basis of these DSC measurements, there is little to recommend this compound as a heat-storage material.

$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Potassium alum, an inexpensive hydrate, was examined as a potential candidate for the temperature range 90 to 250°C (see Sect. 12.1.2). The first endotherm showed a transition at 91 to 92°C with an energy of approximately 58 cal/g . The first exotherm exhibited very substantial supercooling: the first thermal effect on cooling occurred at 17°C , and the energy release was about one-third that noted in the first endotherm. The next endotherm showed the same transition temperature, 91 to 92°C , but with a greatly reduced absorption of energy. The second exotherm also showed an initial freezing temperature of 17°C with less heat released than in the first exotherm. This very preliminary evaluation suggests that potassium alum behaves like $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$: self-nucleation occurs at temperatures far below the melting point, and incongruent melting leads to a marked loss in energy storage capacity.

1. D. R. Biswas, *Sol. Energy*, 19, 99 (1977).

12.1.3 Heat Storage Materials That Melt Between 90 and 250°C

The objective of this investigation is to compile a handbook of compounds and mixtures that melt in

the range of 90 to 250°C . The temperature of 250°C corresponds to the upper limit of the Low-Temperature Thermal Energy Storage Program. The lower temperature, 90°C , represents the upper limit of another study¹ that identified phase-change materials for application at lower temperatures (10 to 90°C).

The initial step in identifying potential candidates involves searching the literature for cost, properties, and effects on safety and health. After the leading candidates are identified, the next steps involve measurement and/or estimation of thermal properties and chemical reactivity in heat storage application. For determining enthalpy of fusion and for assessing the extent of supercooling and thermal decomposition, differential scanning calorimetry is the chief laboratory tool. Values for thermal conductivity, viscosity, heat capacity, and volume expansion on melting are taken from the literature or are estimated. Chemical compatibility of heat storage materials with heat transfer components (containers, heat exchangers, metallic fillers) and with air is predicted from thermochemical information and from other data in the literature. The literature sources used and the procedures applied for screening candidate materials are best shown by way of example taken from organic compounds—the only class of materials surveyed thus far.

First, organic chemicals available in bulk—those listed in each issue of *Chemical Marketing Reporter*—were selected if they cost 50¢/lb or less and melted in the required range. Of the 12 found, five (lactose, sucrose, benzoic acid, oxalic acid, and pentachlorophenol) were immediately eliminated from consideration due to decomposition on melting or hazardous or toxic properties; the description of the compound in *The Merck Index* (9th ed., 1976) was usually sufficient to retain or reject a candidate at this stage. The remaining seven organic compounds, listed in Table 12.2, were ordered on the basis of storage capacity per unit cost. This rough figure of merit, presented in the last column of Table 12.2, is computed as heat of fusion per unit mass divided by the current price for the same unit mass. Of the organic compounds listed, this figure of merit is highest for urea by a considerable margin. Urea also compares favorably with lower-temperature (32 to 50°C) latent-heat materials: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $2000 \text{ kcal/\$}$; paraffin wax, $200 \text{ kcal/\$}$. Thus, urea is worthy of more in-depth evaluation.

Samples of pure urea from Mann Research Laboratory, Orangeburg, N.Y., weighing 2 to 7 mg were examined briefly by means of differential scanning calorimetry with the following salient results: (1) the

Table 12.2. Initial selection of latent-heat thermal-storage materials between 90 and 250°C: organic compounds

Compound	Formula	Melting point ^a (°C)	Cost ^b (¢/lb)	Heat of fusion ^c per unit cost (kcal/¢)
Urea	NH ₂ CONH ₂	133	7	374
Phthalic anhydride	C ₆ H ₄ (CO) ₂ O	130	25.5	66.6
Acetanilide	C ₆ H ₅ NHCOCH ₃	114	30	65 ^d
Anthracene	C ₁₄ H ₁₀	218	42.5	41.2
o-Chlorobenzoic acid	ClC ₆ H ₄ COOH	140	50	39.2
Adipic acid	HOOC(CH ₂) ₄ COOH	152	36	34.5 ^e
Phthalimide	C ₆ H ₄ (CO) ₂ NH	238	40	^f

^aRounded values.

^b*Chemical Marketing Reporter*, Feb. 28, 1977.

^cUnless otherwise indicated, heat of fusion from W. Auer in *Landolt-Börnstein Tabellen*, Band 2, Teil 4, pp. 261–388 (1961).

^dHeat of fusion based on cryoscopic constant given in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2d ed., vol. 1, p. 148.

^eHeat of fusion in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2d ed., vol. 1, p. 406.

^fHeat of fusion unknown.

heat of fusion was found to be 55.6 kcal/kg, slightly less than the originally reported² value of 57.8 kcal/kg, the latter derived from solubility measurements; (2) molten urea supercools substantially (40 to 50°C) below its melting point (132.7°C) before crystallizing; (3) with thermal cycling, both the heat of fusion and melting point gradually decrease, probably caused by thermal decomposition. On the basis of these results, urea is not quite as attractive as it seemed earlier. But before urea is discarded as a candidate, other aspects of its behavior will be investigated such as measuring the extent of supercooling in commercial grades of urea and determining if eutectic mixtures, with urea as the predominant component, are thermally stable. Eutectic temperatures of urea mixed with 10 mole % acetanilide, 20 mole % hydroquinone, and 49 wt % ammonium carbamate are 124, 110, and 98°C respectively.³

In the coming months, we will evaluate other organic compounds in Table 12.2. We have already scanned the *Chemical Marketing Reporter* for inorganic phase-change materials and are gathering the information to make initial selections for further evaluation.

1. G. A. Lane et al., *Isothermal Solar Heat Storage Materials*, ERDA-117 (1975).

2. F. W. Miller and H. R. Dittmar, *J. Am. Chem. Soc.* 56, 848 (1934).

3. J. Timmermans, *Physico-Chemical Constants of Binary Systems in Concentrated Solutions*, Interscience, New York, 1959, vol. I, p. 1153; vol. II, p. 921.

12.2 CRYSTAL STRUCTURE RELATED TO PHASE-CHANGE MATERIALS

H. A. Levy G. C. Lisensky¹

12.2.1 Crystal Structure of Glauber's Salt, Na₂SO₄·10H₂O

Thermal energy storage systems that utilize the 32°C incongruent melting transition in Glauber's salt, sodium sulfate decahydrate, have been tested for a number of years. Two sources of difficulty with this working medium are (1) separation of phases on melting and (2) supercooling of the melt on cooling. To gain an understanding of the molecular basis for its thermal and crystallization behavior, a neutron diffraction study was undertaken.

An x-ray diffraction study by Templeton and co-workers² gave the general nature of the crystal structure, including by inference the approximate hydrogen locations. The zero-point entropy of $R \ln 2$ observed from heat capacity studies³ was postulated as arising for a twofold statistical disorder in the arrangement of hydrogen atoms in certain hydrogen bonds. Although the two arrangements are crystallographically nonequivalent, the postulated structure required equal populations.

The structure was refined from a three-dimensional set of 2636 unique neutron diffraction intensities. Conclusions of the x-ray study were confirmed, including the hydrogen bonding scheme and the equal populations required by the postulated expla-

nations of residual entropy. Accurate parameters for the hydrogen atoms, improved accuracy for all other atoms, and a full description of the thermal displacements of all atoms were provided by the refinement. Figure 12.2 shows the chain of hydrated sodium ions, each adjacent pair doubly bridged by water molecules, which occurs in the structure. Also shown is a remarkably similar chain that occurs in the structure of borax.⁴

An unusual feature of the structure is the apparent thermal displacement of the atoms of the sulfate ion.

Figure 12.3 shows that three of the sulfate oxygen atoms have unusually large thermal displacements in directions suggesting a libration of the ion about the S-O₃ bond direction. An analysis of the data in terms of two distinct equilibrium orientations was carried out: in one orientation, three hydrogen bonds designated in Fig. 12.3 by dashed lines are formed, and in the other, three alternate hydrogen bonds designated by the opposed solid lines exist. The population ratio for the two orientations is 3:7, from which one may compute an energy difference of $-RT \ln (3/7) = 500$

Fig. 12.2. Portion of the chain of hydrated sodium ions linked by water molecules as it occurs in Glauber's salt (above) and borax (below). The disorder to which the residual entropy is attributed involves the alternate orientations shown for the water molecules labeled O8, O9, O16, and O17 in the upper figure.

Fig. 12.3. Sulfate ion and its environment in Glauber's salt. The elongated ellipsoids for 04, 06, and 07 represent the average of two distinct orientations differing by a libration of 29° about the S-O₃ direction. Solid and dashed lines parallel to the long axes of the ellipsoids represent alternate hydrogen bonds. The population of the dashed-line orientation is 30% and is estimated to be 500 cal/mole less stable than the alternate arrangement.

cal/mole. The angular displacement of one orientation from the other is about 29° .

1. Graduate student, California Institute of Technology.
2. H. W. Ruben, D. H. Templeton, R. D. Rosenstein, and I. Olovsson, *J. Am. Chem. Soc.* 83, 820 (1961).
3. K. S. Pitzer and L. V. Coulter, *J. Am. Chem. Soc.* 60, 1310 (1938).
4. See sect. 12.2.2 of this report.

12.2.2 Crystal Structure of Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

The utility of borax as a nucleating agent for the crystallization of Glauber's salt from its melt was first suggested by Telkes¹ on the basis of similarity of cell parameters, similarity of chemical formula, and stability of the solid at temperatures above the melting point of Glauber's salt. For this reason, borax is usually incorporated into working media for thermal energy storage based on Glauber's salt. As an adjunct to our study of the structure of Glauber's salt,² we

have examined the structure of borax by neutron diffraction, primarily to gain insight into the structural basis for its nucleating properties for Glauber's salt.

An x-ray study by Morimoto³ yielded the general structural arrangement: its chemical nature is best described by the formula $\text{Na}_2(\text{H}_2\text{O})_8\text{B}_4\text{O}_5(\text{OH})_4$. Our neutron diffraction study, based on 2373 unique reflections, furnished accurate locations of the hydrogen atom positions and improved accuracy for the heavier atoms. The following features are noteworthy.

The structure contains chains of hydrated sodium ions doubly bridged by water molecules that are remarkably similar to those found in Glauber's salt (see Fig. 12.2). The chains in borax contain inversion centers and diad axes of symmetry that are only approximately present in the sulfate, and the intra-chain hydrogen bonds in borax have an ordered rather than disordered arrangement of hydrogen atoms. The close similarity of the cation chains in the

Fig. 12.4. Views of adjacent cation chains in Glauber's salt (above) and borax (below).

two salts may be important in understanding the nucleating problem.

The similarity of cell parameters, particularly the monoclinic angle β between borax and Glauber's salt that was assumed important for the nucleation process, appears to be coincidental. Figure 12.4 shows views of both structures in which the cation chains are given corresponding orientations and the shear displacements of neighboring chains are portrayed. The magnitude of this shear displacement fixes the β angle. The displacement, while similar in magnitude, is opposite in direction in the two structures. In Glauber's salt, neighboring chains are hydrogen bonded with disordered hydrogen positions, and in borax they are not.

1. M. Telkes, *Ind. Eng. Chem.* 44, 1308 (1952).

2. See sect. 12.2.1.

3. N. Morimoto, *Mineral. J.* 2, 1 (1956).

12.2.3 Sodium Thiosulfate Pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Sodium thiosulfate pentahydrate, which has a semicongruent melting point of 48°C , is a candidate material for low-temperature thermal energy storage. The crystal structure has been determined from x-ray data by Taylor and Beevers¹ and from neutron data

by Padmanabhan and co-workers.² The latter study, consisting of 350 zonal measurements, indicated a degree of nonuniformity in the bond distances, bond angles, and hydrogen bond characteristics that could not be readily accepted although apparently significant in terms of the claimed precision. In particular, it was claimed that one hydrogen atom of a water molecule did not participate in hydrogen bonding.

Structure characteristics deduced from a new neutron diffraction study with 2108 three-dimensional diffraction intensities (Table 12.3) are compared with the earlier results (Table 12.4). The present work eliminates the discrepancies of the earlier study and shows that the hydrogen bonding net includes all the hydrogen atoms.

Figure 12.5 shows a portion of the chain of hydrated sodium ions as it appears in the crystal structure. An unusual feature is the bridging of three adjacent sodium ions by a thiosulfate ion in addition to three shared water molecules.

1. P. G. Taylor and C. A. Beevers, *Acta Crystallogr.* 6, 311 (1952).

2. V. M. Padmanabhan, V. S. Yodava, Q. O. Navarro, A. Garcia, L. Karsono, Il-Huan Suh, and Lin Shi Chien, *Acta Crystallogr. B* 27, 253 (1971).

Fig. 12.5. Portion of the hydrated chain of sodium ions bridged by water molecules and a thiosulfate ion as it occurs in the crystal structure of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

Table 12.3. Water molecule and hydrogen bond features of the crystal structure of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

O—H·····A	Distances (Å)			H—O—H angles (deg)
	O—H	H·····A	O·····A	
O ₄ H ₁ ·····O ₃ H ₂ ·····O ₂	0.967(4) (0.98) ^a	1.863(4) (1.76)	2.824(2) (2.73)	103.4(3) (107.5)
	0.964(4) (0.98)	1.900(4) (1.97)	2.844(2) (2.94)	
O ₅ H ₃ ·····O ₃ ' H ₄ ·····O ₃ ''	0.961(4) (0.96)	1.844(3) (1.82)	2.804(2) (2.77)	104.8(3) (106.2)
	0.964(3) (0.95)	1.951(3) (1.90)	2.904(2) (2.81)	
O ₆ H ₅ ·····O ₄ H ₆ ·····S ₁	0.963(4) (0.94)	1.907(4) (1.88)	2.864(2) (2.73)	104.5(3) (107.6)
	0.957(4) (0.92)	2.401(4) (2.52)	3.352(3) (3.30)	
O ₇ H ₇ ·····S ₁ ' H ₈ ·····O ₈	0.960(4) (0.93)	2.392(4) (2.38)	3.338(4) (3.13)	105.3(3) (108.2)
	0.966(4) (0.93)	1.890(4) (1.88)	2.855(3) (2.79)	
O ₈ H ₉ ·····S ₁ '' H ₁₀ ·····S ₁ '''	0.958(4) (0.95)	2.419(5) (2.68) ^b	3.338(4)	106.8(3) (109.8)
	0.956(4) (0.96)	2.409(4) (2.59)	3.359(4) (3.40)	

^aSecond-line entries in parentheses are from V. M. Padmanabhan, V. S. Yodava, Q. O. Navarro, A. Garcia, L. Karsono, Il-Huan Suh, and Lin Shi Chien, *Acta Crystallogr. B* 27, 253 (1971).

^bNot designated a hydrogen bond in Padmanabhan et al.

Table 12.4. Sodium-oxygen coordination of the crystal structure of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

(Distances in Å)					
	Current work	Earlier work ^a		Current work	Earlier work ^a
Na ₁ —O ₁	2.381(3)	2.25(2)	Na ₂ —O ₁	2.419(3)	2.37(2)
Na ₁ —O ₂	2.436	2.64	Na ₂ —O ₅	2.365	2.34
Na ₁ —O ₄	2.402	2.45	Na ₂ —O ₆	2.331	2.46
Na ₁ —O ₅	2.429	2.51	Na ₂ —O ₇	2.428	2.44
Na ₁ —O ₆	2.433	2.36	Na ₂ —O ₈	2.380	2.64
Na ₁ —O ₇	2.446	2.62			

^aV. M. Padmanabhan, V. S. Yodava, Q. O. Navarro, A. Garcia, L. Karsono, Il-Huan Suh, and Lin Shi Chien, *Acta Crystallogr. B* 27, 253 (1971).

13. Electrochemistry

13.1 MAGNETIC FIELD EFFECTS ON ELECTROCHEMICAL REACTIONS OCCURRING AT METAL/FLOWING- ELECTROLYTE INTERFACES

E. J. Kelly

A study was made to determine whether a magnetic field, such as that associated with a thermonuclear reactor, might adversely affect the corrosion behavior of metallic surfaces in contact with a flowing electrolyte. In metal/flowing-electrolyte systems, electrochemical reactions dependent on the metal/electrolyte interfacial potential difference are affected by an applied magnetic field as a consequence of the Lorentz forces acting on the charged components of the flowing electrolyte. A theoretical analysis of the magnetic field effect was developed, and its validity was established by experiments involving the $\text{Ti}/\text{H}_2\text{SO}_4$ (H_2 -saturated) system. Quantitative agreement between theoretical and experimental results was obtained for the electrochemical behavior of titanium in $1\text{ N H}_2\text{SO}_4$ (mean flow velocity: 0 to 650 cm/sec) over the available range of magnetic flux density (0 to 2.1 T).

A schematic drawing of the electrochemical cell, that is, that segment of a forced-convection loop located between the pole pieces of an electromagnet, is shown in Fig. 13.1. The inner and outer radii (a and b in the schematic) of the Pyrex pipe were 0.953 and 1.27 cm respectively. The axis of the cylindrical cell coincided with the z axis, and the magnetic field was aligned parallel to the x axis. The fluid flow and the magnetic field were directed in the positive z and positive x directions respectively. A pair of identical cylindrical titanium electrodes (M_1 and M_2 in Fig. 13.1) were located opposite one another, their common axis coinciding with the y axis. The titanium electrodes (diameter = 0.397 cm) were mounted through the wall of the pipe, and the surfaces in contact with the electrolyte were polished to conform to the inner surface of the pipe. A pair of identical platinum electrodes (diameter = 0.159 cm), similarly

mounted but displaced 1.27 cm along the z axis, completed the electrochemical cell. In the entire closed loop (reservoir, pump, control valves, and cell), the only metallic surfaces in contact with the electrolyte ($1\text{ N H}_2\text{SO}_4$, $T = 30.0 \pm 0.1^\circ\text{C}$) were the cell electrodes.

For the configuration presented in Fig. 13.1 and described above, it may be shown that, as a consequence of the Lorentz forces acting on the charged components of the electrolyte phase, a potential difference ($\Delta\phi_{\text{MAG}}$) is induced in the electrolyte phase between the two titanium (M_1 and M_2) electrodes (or between the two platinum electrodes). The magnetically induced potential difference is described by the equation

$$\Delta\phi_{\text{MAG}} = 2Bav_m,$$

where

a is the inner radius of the pipe,

v_m is the average flow velocity

$$[v_m = (1/\pi a^2) \int_0^a 2\pi r v dr],$$

B is the applied magnetic flux density.

One may determine $\Delta\phi_{\text{MAG}}$ directly by measuring the open-circuit potential difference between a pair of the oppositely located electrodes.

The electrochemical system chosen for this study, titanium in H_2 -saturated $1\text{ N H}_2\text{SO}_4$, has been studied extensively in the absence of a magnetic field^{1,2} and is one in which the interfacial reactions, the oxidation of titanium to form Ti (III) ions in solution and the hydrogen evolution reaction, are both under activation control. The anodic polarization curve for the titanium electrode located in position M_1 (see Fig. 13.1), that is, the logarithm of the net anodic Faradaic current (i_1) vs the electrode potential (E_1), and the cathodic polarization curve ($\log i_2$ vs E_2) for the titanium electrode located at position M_2 , both determined in the absence of a magnetic field ($\Delta\phi_{\text{MAG}} = 0$), are shown by the solid curves in Fig. 13.2.

ORNL-DWG 76-13800

Fig. 13.1. Schematic drawing of the electrochemical cell segment of the forced-convection loop.

ORNL-DWG 76-15192

Fig. 13.2. Anodic and cathodic polarization curves for the two titanium electrodes, M_1 and M_2 respectively, shown in Fig. 13.1. Curves measured in the absence of a magnetic field ($\Delta\phi_{\text{MAG}} = 0$).

When the two electrodes are externally short-circuited to form an analog of a metallic pipe, and a magnetic field is applied to the flowing electrolyte (see Fig. 13.1 for the directions of v and B), the titanium electrode in position M_1 becomes anodically polarized, while the electrode in position M_2 becomes cathodically polarized, the Faradaic current being equal in magnitude but opposite in sign at the two electrodes. According to theory, the magnitude of the magnetically induced Faradaic current may be determined by simply locating on Fig. 13.2 that current for which $E_2 - E_1 = -\Delta\phi_{\text{MAG}} = -2Bav_m$. Thus the magnetic field effect may be quantitatively evaluated by a simple graphical procedure. In order to prove experimentally the validity of the theory, the two electrodes were connected through an external precision resistor (R_L), and the Faradaic current was determined by measuring the potential difference (iR_L) across the load resistor. Of course, one must take into account the potential difference appearing

across the load resistor; that is, $E_1 - E_2 = \Delta\phi_{\text{MAG}} - IR_L$, a correction indicated in Fig. 13.2.

Figure 13.3 shows the results of an experiment in which R_L was maintained constant at 200 Ω , and the current was measured as a function of the magnetic flux density at a constant flow rate. The currents determined by direct measurement (solid circles), that is, by measuring the potential difference across R_L , and those determined by the application of the equation $E_1 - E_2 = \Delta\phi_{\text{MAG}} - IR_L$ to the polarization curves shown in Fig. 13.2 are in excellent agreement. The partial anodic polarization curve corresponding to just the titanium dissolution reaction is shown by the dashed line in Fig. 13.2. Once E_1 and E_2 have been determined as just described, the actual dissolution rates and hydrogen evolution rates at E_1 and E_2 may be evaluated by means of the dashed curve. The open-circuit corrosion rate (i_{corr}) in the absence of a magnetic field is shown in Fig. 13.2 for comparative purposes. One observes that the maximum enhancement of the titanium dissolution rate in this system is limited by the passivation characteristics of the metal to a factor of $(i_{\text{MAX}}/i_{\text{corr}}) = 2.5$.

Although the experimental work employed discrete titanium electrodes set in the wall of nonconducting Pyrex pipe, the theory was extended to include metallic pipes, that is, the "conducting-wall" case, for which the "wall-shorting" effect was shown to be negligible. In addition to the adverse effect of a magnetic field on the "uniform" corrosion behavior

of metals, the imposition of a magnetic field can also result in enhanced susceptibility to stress-corrosion cracking, localized (pitting or crevice) corrosion, oxidation and reduction of solution species, and electrochemical decomposition of the electrolyte. The aforementioned processes, to name a few, are all potential dependent and, consequently, subject to the magnetic field effect.

1. E. J. Kelly, p. 137 in *Proceedings International Congress on Metallic Corrosion*, 5th, Tokyo, 1972, NACE, Houston, 1974.
2. E. J. Kelly, *J. Electrochem. Soc.* 123, 162 (1976).

13.2 ELECTROCHEMISTRY OF SULFIDES

R. E. Meyer

There has been considerable interest in the electrochemical properties of FeS_2 and other sulfides among investigators interested in the pressure leaching of ore materials. Recently, there has been renewed interest in the electrochemistry of sulfides and chalcogenides because of increased attention to the direct electrochemical conversion of sulfide ores to metals, because of the presence of sulfur in fossil fuels, and because of the use of chalcogenides as catalytic and photoelectric materials. Thus, the study of the electrochemical properties of sulfides is related to many recent research trends in environmental, metallurgical, and energy fields.

Previous investigations of FeS_2 include several studies of high-pressure aqueous oxidation by O_2 and some studies of anodic and cathodic polarization of FeS_2 , mostly in acid solution. Unfortunately, most of the studies of anodic polarization are quite limited in scope, usually with only a single solution at a single temperature. We therefore initiated an extensive study of the anodic oxidation of FeS_2 as a function of a number of variables, including pH, temperature, solution composition, and surface preparation.

In Fig. 13.4 an example is given of a polarization curve for a polished specimen of FeS_2 in deaerated 3 N H_2SO_4 at 25°C and a scan rate of 0.5 mV/sec. The initial open-circuit potential was about +0.36 V vs S.C.E.; however, after the scan, the open-circuit potential shifted in the positive direction by about 0.15 to 0.2 V. When forward and reverse scans were immediately repeated, all subsequent lines would fall essentially on the first reverse scan (cf. line 2 in Fig. 13.4). When polarization was stopped, the open-circuit potential then slowly drifted back to the original open-circuit potential. For these polished

Fig. 13.3. Faradaic current at the titanium electrodes, M_1 and M_2 in Fig. 13.1, when connected through an external resistance of 200 Ω , as a function of the magnetic flux density at constant v_m , that is, as a function of $\Delta\phi_{\text{MAG}}$.

Fig. 13.4 Anodic polarization of polished FeS_2 in $3\text{ N H}_2\text{SO}_4$.

specimens, the slopes of the linear portion, line 2 in Fig. 13.4, varied from about 90 to 110 mV/decade. Only these linear sections of the curves are shown in subsequent figures.

In Fig. 13.5 it is shown that increasing the pH will slightly increase the rate of the reaction at constant potential. The upper portions of the lines at higher pH values are stirring dependent. The effect of temperature shown in Fig. 13.6 corresponds to an effective activation energy of about 14 kcal/mole when the logarithm of the current is plotted vs $1/T$ at a potential of +600 mV vs S.C.E. Polarization curves are shown in Fig. 13.7 for polished FeS_2 specimens in alkaline solutions. Results for 0.1 and 0.01 M NaOH are compared with results in acidic solutions. The horizontal sections of the curves in alkaline solution are strongly stirring dependent and also dependent on the concentration of hydroxide ion. In these alkaline solutions a reddish-brown film formed on the surface. Analyses of these films showed that the composition was depleted in sulfur compared with FeS_2 and that the mole ratio of Fe to S was about 2:1. X-ray diffraction showed that the film was mostly amorphous, but a few weak lines matching FeO were found. Finally, the height of the plateau in alkaline

Fig. 13.5. Effect of pH on anodic polarization of FeS_2 in acid solutions.

Fig. 13.6. Effect of temperature on anodic polarization of FeS_2 in $0.1\text{ N H}_2\text{SO}_4 + 0.5\text{ M Na}_2\text{SO}_4$.

Fig. 13.7. Anodic polarization of FeS₂ in alkaline solutions.

solution depends on the total amount of film, because its height decreased with time as the electrode was polarized. Analyses of the solution after anodic polarization showed that in acid solution all of the Fe in FeS₂ is oxidized to the ferric ion and that from 75 to 100% of the sulfur is oxidized to the sulfate ion.

In summary, FeS₂ oxidizes readily in alkaline solution at relatively low potentials, but the rate is limited by film formation. In acid solution, FeS₂ does not oxidize significantly (i.e., at rates greater than about 10 mA/cm²) until the potential reaches about +850 mV vs S.C.E., and ferric sulfate is the major oxidation product. Kinetic evidence seems to indicate that a thin film is formed in acid solution.

14. Thermal Generation of Hydrogen

C. E. Bamberger D. M. Richardson

The search for efficient and economical thermochemical cycles for the production of hydrogen from water continues to merit worldwide attention because of the availability of water and the versatility of hydrogen in most energy-related areas: conservation, transmission, storage, conversion, etc. As in previous years we have chosen the experimental approach over the calculational approach, and our goal continues to be the identification of chemical (established or new) reactions conducive to the development of new thermochemical cycles and the further examination of already identified cycles in order to improve and develop them or discard them.

The main criteria for considering that an identified cycle deserves further study are that it be composed by reactions which are simple, reach completion (or nearly do), do not have parasitic by-products, and use elements that are fairly abundant and hopefully not toxic; the cycle itself should work at a maximum temperature of 1000°C or less and exhibit an overall efficiency of conversion (heat to hydrogen) larger than that of water electrolysis. The latter, an estimate of the efficiency of the cycle, is the more difficult information to obtain for our cycles because the majority of them involve compounds which are new or which have not been studied sufficiently so as to have available thermodynamic data. Thus, this work requires the chemical and structural identification of new compounds before their thermodynamic data can be obtained.

The following new cycles (two) have been completely identified and one cycle has been partially identified; additionally some reactions of earlier reported cycles¹ have been further studied:

I. Cr(III)/Sr(OH)₂

where s, l, g, and d refer, respectively, to the solid, liquid, gaseous, and dissolved states.

Although this cycle resembles closely the one of Cr(III)/Ba(OH)₂ reported last year,¹ the higher solubility of SrCrO₄ allows for an easier separation of the products of reaction (3) than the equivalent products from the barium cycle.

II. Cu⁰/Ba(OH)₂; F⁻

This cycle, to our knowledge, is the first one to use fluoride compounds; however, we consider the possible corrosion problems tractable due to the relatively low temperatures in which they participate. In reality the HF is obtained as an aqueous solution, a condensate in (7), and can be used as such in (6), thus not requiring any handling of gaseous HF.

III. Co(II)/Ba(OH)₂

We have determined that $y = 2.33$ for $x = 1$, and $y = 3.33$ for $x = 2$; thus $\text{CoO}_{y-x} = \text{CoO}_{1.33}$ or Co_3O_4 . The double oxides Ba_xCoO_y are still being studied because x-ray diffraction indicates that they are as yet unidentified, new compounds. However, CoO obtained in (11) has been reused in (9), evolving H_2 and completing a full cycle.

IV. Thermal decomposition of PbCrO_4

Although it appears to be one of the more unstable chromates, the thermal decomposition of PbCrO_4 was investigated because there are conflicting reports in the literature as to its products of decomposition.

When the temperature does not exceed 800°C , it was confirmed that the reaction proceeds according to

Above 800°C , the amount of oxygen being evolved corresponds to a reaction such as

The solid product contained $\text{PbCrO}_4 \cdot \text{PbO}$ and unidentifiable compound(s). In order to close two different thermochemical cycles, it is necessary that either one of the following reactions takes place:

Neither one occurred to any practical extent; thus, cycles based on lead and chromium are being abandoned. A noteworthy finding is that the x-ray diffraction pattern of $\text{PbCrO}_4 \cdot \text{PbO}$ is the same as that of $\text{PbCrO}_4 \cdot \text{Pb(OH)}_2$, both reported in the ASTM cards. Since details for the preparation of the latter cannot be found, we infer that its stoichiometry may be wrong and that no hydroxyl groups are present.

V. Cr(VI)/KOH

The reaction

has been performed in the past with a large excess of KOH (about 200 times the stoichiometric amount) as part of a Cr/K cycle. Attempts to reduce such excess resulted in very low oxygen evolution. Several samples of pure K_3CrO_4 have been synthesized for determination of enthalpy of formation by solution calorimetry in order to understand this and other reactions of K_3CrO_4 . Although the cycle¹ is feasible, the presence of a large amount of KOH with the reaction product presently renders the cycle impractical.

VI. Mixed valency lead oxyiodides²

We have found that massicot, the yellow orthorhombic variation of PbO , reacts with iodine at room temperature leading to the formation of lead oxyiodide(s) containing lead in the 2+ and 4+ states. X-ray diffraction analysis indicates that two types of structures are predominant. These correspond to the general stoichiometries $(\text{Pb(II)})_{1.5}, \text{Pb(IV)}_{0.5}\text{O}_2\text{I}$ and $(\text{Pb(II)}), \text{Pb(IV)}\text{O}_2\text{I}_2$. Because the formation of such compounds can be achieved at room temperature by reaction of PbO with aqueous solutions of I_2 and to a lesser extent with gaseous I_2 , PbO can be visualized as a trapping agent for I_2 in nuclear technology.³

1. Chem. Div. Annu. Prog. Rep. Nov. 1, 1975, ORNL-5111, p. 119.

2. In collaboration with M. A. Bredig, consultant to the Chemistry Division.

3. D. M. Richardson and C. E. Bamberger, "Solid Sorbent for Trapping Iodine," U.S. Pat. 3,880,619 (Apr. 29, 1975).

15. Chemistry in Support of the Nuclear Fuel Cycle

A. D. Kelmers
M. R. Bennett

L. Maya
D. Y. Valentine

The work concerned with the development of aqueous processes for LMFBR fuel is not reported here, in compliance with the regulations which stipulate that such information must be distributed solely under the category UC-79—Liquid-Metal Fast Breeder Reactors. The results of our work have been summarized in the *LMFBR Fuel Recycle Program Progress Report for Period Oct. 1 to Dec. 31, 1976*, ORNL/TM-5768.

The associated research in LWR fuel reprocessing is being reported separately in a series of quarterly progress reports. The results have been summarized in the *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period July 1 to Sept. 30, 1976*, ORNL/TM-5660 and in the *LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period Oct. 1 to Dec. 31, 1976*, ORNL/TM-5760.

Publications, Patents, Lectures, and Papers Presented at Meetings

COAL-RELATED RESEARCH, CATALYSIS, AND ORGANIC CHEMISTRY

- B. M. Benjamin, "Chemical Bond Cleavage during Asphaltene Formation," Division of Fuel Chemistry, 173rd American Chemical Society National Meeting, New Orleans, La., Mar. 20-25, 1977.
- B. M. Benjamin, "High-Resolution NMR Spectroscopy," Lectures for In-House Continuing Education Program, Spring, 1976.
- C. J. Collins, B. M. Benjamin, M. Hanack, and H. Stutz, "An Isotope Effect Study of Triple Bond Participation during a Homopropargyl Rearrangement," *J. Am. Chem. Soc.* **99**, 1669 (1977); Abstracts Am. Chem. Soc., 172d Meeting, San Francisco, Cal., Aug. 30-Sept. 3, 1976, ORG No. 220.
- C. J. Collins, V. F. Raaen, B. M. Benjamin, and G. W. Kabalka, "Carbon-Carbon Cleavage during Asphaltene Formation," *Fuel* **56**, 107 (1977).
- C. J. Collins, "The Role of the Counter-Ion in Product Control," Seminar, West Virginia University, Morgantown, Nov. 10, 1976.
- E. L. Fuller, Jr., "Surface Properties of a Cobalt Oxide-Molybdenum Oxide Catalyst," 172d American Chemical Society National Meeting, San Francisco, Calif., Aug. 30-Sept. 3, 1976.
- E. L. Fuller, Jr.,* and P. A. Agron, "Surface Properties of Catalysts: Cobalt Molybdate," 28th American Chemical Society Southeastern Regional Meeting, Gatlinburg, Tenn., Oct. 27-29, 1976.
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- E. J. Kelly, "Magnetic Field Effects on Electrochemical Reactions," ORAU Traveling Lecture, University of New Orleans, New Orleans, La., Nov. 19, 1976.
- E. J. Kelly, "Electrochemical Behavior of Titanium," ORAU Traveling Lecture, University of Alabama, Tuscaloosa, Ala., Mar. 23, 1977.
- R. E. Meyer, W. J. McDowell, P. F. Dittner, R. J. Silva, and J. R. Tarrant, "Determination of the Half-Wave Potential of Nobelium," *J. Inorg. Nucl. Chem.* 38, 1171 (1976).

- F. A. Posey* and A. A. Palko, "Use of Porous and Packed-Bed Electrodes for Removal and Recovery of Metals from Flowing Streams," Symposium on Engineering Analysis and Scale-Up of Electrochemical Systems, 149th Meeting, Electrochemical Society, Washington, D.C., May 2-7, 1976 (invited paper).

*Denotes speaker.

1. Chemical Technology Division.

THERMAL GENERATION OF HYDROGEN

- C. E. Bamberger and W. R. Grimes,¹ "Thermochemical Production of Hydrogen," U.S. Pat. 3,919,406 (Nov. 11, 1975).
- C. E. Bamberger and D. M. Richardson, "Chemical Cycle for Thermochemical Production of Hydrogen from Water," U.S. Pat. 3,927,192 (Dec. 16, 1975).
- C. E. Bamberger, D. M. Richardson, and W. R. Grimes,¹ "Process for Generating Hydrogen," U.S. Pat. 3,929,979 (Dec. 30, 1975).
- C. E. Bamberger and D. M. Richardson, "Process for Thermochemically Producing Hydrogen," U.S. Pat. 3,996,343 (Dec. 7, 1976).
- C. E. Bamberger and D. M. Richardson, "Thermochemical Process for the Production of Hydrogen Using Chromium and Barium Compound," U.S. Pat. 4,005,184 (Jan. 25, 1977).
- C. E. Bamberger and D. M. Richardson, "Thermochemical Decomposition of Water Based on Reactions of Chromium and Strontium Compounds," *Chem. Technol.* 6(5), 330 (1976). (Paper presented at symposium on Thermochemical Production of Hydrogen, Division of Fuel Chemistry, 171st American Chemical Society National Meeting, New York, 1976.)
- C. E. Bamberger and D. M. Richardson, "Production of Hydrogen from Water by Thermochemical Cycles," *Cryogenics* 16, 197 (1976).
- C. E. Bamberger and D. M. Richardson, "Thermochemical Production of Hydrogen from Water," *Trans. Am. Nucl. Soc.* 23, 105 (1976). (Invited paper presented at 1976 Annual Meeting of the ANS, Toronto, Canada, June 1976.)
- C. E. Bamberger and D. M. Richardson, "On the Hydrolysis of Manganous Chloride," *J. Inorg. Nucl. Chem.* 39, 150 (1977).
- C. E. Bamberger and J. H. DeVan,² "Materials Problems in Large Scale Production of Hydrogen from Water and in Hydrogen Storage," Symposium on Materials Requirements for Unconventional Energy Systems, TMS-AIME Fall Meeting, Niagara Falls, N.Y., September 1976.
- C. E. Bamberger, "New Thermochemical Cycles for Hydrogen Production," Chemistry Division Seminar, ORNL, Feb. 25, 1977.

1. Chemical Technology Division.

2. Metals and Ceramics Division.

CHEMISTRY IN SUPPORT OF THE NUCLEAR FUEL CYCLE

- A. D. Kelmers, "Chemistry of Plutonium Reducing Agents," presented at Savannah River Laboratory, Aiken, S.C., Jan. 28, 1977.
- L. Maya, "Ruthenium Chemistry in the Purex Process," presented at Savannah River Laboratory, Aiken S.C., Jan. 28, 1977.

MISCELLANEOUS TOPICS

- E. L. Fuller, Jr., "Studies of Lunar Soils and Their Reactions with Atmospheric Vapors," Clarkson College of Technology, Colloid and Surface Science Colloquium, Potsdam, N.Y., Nov. 25, 1976.
- E. L. Fuller, Jr., "The Reactions of Atmospheric Vapors with Lunar Soil (14003)," IUPAC 50th Colloid and Surface Science Symposium, San Juan, P.R., June 21-25, 1976.
- E. L. Fuller, Jr., R. W. Hendricks, and J. S. Lin,* "Small Angle X-Ray Scattering: Supported Cobalt Molybdate Catalyst," Am. Crystallogr. Soc., July 20-24, 1976.
- E. L. Fuller, Jr., "Physical Adsorption of Gases on Lunar Soils," Gordon Conferences: Chemistry at Interfaces, July 18, 1976.
- E. L. Fuller, Jr., and P. A. Agron, "Sorption of Water, Carbon Dioxide, and Nitrogen by Sol-Gel Thorium Oxide," *J. Colloid Interface Sci.* 57, 193-200 (1976).
- E. L. Fuller, Jr., "Interaction of Gases with Lunar Materials (12001): Textural Changes Induced by Sorbed Water," *J. Colloid Interface Sci.* 55, 358-69 (1976).
- E. L. Fuller, Jr., "The Reactions of Atmospheric Vapors with Lunar Soil (14003)," pp. 47-62 in *Colloid and Interfacial Science*, Vol. III, Chap. 5, ed. M. Kerker, Academic Press, New York, 1976.
- E. L. Fuller, Jr., and P. A. Agron, *The Reactions of Atmospheric Vapors with Lunar Soil*, ORNL-5129 (March 1976).
- R. B. Gammage¹ and H. F. Holmes, "Alteration of Apollo 17 Orange Fines by Adsorbed Water Vapor," *J. Colloid Interface Sci.* 55, 243 (1976).
- R. B. Gammage¹ and H. F. Holmes, "Blocking of the Water-Lunar Fines Reaction by Air and Water Concentration Effects," *6th Lunar Sci. Conf., Geochim. Cosmochim. Acta*, Suppl. 6, Vol. 3, p. 3305, Pergamon, New York, 1975.
- R. B. Gammage¹ and H. F. Holmes, "Effects of Surface Water on the Adsorption of Inert Gases," p. 1 in *Colloid and Interface Science*, Vol. III, Academic Press, New York, 1976.
- R. B. Gammage*¹ and H. F. Holmes, "Effects of Surface Water on the Adsorption of Inert Gases," International Conference on Colloids and Surfaces, San Juan, Puerto Rico, June 21-25, 1976.
- R. B. Gammage¹ and H. F. Holmes, "Specific Surface Area as a Maturity Index of Lunar Fines," *Earth Planet. Sci. Lett.* 27, 424 (1975).
- H. F. Holmes and R. B. Gammage,¹ "Comments on the Shape of Pores Induced in Lunar Fines by Adsorbed Water," *J. Colloid Interface Sci.* 54, 151 (1976).
- H. F. Holmes, P. A. Agron, E. Eichler,² E. L. Fuller, Jr., G. D. O'Kelley, and R. B. Gammage,¹ "Alteration of an Annealed and Irradiated Lunar Fines Sample by Adsorbed Water," *Earth and Planet. Sci. Letters* 28, 33 (1975).
- H. F. Holmes and R. B. Gammage,¹ "Interaction of Gases with Lunar Materials: Revised Results for Apollo 11," *Proc. 6th Lunar Sci. Conf., Geochim. Cosmochim. Acta*, Suppl. 6, Vol. 3, p. 3343, Pergamon, 1975.

*Denotes speaker.

1. Health Physics Division.

2. Deceased.

Supplementary Activities

PROFESSIONAL AND EDUCATIONAL ACTIVITIES

- C. F. Baes, Jr. Lecturer on environmental chemistry in a course entitled "Seminars in Professional Chemistry," at Rensselaer Polytechnic Institute, Apr. 9, 1976.
Participant with F. J. Hurst in a seminar and discussion of ORNL's processes for extracting uranium from phosphoric acid at the Exxon Research and Engineering Company, Linden, N.J., Dec. 3, 1976.
Participant in an ERDA Workshop, "Environmental Effects of Carbon Dioxide from Fossil Fuels Combustion," Miami, Fla., Mar. 7-11, 1977.
- C. E. Bamberger Codirector of course on molten-salt technology, Center for Professional Advancement, New Brunswick, N.J., May 24-26, 1976.
- C. E. Bemis, Jr. Guest scientist Physics Department, Brookhaven National Laboratory, Upton, L.I., N.Y., March 1977.
- J. Braunstein Editor, *Advances in Molten Salt Chemistry*, 1970-present.
Cochairman, International Symposium on Molten Salts, the Electrochemical Society, May 1976.
Lecturer, University of Tennessee-Oak Ridge Graduate School of Biomedical Sciences, 1971-present.
Vice-chairman, 1977 Gordon Conference on Molten Salts and Liquid Metals.
Editor, Molten Salts (Proceedings of the International Symposium), 1976.
Course Director, Molten-Salt Technology, Center for Professional Advancement, New Brunswick, N.J., May 1976.
Panel Member, Workshop on Energy Conservation in the Electrochemical Industries, sponsored by USERDA Conservation Division, Argonne National Laboratory, July 1976.
Panel Member, Workshop on Thermodynamics and Electrochemistry, sponsored by USERDA Division of Physical Research, Materials Science Program, Argonne National Laboratory, May 1977.
- J. H. Burns Participant, ERDA Workshop on Heavy-Element Research, and member of Panel on Actinide Element and Compound Preparations and Properties, May 1976.
- W. R. Busing Secretary-Treasurer, U.S. National Committee for Crystallography, National Academy of Sciences - National Research Council, Jan. 1, 1974-Dec. 31, 1976.
- C. J. Collins Professor of Chemistry, part time, University of Tennessee, Knoxville, January 1964-present.
Member, Advisory Board, *Isotopes in Organic Chemistry*, Elsevier Publishing Co., Amsterdam, Netherlands.
Coholder of NATO Grant No. 814 with Prof. Michael Hanack, University of Tübingen, Germany.
- S. Datz Associate Editor, *Atomic Data and Nuclear Data Tables*, 1969-present.
Member, National Academy of Sciences - National Research Council Committee on Energy-Related Atomic and Molecular Physics.
Member, Publications Committee, American Institute of Physics.
Member, International Committee, Atomic Collisions in Solids.
Lecturer, Haifa International Workshop: Topics in Atomic Physics Related to Nuclear Experimentation, Haifa, Israel, August 1976.
- R. L. Ferguson Guest scientist ("outside user"), SuperHILAC, Lawrence Berkeley Laboratory, Berkeley, Calif.
- E. L. Fuller, Jr. Steering Committee for International Conferences on Vacuum Microbalance Techniques.
Program Committee for Colloid and Surface Science Symposium, Division of Colloid and Surface Chemistry, American Chemical Society.
Local chairman, 52nd Colloid and Surface Science Symposium to be held in Knoxville, Tenn., June 1978.
Steering Committee for Gordon Conference on Chemistry at Interfaces.
Session Chairman, 28th Southeast Regional American Chemical Society Meeting, October 1976.

- R. L. Hahn Participant, ERDA Workshop on Heavy-Element Research, and member of Panel on Actinide Element and Compound Preparations and Properties, May 1976.
Member, ERDA Transplutonium Program Committee, 1975-present.
Member, Committee on Major Nuclear Facilities, American Chemical Society, Division of Nuclear Chemistry and Technology, 1976-present.
Guest scientist ("outside user"), SuperHILAC, Lawrence Berkeley Laboratory, Berkeley, Calif.
- R. G. Haire Participant, ERDA Workshop on Heavy-Element Research, and member of Panel on Actinide Element and Compound Preparations and Properties, May 1976.
- C. K. Johnson President, American Crystallographic Association, 1977.
Member, U.S. National Committee for Crystallography, National Academy of Sciences - National Research Council, Jan. 1, 1972-Dec. 31, 1978.
Member, National Research Council Committee on Chemical Crystallography, July 1, 1970-June 30, 1976.
Member, Planning Committee for a National Resource for Computational Chemistry, NAS-NRC, Woods Hole, Mass., July 13-16, 1976.
- J. S. Johnson, Jr. Cochairman of seminar, "Membrane Separation Technology," cosponsored by Clemson University and Oak Ridge National Laboratory, Aug. 2-6, 1976, Clemson, S.C.
- N. R. Johnson Member, HHIF Users Liaison Group.
Member, ORIC Program Committee.
ORIC Scheduling Coordinator.
Guest scientist ("outside user"), SuperHILAC, Lawrence Berkeley Laboratory, Berkeley, Calif.
Guest scientist, University of Paris South, Orsay, France, Feb. 16-27, 1977.
Guest scientist, University of Bordeaux, Bordeaux, France, Feb. 27-Mar. 13, 1977.
- M. O. Krause Participant, ERDA Workshop on Heavy-Element Research, and member of Panel on Electronic and Magnetic Properties of the Actinides, May 1976.
Lecturer, NATO Advanced Study Institute on "Photoionization and Other Probes of Many-Electron Interactions," Aug. 31-Sept. 13, 1975, Carry-Le-Rouet, France.
Member, International Advisory Committee and of Program Committee of Second International Conference on Innershell Ionization Phenomena, Mar. 29-Apr. 2, 1976, Freiburg, Germany.
Member, Program Committee of International Conference on the Physics of X-Ray Spectra, Aug. 30-Sept. 2, 1976, NBS, Washington, D.C.
- H. A. Levy Member, Subpanel on Structures, ad hoc Panel to Carry Out a Study of Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons, National Academy of Sciences, March 15-June 15, 1977.
- M. H. Lietzke Professor of Chemistry, part time, University of Tennessee, Knoxville, 1964-present.
- R. Livingston ORNL Liaison Officer for ORNL-University of Tennessee part-time teaching program, 1968-present.
Editorial Board, *The Journal of Magnetic Resonance*, January 1971-present.
Editorial Board, *Magnetic Resonance Review*, September 1971-present.
Member, Executive Committee for the Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Oct. 27-29, 1976.
Judge, Southern Appalachian Science and Engineering Fair, Knoxville, Tenn., April 8, 1976, and March 31, 1977.
- W. L. Marshall 1977 Recipient of the Herty Medal, Georgia Section, American Chemical Society.
Member, National Council, American Chemical Society, 1969-74, 1976-present; Committee on Chemical Education, 1970-74, 1977-present; Subcommittee on High School Chemistry, 1971-74, 1977-present; Steering Committee on Guidelines for Teacher Training, 1975-present.
Member, Working Committee of International Association for the Properties of Steam, 1975-present.
Participant, International Meeting on Physical Data of High-Pressure Fluids, Kyoto, Japan, Sept. 11, 1976.
Participant, Visiting Scientist Program, Tennessee Academy of Science, 1975-present.
- R. E. Mesmer Participant, EPRI Workshop on Denting in PWR Steam Generators, Washington, D.C., December 1976.
- A. H. Narten Member, Study Group on Noncrystalline Structures and Surfaces, ERDA Workshop on X-Ray, Neutron, and Electron Scattering, Apr. 13-15, 1977.
- G. D. O'Kelley Participant, ERDA Workshop on Heavy-Element Research, and member of Panel on Actinide Solution and Separations Chemistry, May 1976.
Professor of Chemistry, part time, University of Tennessee, Knoxville, January 1964-present.
Alternate Councilor, Division of Nuclear Chemistry and Technology, American Chemical Society, 1977-1979.
Symposium Chairman, Centennial Meeting, American Chemical Society, New York, Apr. 4-9, 1976.
Member, National Research Council Committee on Nuclear Science; Chairman, Subcommittee on Radiochemistry, 1974-1977.

- R. M. Pearlstein Lecturer, University of Tennessee—Oak Ridge Graduate School of Biomedical Sciences, 1969—present.
Publications and Program Committees, Division of Biological Physics, American Physics Society.
Coordinator of Solar Energy Research, ORNL.
- R. J. Silva Participant, ERDA Workshop on Heavy-Element Research, and member of Panel on Actinide Solution and
Separations Chemistry, May 1976.
Member, International Committee on Reporting of Actinide Research.
- G. P. Smith Professor of Chemistry, part time, University of Tennessee, Knoxville, January 1964—present.
Program Chairman, 28th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg,
Tenn. Oct. 27–29, 1976.
External examiner, Ph.D. thesis of Ismail K entitled "Physico-chemical Studies of Molten Salt Systems,"
1976, Aligarh Muslim University, Aligarh, India.
- R. W. Stoughton Editorial Advisory Board, *Journal of Inorganic and Nuclear Chemistry*, 1958—present.
Consulting Editor, *Inorganic and Nuclear Chemistry Letters*, 1965—present.

COLLABORATIVE RESEARCH

Institution	Collaborator(s)	Subject	Staff Member(s)
Argonne National Laboratory	K. L. Wolf	Spontaneous fission energetic studies	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Arizona State University Center for Meteorite Studies	C. B. Moore	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Australian Atomic Energy Commission, Lucas Heights, Australia	B. J. Allen M. J. Kenny	Neutron capture cross section of ^{52}Cr	J. Halperin
University of Bordeaux, Bordeaux, France	P. Hubert	Multiple Coulomb excitation measurements in $^{182}, ^{184}, ^{186}\text{W}$	N. R. Johnson
Brookhaven National Laboratory	M. J. LeVine	Coulomb excitation — reorientation and the determination of static quadrupole moments for vibrational-like states in ^{230}Th	C. E. Bemis, Jr.
University of California, San Diego, La Jolla	H. W. Meldner	Possibility of superheavy elements in nuclear explosions	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
University of California, San Diego	K. Lindenberg	Excitons in photosynthetic units	R. P. Hemenger R. M. Pearlstein
Carnegie-Mellon University	A. A. Caretto, Jr. M. Kaplan	Heavy-ion-induced reactions at ORIC	R. L. Ferguson
Central College, Pella, Iowa	P. J. Ogren	Flash photolysis studies of the reactions of methyl and formyl radicals	C. J. Hochanadel T. J. Sworski
Centre College	C. A. Girard	Proton spin relaxation in hydrous melts	J. Braunstein
Centre d'Etudes Nucléaires, Bordeaux, France	F. Hubert	Heavy-ion transfer reactions	R. L. Hahn
University of Chicago	E. Anders S. A. Rice	Primordial radioelements and spallogenic radionuclides in meteorites Structure of water	G. D. O'Kelley A. H. Narten
Clemson University (supported by EPA)	C. A. Brandon	Hyperfiltration for energy conservation	J. S. Johnson, Jr.
Convair Aerospace Division, General Dynamics Corp., San Diego	O. E. Myers	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton

Institution	Collaborator(s)	Subject	Staff Member(s)
Department of Geologic Sciences Cornell University	J. M. Bird	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Denison University	R. R. Winters	Neutron capture cross section of ^{197}Au	J. Halperin
Fermi National Accelerator Laboratory	D. Theriot	Search for superheavy elements in accelerator targets	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
University of Freiburg, Germany	W. Mehlhorn	Electron spectrometry	M. O. Krause
University of Georgia, Geochronology Laboratory	J. E. Noakes	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Gesellschaft für Schwerionenforschung, Darmstadt, Germany	H. H. Gutbrod	Heavy-ion-induced reactions at Lawrence Berkeley Laboratory SuperHILAC	R. L. Ferguson
Harvard University	W. N. Lipscomb	Structure of cyclic peptides	W. E. Thiessen
Indiana University, Bloomington	J. Jastrzebski	Search for high-spin yrast traps in nuclei	N. R. Johnson
Institut de Physique Nucléaire, Orsay, France	Y. LeBeyec	Study of nuclear reactions with Ar and Kr beams	R. L. Hahn
International Paper Co. (supported by EPA)	L. J. Breithaupt	Pilot plant tests of dynamic membranes for treatment of kraft pulping effluents	J. S. Johnson, Jr.
University of Kentucky	S. W. Yates	Properties of ^{164}Er in the band-crossing region	N. R. Johnson E. Eichler
	S. W. Yates	Lifetime measurements of high angular momentum states by the Doppler-shift recoil-distance technique	N. R. Johnson
Lawrence Berkeley Laboratory	A. Ghiorso	Search for $^{260}104$ via the $^{249}\text{Bk} + ^{15}\text{N}$ reaction	R. J. Silva
	A. Ghiorso G. T. Seaborg E. Cheifetz R. C. Jared E. R. Guisti S. G. Thompson M. W. Guidry R. M. Diamond F. S. Stephens	Search for superheavy elements via the $^{48}\text{Ca} +$ ^{248}Cm reaction	R. J. Silva
		Search for superheavy elements in nature	J. Halperin R. J. Silva R. W. Stoughton
	M. W. Guidry	Lifetime measurements of high-spin states in ^{232}Th , ^{164}Er , and ^{162}Dy following Coulomb excitation with ^{84}Kr and ^{136}Xe	N. R. Johnson E. Eichler
		Study of nuclear reactions with Ar and Kr beams	R. L. Hahn
Lawrence Berkeley Laboratory SuperHILAC	M. S. Zisman A. Ghiorso	Search for superheavy elements in accelerator targets	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Lawrence Livermore Laboratory	E. K. Hulet R. W. Lougheed	Production, identification, and the alpha- and spontaneous-fission-decay characteris- tics of $^{262}105$	C. E. Bemis, Jr.
	M. G. Mustafa	Theoretical calculation of fission properties of actinide and transactinide nuclei	R. L. Ferguson
	E. K. Hulet R. W. Lougheed	Fission of actinide and transactinide nuclei	R. L. Ferguson

Institution	Collaborator(s)	Subject	Staff Member(s)
Los Alamos Scientific Laboratory	H. C. Britt B. H. Erkkila P. D. Goldstone R. H. Stokes G. A. Cowan J. R. Nix	Heavy-ion-induced reactions at Lawrence Berkeley Laboratory SuperHILAC	R. L. Ferguson
		Possibility of superheavy elements in nuclear explosions	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton C. E. Bemis, Jr.
	J. R. Nix	Review and evaluation of superheavy element claims, research, and prospects	J. Braunstein
University of Maine at Presque Isle	T. B. Tripp	Thermodynamics of concentrated aqueous electrolytes	R. P. Hemenger R. M. Pearlstein
MIT, Cambridge, Mass.	R. J. Silbey	Excitons in photosynthetic units	N. R. Johnson
Michigan State University, East Lansing	T. L. Khoo C. H. King B. A. Brown	Search for high-spin yrast traps in nuclei	N. R. Johnson
Nagoya University, Japan	H. Yamada T. Katoh	Properties of excited 0^+ states and beta, gamma mixing effects in ^{156}Gd	G. D. O'Kelley
NASA Johnson Space Center	E. Schonfeld	Primordial radioelements and spallogenic radionuclides in meteorites	R. M. Pearlstein W. B. Whitten
New York University	N. E. Geacintov	Linear dichroism of chlorophyll-proteins	J. Halperin
State University of New York at Albany	J. B. Garg	Capture cross section of $^{63,65}\text{Cu}$	N. R. Johnson
University of Paris South, Orsay	H. Sergolle C. Raulette J. Vanhorenbeck J. Lagrange P. Colombani	Multiple Coulomb excitation measurements in $^{182,184,186}\text{W}$	N. R. Johnson
Purdue University	P. C. Simms S. Popick P. J. Daly H. Haelppi S. K. Saha	Lifetime measurements of high angular momentum states by the Doppler-shift recoil-distance technique	N. R. Johnson
Research Institute of Physics, Stockholm	T. Lindblad	Lifetime measurements of high angular momentum states by the Doppler-shift recoil-distance technique	N. R. Johnson
Rice University, Houston, Department of Geology	J. A. S. Adams	Search for unknown radioactivities in nature	R. V. Gentry J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
University of Rochester	M. Blann	Heavy-ion-induced reactions at Lawrence Berkeley Laboratory SuperHILAC	R. L. Ferguson
St. Louis University	J. H. Barker	Gamma-ray multiplicities in evaporation residues following compound-nucleus reactions	N. R. Johnson E. Eichler
Science Applications, Inc., Palo Alto	J. Maly	Search for superheavy elements in nature and in accelerator targets	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton

Institution	Collaborator(s)	Subject	Staff Member(s)
Stanford Linear Accelerator Center	D. Walz	Search for superheavy elements in accelerator targets and in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Stevens Institute of Technology, Hoboken, N.J.	F. T. Jones	Radiation chemistry of deaerated aqueous bromide ion solutions	T. J. Sworski
University of Tennessee	L. L. Riedinger A. C. Kahler C. R. Bingham Reidar Huglen L. L. Riedinger A. C. Kahler M. W. Guidry L. L. Riedinger	Studies of the "back-bending" effect in nuclei Resonance Raman spectro-electrochemistry Lifetime measurements of high angular momentum states by the Doppler-shift recoil-distance technique Lifetime measurements in ^{165}Yb high-spin states in nuclei from compound-nucleus reactions	N. R. Johnson G. M. Begun N. R. Johnson E. Eichler N. R. Johnson
Thomas More College, Covington, Ky.	Joseph Lang	Structure of <i>o</i> -terphenyl	G. M. Brown
Tokyo Institute of Technology	M. Fujioka M. Sekikawa	Properties of excited 0^+ states and β - γ mixing effects in ^{156}Gd	N. R. Johnson
Tokyo Metropolitan University	H. Nakahara	Heavy-ion-induced reactions at ORIC	R. L. Ferguson
Chemical Institute, The University Tübingen, Tübingen, Germany	M. Hanack H. Stutz	Isotope effects	C. J. Collins B. M. Benjamin
Union Carbide Corporation, Linde Laboratories	G. J. Nihart	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
U.S. Geological Survey	J. H. McCarthy	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
UNISOR Consortium	K. S. R. Sastry et al. L. L. Riedinger C. R. Bingham J. L. Wood R. W. Fink	Precession of gamma-gamma correlation in ^{126}Xe Decay of ^{195}Pb , ^{197}Pb	N. R. Johnson G. D. O'Kelley
Department of Chemistry, University of Utah, Salt Lake City	P. Stang D. P. Fox	Unsaturated carbenes	C. J. Collins
Vanderbilt University	J. H. Hamilton J. H. Hamilton R. Ronningen R. Hichwa	Properties of excited 0^+ states and β - γ mixing effects in ^{156}Gd Properties of ^{164}Er in the band-crossing region	N. R. Johnson N. R. Johnson E. Eichler
Washington University, St. Louis, Mo.	D. Sarantites S. Gronemeyer D. Sarantites J. Urbon D. Sarantites D. Sarantites L. Westerberg	Gamma-ray multiplicities in evaporation residues following compound-nucleus reactions Lifetime measurements of high angular momentum states by the Doppler-shift recoil-distance technique Heavy-ion-induced reactions at ORIC Search for high-spin yrast traps in nuclei	N. R. Johnson E. Eichler N. R. Johnson R. L. Ferguson N. R. Johnson

Institution	Collaborator(s)	Subject	Staff Member(s)
University of Washington, Seattle	Elinor Adman L. H. Jensen	Structure refinement of macromolecular catalysts	G. M. Brown
Weizmann Institute of Science (sponsored by U.S.-Israel Binational Foundation)	G. Tanny	Dynamic polyelectrolyte membranes for hyperfiltration	J. S. Johnson, Jr.
Yonsei University, Seoul, Democratic Peoples Republic of Korea	A. H. Ahn	Properties of excited 0^+ states and β - γ mixing effects in ^{156}Gd	N. R. Johnson

VISITING SCIENTISTS

Name	Affiliation	ORNL Research Program	Sponsor
A. M. La Gamma de Batistoni	Comision Nacional de Energia Atomica Argentina	Isotopic exchange of the hydrogen isotopes in lithium	I.A.E.A. (F. J. Smith)
L. Blum	University of Puerto Rico, Rio Piedras	Structure of liquids	Oak Ridge Associated Universities (A. H. Narten)
C. P. Brock	University of Kentucky, Lexington	Structural chemistry	Oak Ridge Associated Universities (H. A. Levy)
C. J. Fritchie, Jr.	Tulane University, New Orleans, La.	Structural chemistry	Tulane University (H. A. Levy)
S. W. Hawkinson	University of Tennessee, Knoxville	Structural chemistry	University of Tennessee (W. E. Thiessen)
P. Hubert	Centre d'Études Nucléaires, Bordeaux, France	Nuclear chemistry	N. R. Johnson E. Eichler
Radar Huglen	University of Tennessee, Knoxville	Raman spectroscopy of molten salts	G. P. Smith
G. L. Johnson	Kenyon College, Gambier, Ohio	Coordination of titanium in borate melts	G. P. Smith
D. S. Jones	University of North Carolina, Charlotte	Structural chemistry	Oak Ridge Associated Universities (H. A. Levy)
Stanley L. Klemetson	North Dakota State University, Fargo	Filtration of coal-conversion effluents	NSF
M. L. Poutsma	Union Carbide Corporate Research Laboratory, Tarrytown, New York	Homogeneous catalysis	G. P. Smith
A. D. Rae	University of New South Wales, Kensington, Australia	Structural chemistry	University of New South Wales (W. R. Busing)
S. I. Sandler	University of Delaware, Newark	X-ray diffraction studies of liquid hydrocarbons	Oak Ridge Associated Universities (A. H. Narten)
Eugene Schwartz	DePauw University	Aqueous chemistry	Great Lakes Colleges Program
R. Triolo	University of Palermo, Italy	Neutron diffraction from aqueous solution	NATO Fellow (A. H. Narten)
C. E. Vallet	University of Provence, Marseilles, France	Electrochemistry of molten salts	J. Braunstein
S. W. Yates	University of Kentucky, Lexington	Nuclear chemistry	N. R. Johnson

GRADUATE STUDENTS

Name	Major Professor and/or Institution	Staff Advisor	Field of Research	Sponsor
R. Agraval	S. I. Sandler, University of Delaware, Newark	A. H. Narten	Structure of liquids	
C. L. Barnes	S. W. Hawkinson, University of Tennessee	W. R. Busing	Structural chemistry	
R. E. Cassady	S. W. Hawkinson, University of Tennessee	W. R. Busing	Structural chemistry	
L. L. Collins, Jr.	G. D. O'Kelley, University of Tennessee	G. D. O'Kelley	Nuclear spectroscopy	University of Tennessee
J. P. Fillers	S. W. Hawkinson, University of Tennessee	W. R. Busing	Structural chemistry	
E. C. Kostansek	W. N. Lipscomb, Harvard University, Cambridge, Mass.	W. E. Thiessen	Structural chemistry	
M.-S. Kuo	C. P. Brock, University of Kentucky, Lexington	H. A. Levy	Structural chemistry	
R. A. Muntean	G. D. O'Kelley, University of Tennessee	G. D. O'Kelley	Nuclear geochemistry	University of Tennessee
M. K. Pastorcich	M. H. Lietzke, University of Tennessee	M. H. Lietzke	NMR studies	University of Tennessee
William L. Salter	M. H. Lietzke, University of Tennessee	M. H. Lietzke	Potentiometric studies	University of Tennessee
Monte Scharbow	S. L. Klemetson, North Dakota State University	J. S. Johnson, Jr.	Filtration of coal-con- version effluents	NSF
Y. P. Tsao	C. J. Fritchie, Tulane University, New Orleans, La.	H. A. Levy	Structural chemistry	
Li -hau Wu	M. H. Lietzke, University of Tennessee	M. H. Lietzke	Thermodynamic modeling	University of Tennessee

UNDERGRADUATE STUDENTS

Name	Institution	ORNL Research Program	Sponsor
Peter K. Brown	Albion College	Transuranium element nuclear chemistry	Great Lakes Colleges Association
Steven Daniels	Wake Forest University	Physical chemistry of geothermal solutions	ORAU Summer Student Trainee Program
Carl Harris	Tennessee Technological University	High-temperature aqueous chemistry	ORAU Summer Student Trainee Program
J. B. Hendricks III	University of the South	Thermal generation of hydrogen	Southern College University Union
C. Hilborn	Centenary College	Organic chemistry	Southern College University Union
Paul Martinez	East Tennessee State University	Thermal generation of hydrogen	ORAU
Michele Moisis	Kenyon College	Phase behavior of water-alcohol- hydrocarbon systems	Great Lakes Colleges Association
I. A. Nairn	Dartmouth College	Energy transfer in biosystems	ORAU Summer Student Trainee Program

Name	Institution	ORNL Research Program	Sponsor
P. Rafferty	Centre College	Structural chemistry	Southern College University Union
Gregory H. Slocum	DePauw University	Aqueous chemistry	ORAU Summer Student Trainee Program
S. A. Templeton	University of the South	Phase behavior of aqueous-alcohol-surfactant-hydrocarbon systems	Southern College University Union
A. Titterton	Denison College	Organic chemistry	Southern College University Union
M. Warner	Centenary College	Organic chemistry	Southern College University Union

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